KINETICS OF THE CATALYTIC OXIDATION OF PHTHALIC ANHYDRIDE

by

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1. Introduction

Phthalic-anhydride (PA) is produced by oxidation of o-xylene or naphthalene. Ninety percent of the 2 million meton annual production is used in the manufacture of plasticizers, alkyd resins, and polyesters. Almost all PA production is based on catalytic vapor phase air oxidation processes. These processes use catalysts that are based on vanadium pentoxide. Present process technologies produce PA at 75 and 85% of theoretical yield. The 75 mole % yield is obtained from o-xylene, the more abundant of the two feedstocks.

Purpose of this research was to investigate PA production and its combustion, in order to study sources of the reduced yields. Low yields have been attributed to late combustion of the PA product and/or to rupture of the aromatic ring during sidechain oxidations that produce PA.

If PA combustion occurs slowly, relative to PA production, as revealed by kinetic studies, the reduced industrial yields may be attributed to early rupture of the aromatic ring, rather than to over-oxidation of the PA produced.

Conversely, if PA combustion occurs rapidly on catalyst or container surfaces, the yield problem is most likely due to PA over-oxidations.

Maleic anhydride (MA) is a by-product of PA production. The MA can originate from either early or late degradive routes. Location in the reaction scheme where MA formation begins may be a clue to the step where some of the degradation begins.

This investigation was directed to locate the earliest source of MA in the reaction scheme, and to make a kinetic study of the oxidation of PA.

2. Summary and Conclusions

(1) Air oxidations of o-xylene to products were conducted in an aluminum tubular reactor using a series of V_2O_5 catalysts. These catalysts differed in their selectivity. Product distribution diagrams for each catalyst over the temperature range 350-600°C showed that carbon oxides were produced at low temperature from the initial oxidative attack on o-xylene. MA was not detected until o-tolualdehyde was present as an intermediate. Six minor products of o-xylene et seq. were evident. These minor products augment the usual products: o-tolualdehyde, o-toluic acid, phthalide, PA, MA, carbon oxides, benzoic acid, tars and water.

Oxidations of PA et seq. on V_2O_5 yielded four of the above six minor products, plus MA, carbon oxides, tars and water. Benzoic acid was not a product of PA. Acetylene and acrolein were identified by IR, and o-benzoquinone was another probable minor product. It was concluded that MA is primarily formed from PA oxidation.

MA oxidation yielded carbon oxides and water, plus three of the four minor products found from PA et seq.

(2) Kinetics of PA oxidation were measured, at temperatures from 300 to 600°C, on several V_2O_5 catalysts and on catalytic surfaces. Contact times were varied from 0.1 to 0.6 second. PA concentration was varied by a factor of 20, ranging up to 0.87% volume in air.

The kinetics followed a Langmuir-Hinshelwood heterogeneous rate law that was pseudo zero order in oxygen:

$$r = \frac{k_1 P_{PA}}{1+k_2P_{PA}}$$

Rate constants and their temperature dependence varied among catalysts and the various catalytic surfaces examined.

3. Literature Survey

A. Process Survey

Phthalic anhydride (PA) is industrially produced by the air oxidation of naphthalene or o-xylene.[1] Maximum yields have, over the years, increased to 77 mole % from o-xylene[2,3] and 85 mole % from naphthalene.[4-6] Vapor phase oxidations for PA production are conducted on fixed or fluidized beds of catalysts containing vanadia (V_2O_5). One liquid phase oxidation process is in operation. Industrial PA plants are built using licensed processes; these guarantee performance based upon the design, technology and catalyst provided by the licensors.[7]

Fixed bed processes used for PA production are summarized in table 1, according to licensor, feedstock, number of plants, and total plant capacity in the western world. Greatest capacity is based upon the von Heyden (Lurgi, Chemiebau) processes, using naphthalene or o-xylene feedstock. The Badische Anilin- und Soda Fabrik (BASF) process is based solely on o-xylene feed. Most recent versions of von Heyden and BASF processes dominate present fixed bed PA construction. The Rhone-Progil process gives lower PA yield and has been licensed to a more limited extent. The von Heyden, BASF and Rhone-Progil processes now available are low temperature, high space velocity processes. Much of the early von Heyden technology was based upon low temperature, lower space velocity catalysts.

Table 1

Free World Fixed Bed PA Processes (1973)

Licensor	Feedstock	No. of Plants	Total Capacity Metons/year	References
von Heyden (Lurgi) (Chemibau)	o-xylene	41	505,000	3, 8-13
	naphthalene	24	295,000	
BASF	o-xylene	17	685,000	14-20
Rhone-Progil (Pechiney-St. Globain)	o-xylene	3	86,000	7,21
	naphthalene	1	40,000	
Ruhröl	o-xylene	4	ca.45,000	7,22
Allied Chemical	naphthalene	2	52,000	7
Scientific Design	o-xylene	1	9,000	7, 23-26
	naphthalene	1	14,000	
Monsanto Chemical	naphthalene	1	18,000	7,27
Chevron Chemical	o-xylene	1	14,000	7,28,29
Alusuisse	o-xylene	1	est. 10,000	7
Ftalital	o-xylene	1	est. 10,000	7

Other processes shown in Table 1 operate at higher temperature, were developed earlier, and do not produce comparable yields to those obtained with the current von Heyden and BASF processes.

Fluid bed processes for PA production are summarized in table 2. Fluid bed processes had an inherant advantage that larger plants could be built, with some reduction in capital investment over earlier fixed bed processes. The fluid bed processes operate exclusively with naphthalene feedstock. One plant was built for o-xylene feedstock, but was decommissioned shortly thereafter.

Table 2

Free World Fluid Bed PA Processes (1973)

Licensor	Feedstock	No. of Plants	Total Capacity Metons/year	References
Sherwin-Williams (Badger)	naphthalene	14	286,000	4-7, 30
	o-xylene	(1)	(34,000) decommissioned	7, 27
United Coke & Chemicals, Ltd.	naphthalene	3	39,000	31-34
American Cyanamid (Koppers)	naphthalene	1	32,000	7, 46-48

Liquid phase oxidation of o-xylene can produce phthalic acid, analogous to production of terephthalic acid from p-xylene. Plants have been built using two comparable processes for o-xylene oxidation. Progil now operates the only plant for PA using a liquid phase oxidation process as shown in table 3.

Table 3

Free World Liquid Phase PA Processes (1973)

Licensor	Feedstock	No. of Plants	Total Capacity Metons/year	References
Amoco	(o-xylene) diverted to p-xylene	(1)	(7,000)	7, 35,36
Progil	o-xylene	1	15,000	7, 27,37,38

An overall summary of PA production by feedstock and type of process is shown in table 4. Almost twice as much PA is produced from o-xylene as is produced from naphthalene. Fixed bed processes predominate and no PA is produced from o-xylene by fluid bed processes.

This table indicates that the 1973 western world capacity for production of PA was 2.1 million metons/year.

Table 4

Free World PA Capacity (1973)

Process	Fixed bed		Fluid bed		Liquid Phase		Total	
Feedstock	No. of Plants	Thousand Metons per yr.	No. of Plants	Thousand Metons per yr.	No. of Plants	Thousand Metons per yr.	No. of Plants	Thousand Metons per yr.
naphthalene	29	419	18	357	0	0	47	776
o-xylene	67	1344	0	0	1	15	68	1359
Total	96	1763	18	357	1	15	115	2135

3. Literature Search

B. Process Technology

Process technology of PA production from o-xylene of 96$^+$% purity is primarily based upon air oxidation on vanadia catalysts. Fixed bed plants operate with a feed stream containing 1 mole % o-xylene in air, in order to remain below the lower explosive limit. High exothermic heat of reaction is removed from reactor tubes by heat transfer to molten salts at about 360°C. Product collection is by desublimation in switch condensers. Product is purified by distillation, to separate PA from maleic anhydride (MA), tars, and small amounts of benzoic acid. Maximum product yields claimed are 105 lb. PA per 100 lb. of 96% o-xylene, or 77 mole %. These product yields are low, due to byproduct formation and some combustion to carbon oxides and water. PA, byproducts, and combustion products are formed via oxidative reactions involving the two methyl sidechains of o-xylene, and via aromatic ring rupture.

A typical flow diagram of the BASF fixed bed process[8] for PA production is shown in Figure 1. The heart of the process is a reactor tube bundle consisting of up to 10,000 parallel reactor tubes. Each 3 meter stainless steel reactor tube is filled with catalyst. Tube diameter is standardized at 2.5 cm for packing efficiency in the tube bundles, and to facilitate heat transfer to the salt bath. Due to the highly exothermic nature of the oxidation reaction, and to excessive formation of byproducts at elevated temperature, catalyst hot spot temperature is not allowed to rise above 410°C. Air

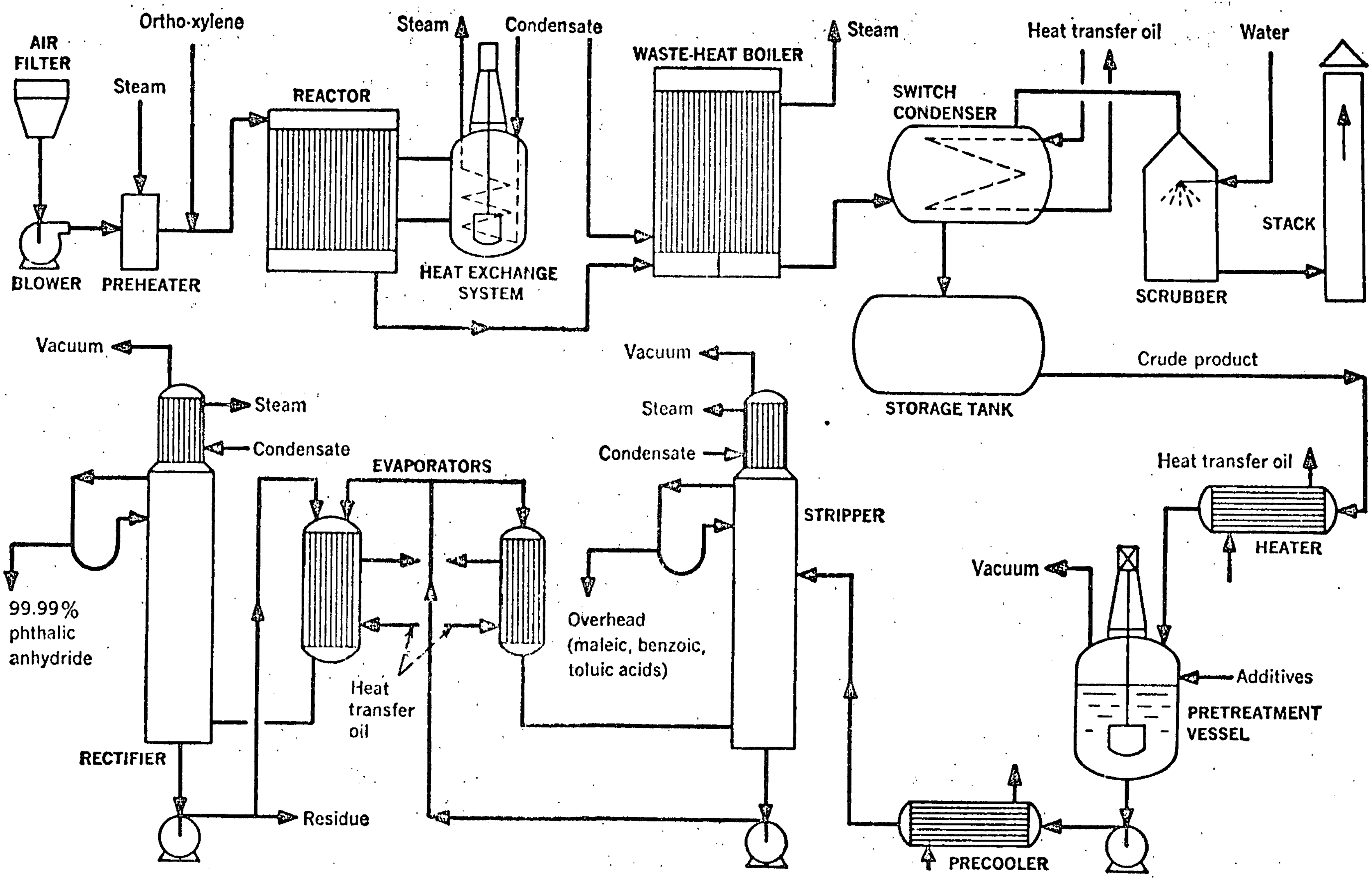


Figure 1

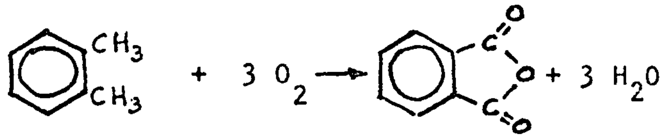
BASF Fixed Bed Process for PA Production[18] flowrates of 4-5 M^3 (STP) per hr. per tube yield space velocities of 13,600 - 17,000 hr.,$^{-1}$ based on salt bath temperature and void volume of the reactor tube. These space velocities are equivalent to contact times of 0.21-0.26 second.

Catalysts

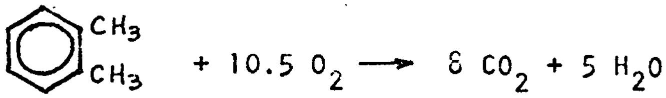
Catalysts of the earlier high temperature fixed bed processes were V_2O_5, either fused or surface coated on porous silica, alumina or SiC carriers for surface-area improvement. These catalysts were operated at 425-500°C with contact times of about 0.1 second. Activity and selectivity of V_2O_5 was modified by addition of K_2SO_4 and $K_2S_2O_7$. These additions permit PA formation at tube temperatures as low as 360°C. Low temperature operation reduces formation of carbon oxides due to ring rupture. Since $K_2S_2O_7$ slowly loses SO_3 during operation, and sulfur compounds are oxidized to SO_3 on V_2O_5, small amounts of sulfur are introduced into the feedstock to maintain uniform activity of $K_2S_2O_7$-containing catalysts. Small amounts of P_2O_5, TiO_2 and heavy metal oxides have, on occasion, been added to V_2O_5 as catalyst promoters and deactivators. Carrier substrate composition and porosity have been varied. Proprietary industrial catalysts have been optimized for catalyst life, low pressure drop, mechanical strength, yield and selectivity to PA at high space velocity. All of the multicomponent catalysts are V_2O_5 based.

Heat of reaction

Overall exothermic reactions involved in the oxidation of o-xylene to PA are:



$\Delta H=-308.$Kcal/mole



$\Delta H=-1092.$Kcal/mole

These two reactions oversimplify the process, as is shown by more detailed reaction schemes.[156] However, these large reaction exotherms lead to a heat release, at 75 mole % conversion of o-xylene to PA and 25 mole % to complete combustion products, of 504. Kcal/mole. This is the approximate amount of heat produced in operating processes. Much of this heat is transferred via a circulated molten salt bath for high pressure, superheated process steam generation.

Process Details

A trade literature summary relative to processes for PA production follows. This is presented chronologically, and divided according to type of licensed process.

Fixed Bed Processes

for either naphthalene or o-xylene

Following disclosure[61] of the process for catalytic vapor phase oxidation of naphthalene or o-xylene to PA in 1917, plants were built based upon readily available coal tar naphthalene feedstock. The process rendered prior chemical oxidations of naphthalene uneconomic, and production of PA approached 3000 metons by 1928. Plants were operated using vanadia containing catalysts at 450-500°C and at low space velocity to yield 50-60 mole % PA. Bundles of many parallel tubular reactors were immersed in a molten salt bath for temperature control and removal of the exothermic heat of reaction.[125] Catalyst activity and selectivity has been improved over the years to increase yield and product purity. Tubular reactor configurations have remained substantially unchanged.

Fixed bed processes may now be used with either naphthalene or o-xylene feedstocks. Although the reactors and catalysts are similar, entire plants are not directly convertable due to different feed and recovery section details, and to different amounts of heat release obtained from oxidation of the two feedstocks.

1. von Heyden Process

Forbath (1962) provided a process diagram of the von Heyden fixed bed process for PA production from either o-xylene or naphthalene.[12] This process is licensed by Chemibau Dr. A. Zieren GmbH and by Lurgi Gesellschaft. Differences between plants offered by the two licensors lie in design and engineering detail, particularly in the recovery section.[7] Guaranteed yields for the process are 92.5 lb. PA/100 lb. 95% o-xylene, (70 mole %), and 91 lb. PA/100 lb. 95% naphthalene, (83 mole %). Byproducts from o-xylene feed are benzoic acid, MA and residual tarry bottoms. The von Heyden catalyst contains V_2O_5 plus inhibitors on silica. Shape of the catalyst is extruded short cylinders, for low bed pressure drop. This catalyst is believed to be Kontakt-WO, which operates at 360°C bath temperature and space velocity of 6000 $hr.^{-1}$ (0.6 sec. contact time).[40]

Guccione (1965) disclosed details of a commercial plant, with four reactors, using the von Heyden process for PA production from 95% o-xylene. Yield is approximately 100 lb. PA/100 lb. o-xylene, or 75 mole %. The plant was designed to operate at a salt bath temperature of 355-370°C. Byproducts are 2-3% of MA and benzoic acid. Reaction enthalpy is primarily recovered as 300 psig superheated steam. Product recovery is by switch condensers, followed by distillation.[13]

Chemibau (1966) announced introduction of the new von Heyden Kontakt-S catalyst for production of PA from o-xylene.[41] This V_2O_5 containing catalyst operates at low temperature and high space velocity to give consistent high yields.

Vedrilla (1967) presented further information on the low temperature high space velocity von Heyden Kontakt-S catalyst for oxidation of o-xylene to PA.[39] This catalyst is originally activated by SO_2, and high activity is maintained by using small amounts of sulfur dissolved in the o-xylene. Operation is at 360°C with a space velocity of about 14000 $hr.^{-1}$ This space velocity is equivalent to a contact time of 0.25 sec.

Chemische Fabrik von Heyden (1969) announced that consistent PA yields of 97-98% wt. (guaranteed 95-96% wt.) were produced from o-xylene with their Kontakt-S catalyst. Key elements of this catalyst were reduced bed pressure drop and extended service life. Reactor design uses 12,000 tubes per bundle. Further catalyst development was reported to be in progress.[27]

Chemische Fabrik von Heyden (1971) disclosed operating parameters and activation instructions for Kontakt-WO and Kontakt-S for the oxidation of o-xylene to PA.[40] Both catalysts operate at a salt bath temperature of 360°C, using 1 mole % o-xylene in air. Kontakt WO used air flow at 1.8 cubic meters (STP)/hr per 2.5 meter tube of 2.5 cm. inner diameter. Kontakt-S used an air flow of 4 cubic meters/hr./tube. Both catalysts required SO_2 activation, and continuous use of 0.1-0.4 wt % sulfur in the o-xylene feedstock to maintain catalyst activity.[40]

Hydrocarbon processing (1965-1973) presented flowsheets and process summaries of the von Heyden (Lurgi, Chemibau) process for fixed bed production of PA.[8-11] Yields were reported as 102-105 lb. PA/100 lb. 96^+% o-xylene, and 94-98 lb. PA/100 lb. naphthalene. Catalyst life was claimed to be 3 years, minimum.

Lurgi Gesellschaft (1974) announced two years plant operation using an improved high space velocity o-xylene to PA catalyst.[3] Yield was 105 wt % PA based on 96.5% o-xylene.

2. BASF Process

BASF (1967) announced a large, improved, high space velocity fixed bed process for PA production. Catalyst used does not require sulfur activation, and yields of PA from o-xylene were reportedly higher than with other processes. Reactor yields of 106 lb. PA/100 lb o-xylene are claimed, with overall system recovery of 103 lb. of PA. A standard reactor contains 8900 tubes that are 3 meters long and have a 2.5 cm inner diameter.[14,15]

Elwood (1969) presented a flow diagram and process summary of BASF process plants for o-xylene oxidation to PA. The catalyst is surface coated, has high surface area, contains V_2O_5, and operates at 375°C. No SO_2 activation is required.[16]

Hydrocarbon Processing (1969-1973) presented flowsheet and abbreviated process summary of the BASF fixed bed process. Distilled PA, MA and benzoic acid products are formed.[17-19]

Key to the BASF process lies in patents by Reuter et al (1973). They taught, in a series of four patents, the technique for producing high surface area, selective catalysts for the air oxidation of o-xylene to PA. Steatite substrate was surface coated with anatase (TiO_2) 72% wt, ZrO_2 22%, and V_2O_5 6%. Formamide was a key solvent ingredient for producing the high surface area of the coating. It is claimed that 110 wt %, (79 mole %) PA is produced at 380°C, using high space velocity and 1 mole % o-xylene feed in air.[42,43]

Friedrichsen and Goehre (1973) gave details of a second new catalyst type in another BASF patent. Steatite was surface coated with anatase (TiO_2), V_2O_5, and a small amount of P_2O_5. This yielded a high surface area catalyst containing 6% wt V_2O_5 and 0.3% P_2O_5. Using this catalyst at high space velocity, 77 mole % PA and a trivial amount of phthalide were produced at 360° bath temp (480°C hotspot temperature) from 1 mole % o-xylene feed in air. Claimed catalyst life was about 3 years.[44]

BASF (1973) announced consistent, long term plant production yields of 103 lb. PA/100 lb. of 95% o-xylene, and stable catalyst activity for their improved process and high space velocity catalyst.[20]

3. Rhone-Progil Process

Zimmer (1974) presented details of an improved Pechiney-Saint Globain process for production of PA from o-xylene. A V_2O_5 containing catalyst is operated at 360-380°C without requiring sulfur in the feedstock, or SO_2 activation of the catalyst. Product yield claimed is 95 wt % (68 mole %). Tail gases containing MA are burned in a catalytic incinerator for pollution control. Byproducts are benzoic acid and tars.[21]

The above three low temperature, high space velocity processes produce greater product yield than the higher temperature processes that follow. The earlier of these high temperature processes used unpromoted V_2O_5 on various carrier substrates.

Catalysts & Chemicals International (1973) stated that they had discontinued work with unpromoted V_2O_5 catalysts in 1970.[45] Typical of these superceded high temperature processes are Ruhröl, Scientific Design, and Oronite (Chevron) Chemical.

4. Ruhröl Process

Ibing (1967) offered details of the Ruhröl fixed bed process for producing PA from o-xylene using a V_2O_5 high temperature, high space velocity catalyst. It was claimed that yield was comparable with that of the von Heyden process. Significant amounts of MA were produced; technology was offered for its recovery and isomerization to fumaric acid.[22]

5. Scientific Design Process

Landau and Simon (1962) reported that the Scientific Design process yielded 85-95 lb. PA/100 lb. o-xylene. This was accompanied by appreciable amounts of MA, which can be recovered and isomerized to fumaric acid. They predicted a continuing trend to o-xylene feedstock, due to limited supplies of coal tar naphthalene, and the inherently higher cost of petrochemical naphthalene.[35]

Scientific Design (1960, 1961) disclosed that they had developed a new catalyst[23] that performed equally well with naphthalene or o-xylene feedstocks for the production of PA. Yields claimed were 85-95 lb. PA/lb. of o-xylene.[24] Normal feedstocks are coal tar naphthalene (95% pure), petrochemical naphthalene (99% pure), or o-xylene (95% pure).

6. Oronite Chemical Process

Callaham (1946) and Levine (1947) presented flow diagram and preliminary process summary for the first plant to commercially produce PA by the V_2O_5 catalyzed oxidation of o-xylene.[28,29] Temperatures were 400-475°C with 0.4-0.6 sec. contact times. Yield claimed was 90-95 lb. of PA/100 lb. 95% o-xylene. According to trade sources[24] consistent yield was nearer to 75 lb. PA/100 lb. o-xylene. More recent plant installations by the parent company, Standard Oil Co. of California, have used the von Heyden (Lurgi) process.

Naphthalene Fluid Bed Processes

Fluid bed processes were developed for oxidation of naphthalene to PA by Sherwin Williams, American Cyanamid, United Coke and Carbide, and BASF.

1. Sherwin Williams Process

Lee (1945) presented process summary of the Sherwin Williams fluidized bed process for naphthalene oxidation to PA.[30] Feed concentrations in the explosive range were possible because the fluidized catalyst would eliminate hotspots and quench any possible explosion wave. The fluid bed design inherently made larger plants possible than with bundles of thousands of fixed bed tubular reactors. Yields of about 65 mole % were significantly lower than 70-80 mole % then achieved in fixed bed reactors.[28]

Hydrocarbon Processing (1971, 1969, 1967) presented flow diagram and process survey of the Sherwin Williams process. It was claimed this process was applicable to o-xylene feed in 1967, but the claim was subsequently withdrawn. Fluid bed temperature was 345-385°C.[4-6]

Union Carbide (1975) reported shutdown of their 41,000 meton/year plant for the production of PA from petroleum naphthalene.[182] Reason given for the closure was that this plant, built more than a decade ago, had become non-competitive with plants using o-xylene feedstock.

2. American Cyanamid Process

Fugate and Tribit (1954) taught that the fluid bed yield of PA from naphthalene could exceed 100 lb. PA/lb. naphthalene, (87 mole %), at 330-370°C and mean residence times of 5 to 8.5 seconds.[46] Catalyst used was a V_2O_5 - $K_2S_2O_7$ on silica catalyst activated with Ag and/or CeO_2. This fluid bed yield exceeded usual fixed bed yields of 85 wt % (75 mole %) PA from naphthalene.

An American Cyanamid patent (1956) taught that use of a fluidized bed of high surface area, silver activated V_2O_5/K_2SO_4 on silica gel catalyst oxidized naphthalene to PA at 320-410°C. A quench zone was necessary to rapidly cool the reaction products to 200-300°C and prevent PA combustion. PA yield averaged 85 mole %.[47]

Chomitz and Rathjens (1961) taught that naphthalene could be oxidized in a fluid bed at 320-380°C on a high surface area catalyst containing V_2O_5 - K_2SO_4 on silica gel. Yield was 106 lb. PA/100 lb. naphthalene (92 mole %). The PA product contained no naphthoquinone byproduct, in contrast to a usual content of 0.6% naphthoquinone.[48]

3. United Coke and Chemicals Process

UCC similarly developed fluid bed technology and catalyst for naphthalene oxidation.

Pinchbeck and Popper (1958) taught manufacture of attrition resistant V_2O_5 - K_2SO_4 on silica gel catalysts for use in fluid bed oxidation of naphthalene.[49]

A United Coke and Chemical (1962) patent taught the method of preparing a V_2O_5 - $K_2S_2O_7$ on silica gel catalyst for the air oxidation of naphthalene in fluidized bed.[50]

Riley (1965) taught the method of absorbing a glassy melt of V_2O_5 - $K_2S_2O_7$ on silica gel. Resulting fluidized bed catalyst was used for naphthalene oxidation.[51]

Pinchbeck and Markham (1968) reviewed status of the fluidized bed process for PA production from naphthalene. Catalyst attrition, fines filtration problems, and combustion of PA product were overcome by using the United Coke and Chemical V_2O_5 - $K_2S_2O_7$ on SiO_2 catalyst. Naphthalene shortage has limited recent installation of the fluid bed process. Attmepts to utilize o-xylene as feedstock has resulted in severely reduced PA yields. These reduced yields are not competitive with those from fixed bed processes.[53]

Hydrocarbon Processing (1969, 1967, 1965) presented process surveys of the UCC process for oxidation of naphthalene to PA.[31-33]

4. BASF Process

Nonnenmacher et al (1963) taught that the high surface area BASF catalyst, for the air oxidation of naphthalene to PA in fluidized bed, contained $V_2O_5/K_2S_2O_7$, $Na_2S_2O_7$/silica gel, and was operative at 320-350°C. This catalyst had improved selectivity to PA when the naphthalene feed stream contained about 0.08% sulfur. It yielded 83-86 mole % PA, with the highest yield occurring at the lower bed temperatures.[52]

Successful development of large fluid bed processes for naphthalene oxidation to PA is attested by the amount of industrial capacity shown in table 2 for the Sherwin Williams and United Coke and Carbide processes. Developmental problems that were ultimately overcome involved: catalyst development to reduce attrition, catalyst optimization to reduce activity and prevent post combustion of PA during the long contact times, and filter systems for recovery and recirculation of catalyst fines. Sulfur-free petroleum-derived naphthalene allowed product yield from fluid bed processes to approach, but not meet, those attainable in fixed bed processes. Overall economics favored the larger fluid bed processes. Greater catalyst inventory and attrition plus reduced yield were offset by lower plant and operating costs. Smaller operating costs were due to lower pumping cost due to reduction of the air/xylene ratio by a factor of 3, and somewhat better recovery of product from the more concentrated product stream.

Duckworth (1969), in a review of PA production, predicted the next major breakthrough would come from the development of catalysts giving better yields and lower attrition for the fluid bed oxidation of o-xylene to PA.[34]

O-Xylene Fluid Bed Processes

In contrast to economic operation of fluid bed reactors with naphthalene feedstock, numerous attempts were made to obtain yields with o-xylene that approached those attainable in fixed bed reactors.

Nonnenmacher 1963 taught that use of $V_2O_5/K_2S_2O_7$ on silica, with various modifications and metal oxide promoters yielded a fluidized catalyst. This catalyst converted o-xylene in yields of 50-57 mole % PA at 300-340°C and 30 sec. mean contact time. Catalyst deactivation over a period of 50-100 hours was prevented by the continuous small addition of SO_2 with the feedstream. The BASF reactor was made of quartz. Austenitic Ni-Cr stainless steel was preferred for plant operation because iron resulted in increased combustion of PA to carbon oxides.[52] The 50-57 mole % yields compare with around 70% in fixed bed o-xylene processes.

Considerable effort was expended to use bromine compounds to improve selectivity to PA.

Burney and Hoff (1960) taught that continuous introduction of traces of volatile bromine compounds improved the selectivity of supported V_2O_5 when used for the air oxidation of naphthalene to PA at 450-500°C in a fixed bed. They presented data supporting the use of 0.2 wt. % ethylene dibromide, relative to o-xylene feedstock, during fluidized bed oxidation to PA. In their reactor system catalyst was reoxidized from V_2O_3 to V_2O_5 with air at 590°C in a separate catalyst regenerator.[55]

Nonnenmacher et al (1962, 1965) taught that bromine compounds, introduced at 0.5 wt % Br based on o-xylene, raised fluid bed yields of PA to about 60 mole %.[56] Chlorine compounds, introduced at 2.5 wt % Cl based on o-xylene, also gave 60 mole % PA.[57]

Chemical Process Corp (1967) taught use of aluminum for corrosion resistance, in the recovery system of o-xylene oxidation to PA, in the presence of bromine compounds. HBr formed in the process was particularly corrosive to other structural materials and resulted in structural problems plus an off-colored and contaminated PA product.[58]

Egbert et al (1967, 1968) taught that $V_2O_5/K_2S_2O_7$ on silica fluidized catalyst could be used at 327-366°C for oxidation of o-xylene to PA at a space velocity of 350 $hr.^{-1}$ in the presence of HBr at 1% wt based on o-xylene. The reactor was operated at 2.5 atm exit pressure to facilitate product recovery. Mean contact times of 8 to 20 seconds were advocated. It was claimed that 6 times more elemental bromine was required when the bromine was injected as ethylene dibromide rather than as Br_2 or HBr. Yields up to 70 mole % varied with bromine amount and bed temperature.[59]

Badger (1968) commercialized use of volatile bromine compounds to modify fluid catalyst behavior during oxidation of o-xylene to PA. Combustion products were reduced.[60] It was reported that the plant was decommissioned in 1969, presumably due to poor yield and HBr corrosion problems.[27]

O-Xylene Liquid Phase Process

Liquid phase oxidation processes were developed because meta and paraxylene could not be oxidized in the vapor phase to commercially feasible yields of isophthalic and terephthalic acids. Successful processes were developed and are widely used for terephthalic acid. These same processes are directly applicable to liquid phase oxidation of o-xylene to phthalic acid, which can be dehydrated to PA.

1. Amoco Process

Barker and Saffer (1958) taught that mixed xylenes could be air oxidized in the liquid phase to the corresponding acids. Catalysts were salts of manganese, cobalt and molybdenum, plus bromine compounds that were soluble in an acetic acid solvent.[25]

Burney and Coworkers (1959) presented flow diagram and operating parameters of the Amoco plant using the liquid phase oxidation process. Air requirement is 110% of theoretical. Reaction temperature is 125-275°C, and pressures to 40 atm are used to maintain the liquid phase and to increase the oxygen partial pressure in the system. When o-xylene is oxidized, the products are phthalic and benzoic acids.[26]

Landau and Simon (1962) reviewed liquid phase oxidation processes.[35]

Kafidelis et al (1964) described in detail the production of PA by the Amoco liquid phase oxidation of o-xylene.[36] The process operated on o-xylene originally, but was shifted to p-xylene as demand for terephthalic acid increased.

2. Progil Process

Socíété Progil (1966) announced commercial application of their liquid phase process for the oxidation of o-xylene to PA.[38] The process uses a three stage reaction system with controlled oxygen to each reactor. Phthalic acid is crystallized from reaction solvent, dehydrated to PA and distilled. Yields up to 88 mole % PA were obtained from o-xylene.[39]

3. Soviet Process

Trusov and Neilands (1972) described their catalytic air oxidation of o-xylene over cobalt acetate bromide in acetic acid. Products were o-tolualdehyde, o-cresol, o-methylbenzyl bromide, o-toluic acid, phthalic acid, PA, phthalide and o-formylbenzoic acid. Phthalide was an intermediate from o-xylene to phthalic acid.[54]

3. Literature Search

C. Kinetics and Mechanism

Knowledge about the reaction scheme and kinetics of o-xylene oxidation to PA, intermediates, byproducts and combustion products, has progressed in an evolutionary manner. Reaction schemes, developed by investigators working with fixed and fluid beds are mutually supportive, but kinetics proposed vary widely. Kinetic variations may be related to different catalysts, experimental conditions, and different types of reactors used by the investigators. Therefore, this literature survey is separated into separate sections devoted to xylene et seq. oxidation by fixed bed, and by fluid bed, to PA oxidation, and to MA oxidation studies. Naphthalene oxidation to PA is included, since information on the degradation of PA to MA and combustion products is an integral part of naphthalene oxidation schemes and kinetics.

Fixed Bed o-Xylene Oxidation

Gibbs (1917) taught that xylenes and air, passed over V_2O_5 at 350-550°C, gave methylbenzaldehydes, phthalaldehydes, benzenedicarboxylic acids plus some toluic acid, benzoic acid and benzaldehyde. Naphthalene, under similar conditions gave PA, phthalic acid, 1,4-naphthoquinone and benzoic acid. He found oxides of Sb, Bi, Cr, W and U effective, but preferred oxides of V or Mo.[61]

Mittasch and Luther (1924) taught that active silica gel was an effective catalyst for the air oxidation of hydrocarbons at 350°C.[64]

Craver (1927) taught that o-xylene could be air oxidized to o-tolualdehyde at 550°C on oxides of W, Mo, U or Ta using contact times of 0.3-0.4 second. Approximately 50% o-tolualdehyde was produced on

UO_3 or MoO_3 at 600°C, without appreciable formation of PA, MA or complete combustion products. Oxides of vanadium catalyzed formation of o-tolualdehyde, PA, MA and carbon dioxide.[62]

Maxted (1938) in his study of aromatic oxidations, used tin vanadate catalyst in a quartz flowtube at 290°C and low space velocity of 800 hr^{-1} to air oxidize o-xylene to PA.[63] Yields to 59 mole % PA were obtained. Bismuth vanadate gave similar results at 390°C. Similar catalysts had been used for the oxidation of naphthalene to PA.[154]

Buylla and Pertierra (1933) noted that air oxidation of o-xylene on V_2O_5 catalyst at 450°C produced PA, as did the oxidation of naphthalene.[65]

Parks and Allard (1939) investigated the air oxidation of o-xylene at contact times below 0.01 second and at low conversions per pass. They used a variety of vanadium containing catalysts at 320-530°C. They found that the air/xylene ratio controlled the extent of oxidation. At low air/xylene ratios, o-tolualdehyde was produced exclusively. At ratios near 10 times theoretical air, PA was the main product. Although tin vanadate was effective for producing PA at temperatures as low as 320°C, they obtained best PA yields of above 50% with V_2O_5 at 530°C. Benzoic acid was not detected in their products, but they did show that it was readily formed from the ethylbenzene in impure feedstocks. They found TiO_2, ZrO_2, MoO_3, WO_3, activated Al_2O_3 and $FeCrO_4$ produced carbon oxides rather than PA or tolualdehyde. They concluded that a high surface area of V_2O_5 on "Alfrax" (Al_2O_3) was their optimum catalyst for PA prodection.[66]

Morrell and Beach (1948) taught that o-toluic acid can be oxidized on V_2O_5, under conditions similar to those used for o-xylene oxidation, to form PA with 95 mole % yield.[67]

Levine (1948) taught that V_2O_5 deposited on a granular Al metal support catalyzed the air oxidation of 1 mole % o-xylene to PA in 68 mole % yield, at 500-600°C with a contact time of 0.12 second.[68]

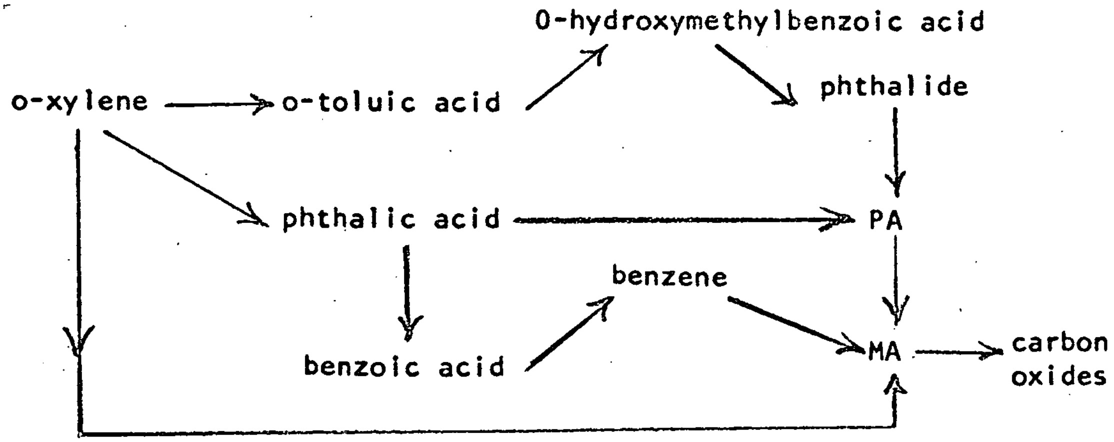
Toland (1951) taught that minor amounts of sulfur dioxide in the feedstock served to reduce activity of the V_2O_5 catalyst and to spread out the hotspot in tubular reactors.[69]

Gulati and Bhattacharyya (1953, 1954) oxidized o-xylene with air at 360°C, using V_2O_5 on kieselguhr, to produce PA and MA plus traces of o-tolualdehyde and quinone. No o-toluic acid was detected. At a space velocity of 6200 $hr,^{-1}$ o-xylene was converted to 43% PA and 11% MA.[70] In a second paper,[71] they reported o-xylene oxidation using fused and unsupported V_2O_5 at 460°C. Using a molar air/xylene ratio of 362, at space velocity 5700 $hr,^{-1}$ they obtained o-xylene conversions of 58% to PA, 9% to MA and 19% to carbon dioxide. Equal volumes of supported V_2O_5 were reported to yield less PA, more MA, and more carbon dioxide.

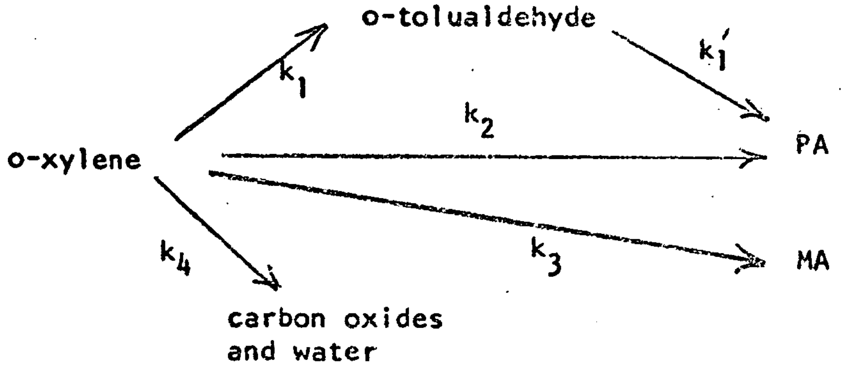
Levine (1955) summarized state of the art for o-xylene oxidation to PA.[72] Using a supported V_2O_5 catalyst, 1 mole % o-xylene is air oxidized in parallel tubular reactors with a 500-600°C hotspot. PA yields were 68 mole%. At hotspot temperatures below 525°C excessive amounts of tolualdehyde are formed; above 600°C, excessive over-oxidation of PA occurs. Catalyst deactivation occurs over a period of months and contact time may be increased several fold by reducing throughput, but o-xylene conversion to PA remains constant. Mechanism postulated for oxidation on the catalyst surface involves redox, with V_2O_5 being reduced by the hydrocarbon and reoxidized by air. Without excess air to reoxidize the catalyst to V_2O_5, the catalyst is rapidly deactivated.

Percentage carbon distribution in products from commercial fixed bed o-xylene oxidation was reported as PA 60.2, carbon dioxide 19.0, MA 7.5, carbon monoxide 7.5, aromatic aldehydes 3.4, hydrocarbons 2.0, benzoic and toluic acids 0.2, phthalide 0.2, plus acrolein and methylacrolein 0.04. Aromatic aldehydes are interpreted to mean o-tolualdehyde, plus traces of o-formylbenzoic acid and phthalaldehyde (o-formylbenzaldehyde). The proportion of phthalide and aldehydes increased at low temperatures and low air/xylene ratios, while the MA and carbon oxides proportion increased at high temperatures and high air/xylene ratios. Metal and metal oxide catalyzed decarboxylation of a carboxylic acid group was reportedly easy at elevated temperatures. Benzoic acid may be formed by decarboxylation of one acid group.

PA was declared to be more stable to ring rupture than o-xylene, due to the stabilizing presence of the additional anhydride ring. Oxidations of meta and para-xylenes yield MA due to ring rupture, and yield minor amounts of tolualdehydes, but yield no significant amounts of isophthalic and terephthalic acids. These acids are not recovered becaude the stable anhydride structure cannot form. Major elements of Levine's o-xylene to PA reaction scheme are shown in the diagram below:



Simard et al (1955) used V_2O_5 on SiC catalyst in a tubular non-isothermal reactor to air oxidize 1.1 mole % o-xylene.[73] Maximum PA was produced at 0.26 sec. contact time with 460°C tube bath temperature and a 490°C hotspot. Purity of the o-xylene was 93%. The ratio of CO_2 to CO formed was 5.3, and conversion to combined PA and MA was 58 mole %. When o-xylene concentration in the feed was raised to 3.3 mole %, the catalyst was deactivated within 3 to 4 minutes. Starting with another stable operational catalyst bed, the reduction of o-xylene concentration from 1.1 to 0.5 mole % roughly doubled catalyst activity. Post mortems of operational catalyst beds showed some reduction of the V_2O_5 to both V_2O_4 and $V_2O_{4.34}$. Catalyst reduction was related to reaction zone and temperature profile. They postulated a redox mechanism that involves: (1) chemisorption of hydrocarbon, (2) reaction with catalyst oxygen ions, (3) desorption of products, and finally (4) replenishment of catalyst oxygen. Oxygen uptake by $V_2O_{4.34}$ at 400-500°C was found to be independent of oxygen pressure above 10-20 mm. This fast oxygen adsorption led to the conclusion that step (4), the chemisorption and dissociation of oxygen, was not a rate determining step in the oxidation of o-xylene on V_2O_5 catalysts. In a subsequent paper,[74] Simard and co-workers (1956) reversed their 1955 conclusion regarding oxygen adsorption and the rate determining step of the redox reaction. Further experiments were conducted at 400-500°C on the same V_2O_5 on SiC catalyst using 0.01-0.06 second contact times. Conversions of 0.4-1.4 mole % o-xylene were below 25% at several oxygen concentrations. These investigators reported that a 0.5 power oxygen dependence existed for all reactions at the new short contact times. Since chemisorption of oxygen would be expected to show a square root dependence on oxygen pressure, they concluded that the rate determining step must be oxidation of the catalyst by gaseous oxygen. They proposed a simplified reaction scheme, that contained their observed major products:



Reactions k_1 and k_1' were first order in reactant. Reactions k_2, k_3 and k_4 were zero order.

Leibnitz et al (1957) investigated the effect of V_2O_5 content and catalyst porosity in V_2O_5 promoted with 0.2% Ag on a sintered silicic acid carrier.[75] o-Xylene was oxidized to PA at 550°C on catalysts with pore radii of 20 and 40 microns. Under uniform experimental conditions, the maximum PA yield was obtained using the catalyst with the highest V_2O_5 content and largest pore radius. Conversion was directly proportional to temperature and oxygen excess, and inversely proportional to space velocity.

Bhattacharyya and Gulati (1958) studied oxidation of o-xylene to PA using a variety of catalysts.[76] These catalysts included fused and unfused V_2O_5, both promoted and unpromoted, on various carriers. Fused V_2O_5 on pumice gave optimum performance at 490°C, using 0.3-0.4 mole %

o-xylene in air, at space velocity 5650 $hr.^{-1}$ This space velocity is equivalent to a contact time of 0.64 sec. Conversion of o-xylene to PA averaged 51 mole %, to MA was 10%, and to carbon dioxide was 18%. Quinone, in trace amounts, was the only minor product reported. Use of pure oxygen, instead of air, permitted raising xylene concentration and the space time yield of PA. Pure oxygen did not change the fraction of xylene completely oxidized, nor did it significantly alter the percentage conversions to PA and MA. Continued attempts to oxidize meta and para-xylene to corresponding isophthalic and terephthalic acids were unsuccessful.

Sherwood (1958) reviewed industrial experience with the oxidation of o-xylene to PA. Contemporary catalysts were 10% V_2O_5 on alundum or pumice support, and 10% of V_2O_5, containing 20-30% K_2SO_4, on silica gel.[77]

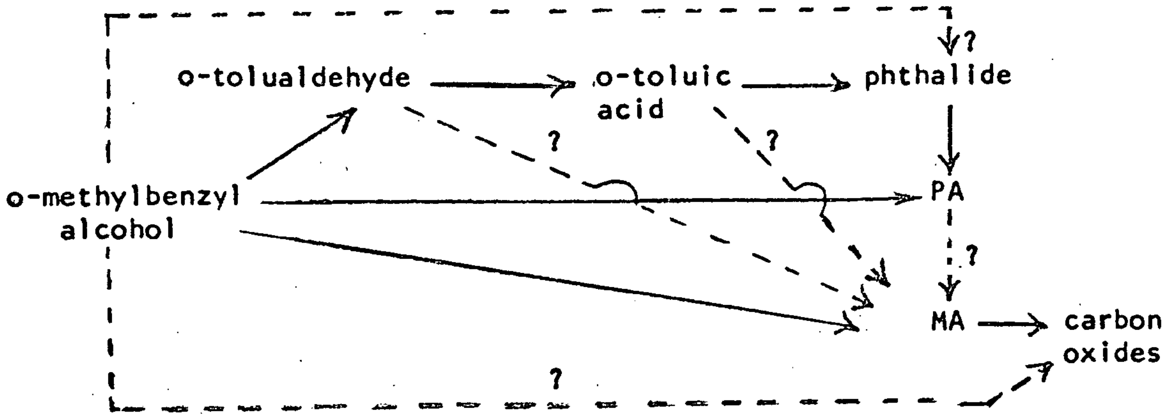
Dixon & Longfield (1960) reported that a small fraction of MA, formed from o-xylene oxidations, is citraconic acid (methyl maleic acid).[78]

Bernardini et al (1965) reported their analysis of the products of o-xylene oxidation on V_2O_5. The following products represent 97-98% of the reaction products: PA, MA, citraconic anhydride, o-toluic acid, benzyl alcohol, o-tolualdehyde, phthalide, carbon oxides, acid phthalate of o-methylbenzyl alcohol, water, and unreacted o-xylene.[79]

Vrbaski and Mathews (1965) studied the oxidation of o-methylbenzyl alcohol (OMBA) over fused V_2O_5 at 280-460°C in a glass flow system.[80] Contact times were varied from 0.075 to 0.6 sec. under near isothermal conditions. Homogeneous oxidation, judged by lack of reaction in the empty flow system, was negligible. Feed stream contained up to 1.1 mole % o-methylbenzyl alcohol in air. Isolatable products were o-tolualdehyde, per-o-toluic acid, o-toluic acid, phthalide, PA, MA and carbon oxides. Traces of o-xylene resulted from disproportionation of 2 moles of o-methylbenzyl alcohol, and occasional traces of o-formylbenzyl alcohol were found. No toluene, bitolyl or benzoic acid were detected. Birth and decay of product concentrations, as a function of reaction temperature, were used to determine the reaction sequences involved.

Consistent minima in MA and carbon oxide concentrations were observed as phthalide concentrations fell and PA concentrations rose. These minima were interpreted as evidence that phthalide was being combusted, and that phthalide was a precursor of PA.

At temperatures above 425°C, the decay of PA was accompanied by increasing amounts of MA and carbon oxides, indicating PA combustion. The derived overall reaction scheme is given as:



The activation energy for o-methylbenzyl alcohol oxidation was 20 Kcal/mole over the limited range 300-350°C. The reaction order was 0.48 in OMBA, and showed a 0.5 dependence on oxygen concentration below 0.2 atm. The rate constant for OMBA disappearance is given by $\ln k = 3.28-20000/RT$. Postulated reaction mechanism is that adsorbed o-methylbenzyl alcohol is oxidized by oxygen ions in the few surface layers of the V_2O_5 catalyst, or by loosely chemisorbed oxygen atoms on the surface. They cited their unpublished investigations of the oxidation of o-tolualdehyde, o-toluic acid, and phthalide. Under comparable conditions, product distributions and yields were comparable to those obtained from o-methylbenzyl alcohol. Under severe conditions, 82 mole % of PA was formed from o-toluic acid, and 55 mole % of phthalide was formed under milder conditions. No phthalaldehydic acid (o-formylbenzoic acid) was detected under either mild or severe conditions.

Vrbaski (1965), using data of the previous experimental paper,[80] analyzed o-methylbenzyl alcohol disappearance rates over the limited temperature range of 300-350°C.[81] Hinshelwood treatment[82] was used to attempt to fit the data. The Hinshelwood rate law is based upon the assumptions that only oxygen is adsorbed on the catalyst surface, and that there is first order rate dependence on both oxygen and organic reactant concentrations. Below 0.2 atm., the oxygen dependence was about 0.5 and o-methylbenzyl alcohol dependence was 0.48. Vrbaski questioned the adequacy of that Hinshelwood treatment, and suggested that o-methylbenzyl alcohol adsorption on the catalyst surface was rate controlling and that oxidation occurred in the adsorbed state, probably with loosely chemisorbed oxygen on the catalyst surface. Hughes and Adams treatment of data assumed organic reactant adsorption and complex formation on the catalyst surface, a redox reaction with catalyst lattice oxygen, oxidized product desorption and very rapid reoxidation of the catalyst.[83] Application of this method left unanswered questions because it was based upon pseudo zero order oxygen dependency.

Pichler and Obenaus (1965) made a detailed chromatographic study of the oxidation products of 0.6 mole % o-xylene in air.[84] They used tin vanadate catalyst at 336°C with a contact time of 0.5 sec., in a 60 cm long flow reactor. The o-xylene contained 0.5% of other aromatics, primarily m-xylene and toluene, and contained 2.3% of non-aromatic hydrocarbons. Products formed were, in order of diminishing quantity: PA, CO_2, CO, MA, phthalide, o-tolualdehyde, unknown, benzaldehyde, citraconic anhydride, acetic acid, o-toluic acid, and benzoic acid. The unknown was not phthalan (o-xylene oxide) but could have been dimethylmaleic acid anhydride. The benzaldehyde could have originated from decarboxylation of phthalaldehydic acid (o-formylbenzoic acid). Benzoic acid would be the logical oxidation product of benzaldehyde. A parallel reaction scheme is based on the fact that more PA is formed than can result solely from a tolualdehyde et seq. oxidation chain.

The route from o-xylene via tolualdehyde et seq. to PA is:

$$\text{o-xylene} \xrightarrow{O} \text{o-tolualdehyde} \xrightarrow{O} \text{(hydroperoxide} \xrightarrow[O]{H_2O} \text{phthalide} \xrightarrow{O} \text{PA.}$$

Citraconic anhydride and MA presumably originated from ring rupture of o-xylene or intermediate products.

Bernardini and Ramacci (1966) reported, in two papers,[85] that the reaction scheme for o-xylene oxidation to PA on V_2O_5 proceeds via the intermediate compounds o-methylbenzyl alcohol, o-tolualdehyde, o-toluic acid and phthalide. Optimum yield in individual steps varied from 83 to 95 mole %. Overall maximum yield of PA was 65 mole %.

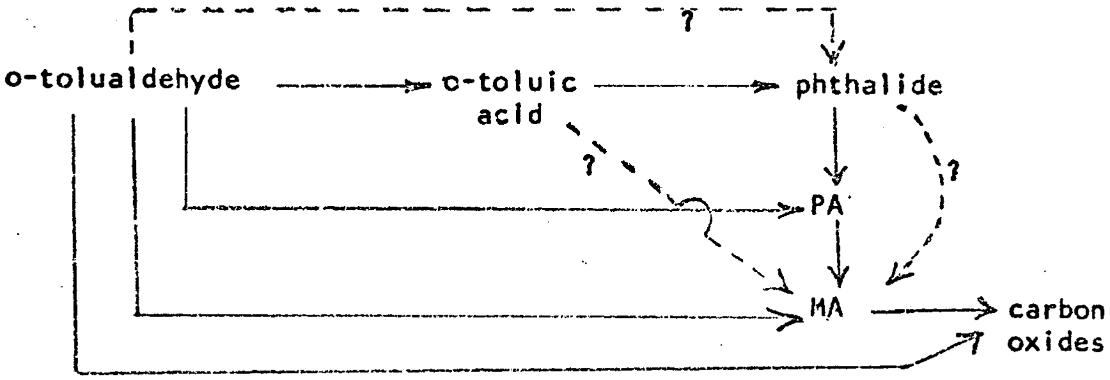
Products of the reaction were PA, MA, citraconic anhydride, phthalide, benzoic acid, o-tolualdehyde, o-toluic acid, unreacted o-xylene, water, carbon oxides, and other unknown products.

Matsumoto et al (1966) studied o-xylene oxidation[86] on V_2O_5-K_2SO_4

catalyst at 2:1 molar ratio of V_2O_5 to K_2SO_4. They concluded that the oxidation proceeds by three parallel paths: (1) PA formation, (2) MA formation, and (3) complete combustion to carbon dioxide. Their studies indicated that the heat of adsorption of PA on the catalyst was so large that inhibition by adsorption of PA on the catalyst surface could not be a significant factor in the mechanism.

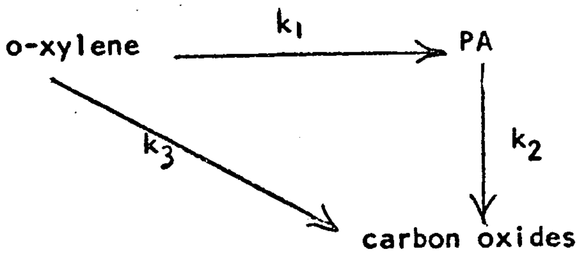
Vrbaski and Matthews (1966) paralleled their earlier work on oxidation of o-methylbenzyl alcohol[80] with this study of the oxidation of o-tolualdehyde.[87] Oxidations were conducted on fused V_2O_5, in a flow system, at contact times of 0.15-0.6 sec. at 360-460°C. The reaction scheme showed four parallel routes of o-tolualdehyde disappearance: (1) stepwise oxidation via o-toluic acid and phthalide to PA, (2) direct oxidation to PA, (3) formation of carbon oxides via MA, and (4) direct oxidation to carbon oxides. Data were analyzed over the more limited temperature range of 370 to 415°C to yield kinetics that were 0.97 order in o-tolualdehyde, and 0.5 order in oxygen when the oxygen concentration was below 0.2 atm. When 0.4 mole % o-tolualdehyde in nitrogen was fed to a fully oxidized V_2O_5 catalyst bed at 420°C and 0.6 sec. contact time, o-tolualdehyde was normally oxidized to PA for the initial period, then PA formation declined and ceased, as carbon oxides formation increased to a maximum. Thereafter, carbon oxides formation exponentially declined with time. At the conclusion of the experiment the catalyst was almost completely reduced to V_2O_4. The experiment led to the interpretation that surface oxygen participated during the initial PA production period, and that this was followed by more severe combustion using lattice oxygen as the catalyst was reduced.

Products during air oxidation of o-tolualdehyde during the most severe oxidations (450°C, 0.6 sec) were, in decreasing amount: PA, carbon oxides, unreacted o-tolualdehyde, MA, phthalide, o-toluic acid, per-o-toluic acid plus o-tolualdehyde peroxide and hydroperoxide, o-xylene, and a trace of o-formylbenzyl alcohol. No toluene or benzoic acid, formed by degradation reactions, were found. Rise and fall of product concentrations with reactor temperature led to the following reaction scheme:



A rate equation for o-tolualdehyde disappearance between 370-415°C was determined to be 0.97 order in o-tolualdehyde. The rate constant was given by: $\ell n\ k = 9.46-24750/RT$.

Froment (1967), in a design paper[88] based upon a two dimensional model, used as an example the following simplified triangular reaction scheme for the oxidation of o-xylene to PA:



Kinetics were assumed to be first order in reactant and pseudo zero order in o-xygen. The rate constants used were:

$$\ln k_1 = 19.837 - 27000/RT$$

$$\ln k_2 = 20.86 - 31400/RT$$

$$\ln k_3 = 18.97 - 28600/RT$$

Pollack (1967) reported V_2O_5 catalyst optimization studies.[89] o-Xylene at 1 mole % in air was oxidized to PA in a 1.1 meter tubular reactor. A 457-532°C hotspot temperature developed. The optimum catalyst for PA yield consisted of 1000 parts porous carrier and 100 parts V_2O_5, promoted with 20 parts of transition metal oxide, and inhibited with 4 parts of alkali metal existent in an undisclosed compound.

This catalyst had a surface area of 1.25 m^2/gm and negligible pore volume of 0.07 cm^3/gm. At a contact time of 0.2 sec., PA production was 70 mole % of o-xylene charged. Products, in decreasing amounts, were PA, CO_2, MA, CO, benzoic acid, phthalide, and o-toluic acid.

Kawasaki and Kogure (1967) analyzed minor condensation products existent in distillation residues from industrial production of PA from o-xylene.[90] They identified xanthone, fluorenone, anthraquinone, p-terphenyl, biphenyl, biphthalyl and 2-hydroxyphenyl-2-carboxylic acid lactone.

Mann and Downie (1968) studied the kinetics of o-xylene oxidation on an industrial V_2O_5/K_2SO_4 on silica catalyst.[91] This catalyst had a surface area of 52 m^2/gm. Contact time of 0.1 sec. was used in a differential, fixed bed, aluminum tubular reactor. Data were taken, at low conversion, using o-xylene concentrations from 0.9 to 3 mole % and oxygen concentrations from 6 to 47 mole %. Kinetic data were taken with a stable catalyst after 100 hours of operation. These data were correlated with a steady state adsorption model. The model assumes an equilibrium adsorption of oxygen on the catalyst surface, and subsequent reaction with gas phase hydrocarbon. This model yields a rate equation for reactant R and oxygen O:

$$r_R = \frac{(k_oC_o)\ (k_RC_R)}{(k_oC_o) + n(k_RC_R)},$$ where n is the stoichiometric number of oxygen moles per mole of reactant.

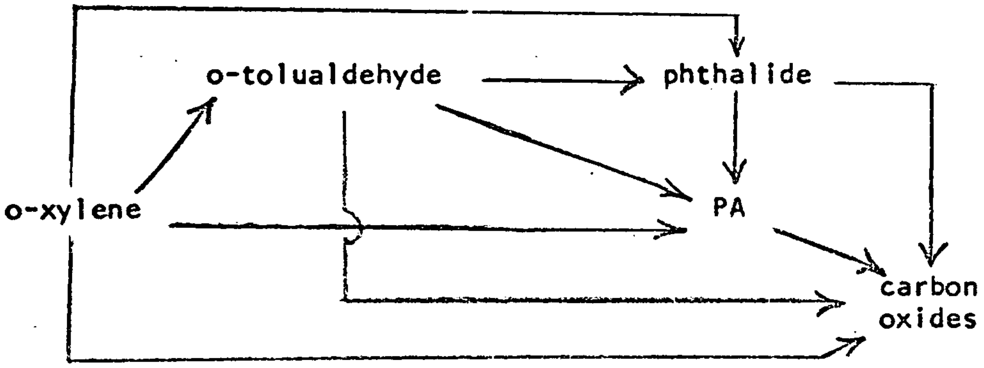
Derived constants were:

$T^{\circ}C$	k_o	k_R	n
300	2.1×10^{-5}	ca 4.2×10^{-4}	2.87
325	4.8×10^{-5}	ca 5.8×10^{-4}	2.87

These constants led to Arrhenius activation energies of E_o = 23 Kcal/mole and E_R = 8.7 Kcal/mole. It is noted that, when $n(k_RC_R) > (k_oC_o)$, the rate is relatively insensitive to the value of k_R.

These investigators used subtraction of blank, to remove catalytic effects of the reactor walls, in correlating the kinetic data. Reaction products were produced in higher than usual concentrations for analysis using 3 mole % o-xylene in 15% oxygen. Products, identified by infrared spectroscopy and gas chromatography, were o-tolualdehyde, o-phthalaldehyde, PA, phthalide, and p-benzoquinone. The last product was obscured by o-xylene in their chromatograph.

Herten and Froment (1968) studied the air oxidation of o-xylene to PA,[92] using a doped V_2O_5 on silica catalyst at 325-402°C. Activity of this catalyst was maintained by small amounts of SO_2 in the feedstream. The quasi-isothermal fixed bed reactor consisted of a 2.5 cm i.d. stainless steel tube containing catalyst and diluent glass beads. The feed contained 0.5-2 mole % o-xylene, and 10.6% to nearly pure oxygen. Product distributions at various reactor temperatures were used to determine the reaction scheme:



The conversion of o-tolualdehyde to phthalide was considered less important than other routes to PA. A simple single parameter rate equation that was first order in xylene and pseudo zero order in oxygen could not be fitted by the data. The three parameter power law equation used for rate of o-xylene disappearance had the form: $r_R = k\ P_O^n\ P_R^m$. Order n with respect to oxygen was constant at 0.3, while order m with respect to o-xylene increased from 0.2 to 0.6 with increasing temperature.

Increase of o-xylene order with increase in temperature led to consideration of an adsorption type rate equation. With assumed pseudo zero order in oxygen, the following two parameter rate equation results: $r_A = \frac{K_R P_A}{1 + k_s P_A}$. Activation energies were 16.2 kcal/mole for k_R, and 23.6 Kcal/mole for k_s.

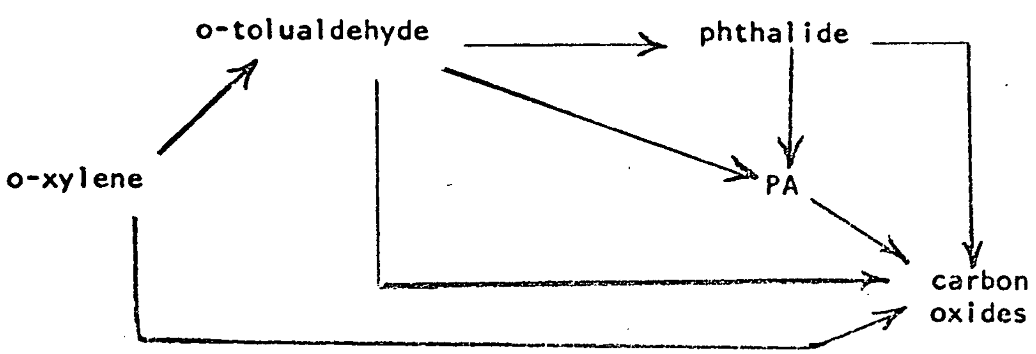
Duckworth (1969), in an industrial review of PA production,[34] cited secondary products from o-xylene oxidation as MA, carbon oxides, benzoic acid plus aldehydes, toluic acid, trimellitic acid and pyromellitic acid. The latter two products have not been reported by experimental investigations.

Juusola et al (1970) reported kinetics of air oxidation of o-xylene[93] in a differential, fixed bed, tubular reactor using the same batch of V_2O_5/K_2SO_4 on silica catalyst as was used by Mann and Downie.[91] A type 304 stainless steel reactor tube was inert when operated uncatalyzed at 290-310°C. The kinetic data were taken with 0.25-1.59 mole % o-xylene, and 2.5-50 mole % oxygen. During blank determinations, type 304 stainless steel was found less reactive than either glass or the type aluminum used in the previous investigation.[91] Kinetic data were corrected for catalyst ageing and activity reduction. Products of the reaction were o-tolualdehyde, p-benzoquinone, carbon dioxide and traces of CO. The product distribution remained essentially constant over the range of conditions studied. Conversions ranged from 0.5 to 6.3 mole % in the differential reactor. Changing order of the reaction rate data with concentration, indicated that one of five adsorption models might be applicable. Of these, the steady state adsorption model was preferred:

$$r_R = \frac{k_o C_o \; k_R C_R}{k_o C_o + n \; k_R C_R}$$, where n is the stoichiometric number for average products, and was 2.13

$\ell n \; k_o = 11.8 - 26000/RT$
$\ell n \; k_R = 16.8 - 28000/RT$

Vanhove and Blanchard (1971) discussed optimization of a V_2O_5 - V_2O_4 - TiO_2 catalyst for the oxidation of o-xylene.[94] Highest selectivity to C_8 products was 74 mole %. This selectivity was achieved with 85% wt. V_2O_5, 2.3% wt. V_2O_4, and 12.5% wt. TiO_2. Products observed at 66% conversion and 450°C were, in decreasing amount: PA, carbon oxides, o-tolualdehyde, phthalide, MA, diphthalaldehyde, benzoic acid, and o-toluic acid. No citraconic or dimethylmaleic anhydrides were observed. They proposed the simplified reaction scheme:



Blanchard and Vanhove (1971) reported, in a second paper,[95] that they had synthesized o-xylene with one C^{14}-labeled methyl group, and oxidized it at 1 mole % in air on V_2O_5 catalyst at 420°C and 30% conversion. O-tolualdehyde, PA and dimethylmaleic anhydride products had molar activity equal to o-xylene charged. Citraconic anhydride had half the o-xylene activity. Carbon oxides had one eighth of o-xylene activity, while MA was inactive. The inactivity of MA showed that all MA resulted from benzene ring rupture. Methyl- and dimethyl-1,4-benzoquinone were postulated as precursors of citraconic anhydride and dimethylmaleic anhydride.

Caldwell (1971) investigated the air oxidation of 1 mole % o-xylene using a commercial V_2O_5 on SiC catalyst.[96] Contact times of ca. 0.3 sec. were used in a type 321 stainless steel flow reactor of 2.5 cm. inner diameter and 2 meter length. Tube temperatures of 380-410°C resulted in catalyst hotspot temperatures of 420-498°C, located near the inlet. PA yields of 60 mole % were virtually independent of tube temperature, catalyst dilution, flow rate, or o-xylene feed concentration. Temperature profile along the reactor tube was not reproducable, being affected by changes in catalyst activity and oxidation state at different locations in the reactor.

Watt (1971) studied air oxidation of o-xylene[97] in a steel spinning basket recycle reactor using a commercial V_2O_5 on SiC catalyst at 391-432°C. O-xylene concentrations of 0.1-1.3 mole % and oxygen concentrations of 10-30 mole % were used at a mean residence time of approximately 5 seconds. Selectivity to PA averaged 25-30% at 432°C, and was seldom greater than 50%. Homogeneous PA combustion was postulated to account for the low selectivity. Carbon dioxide additions to the feed reduced PA yield. Attempts to fit the data for o-xylene disappearance with an adsorption type rate equation of the form: $r_x = \frac{a P_x}{1+b P_x}$ yielded a constant parameter $b = 20 \text{ atm}^{-1}$ over the temperature range. This is equivalent to an o-xylene reaction order of nearly 1. Data for o-xylene disappearance were fitted to a simple rate equation that was first order in o-xylene and zero order in oxygen:

$$r_x = k P_x \qquad \text{where } \ln k = 17.95 - 26300/RT$$

Above 1.6 mole % o-xylene in the feed stream catalyst deactivation occurred. Catalyst activity could be restored by reoxidation in an air stream.

A short nonisothermal fixed bed reactor of 5 cm. inner diameter aluminum was also used to oxidize o-xylene. The previous catalyst was diluted with three times its volume of alundum spheres, and used at a bed depth of 10 cm. This reactor was operated at wall temperature 370-490°C, with 0.5-1.0 mole % oxylene in air. Contact time in the bed was 0.5-2 sec., but product residence time in a large heated void area downstream from the catalyst bed was 1-4 sec. Catalyst bed temperature profile showed an axial hotspot 100°C above wall temperature. Maximum selectivity to PA was 65% at a tube temperature of 400-420°C; selectivity to PA was reduced to 40% at 480°C tube temperature.

The fixed bed reactor was converted to fluidized bed. The same catalyst, ground to small particle size, was used in its air-oxidized state. The short fluidized bed reactor was operated essentially isothermally at 400-520°C using o-xylene at 0.4-2.1 mole % in air. Conversions increased linearly with temperature, from 40-90%. Selectivity to PA was constant at 50% to 500°C, but decreased at higher temperature. These conversions and selectivities were less than anticipated from the recycle reactor data.

Ellis (1972), in a study primarily devoted to reactor modelling, further investigated the air oxidation of 1 mole % o-xylene in air.[98] Work was conducted in the same non-isothermal 2.5 cm. inner diameter tubular reactor, and with the same V_2O_5 on SiC catalyst, as used by Caldwell.[96] Product distributions were measured at tube temperatures of 400-450°C for diluted and undiluted bed depths to 86 cm. Maximum selectivity to PA was 70 mole % in the deeper beds. This selectivity was essentially independent of tube temperature. Catalyst deactivation occurred in the region of the catalyst hotspot when using 1.5 mole % o-xylene.

Kinetic data for rate of o-xylene disappearance were taken in diluted catalyst beds at 375-465°C and at 0.14-1.2 mole % o-xylene. These data were correlated using a rate law that was zero order in oxygen and 0.4 order in o-xylene:

$$r_x = k\, P_x^{0.4}$$

the rate constant, k, varied with temperature according to:

$$\ell n\, k = 22.70 - 36000/RT \quad \text{at } 375\text{-}430^\circ\text{C, and}$$

$$\ell n\, k = 7.31 - 15000/RT \quad \text{at } 435\text{-}465^\circ\text{C.}$$

A Langmuir-Hinshelwood rate equation of the form:

$$r_x = \frac{aP_x}{1+bP_x} \quad \text{was used with fixed parameter } b = 300 \text{ atm.}^{-1}$$

over the temperature range. Parameter a varied with temperature according to

$$\ln a = 23.98 - 33000/RT \qquad \text{at } 375\text{-}430°\text{C, and}$$
$$\ln a = 12.33 - 16000/RT \qquad \text{at } 435\text{-}465°\text{C.}$$

Two experiments were conducted to determine combustion of the PA product. In one, products from o-xylene conversion to PA, containing some unreacted xylene, were passed over soft glass spheres in stainless steel at 500°C, with a 2 sec. contact time. The PA was 50% combusted. A similar experiment, using alundum spheres in aluminum with lower conversion products from a recycle reactor, showed very little combustion of PA.

Data of Calderbank were reported for the oxidation of o-xylene and subsequent products in an aluminum alloy recycle reactor on the same V_2O_5 catalyst. First order rate equations for reactant disappearance were used. Rate constants were given by:

o-xylene	$\ln k = 3.31 - 5600/RT$	(440-570°C)
o-tolualdehyde	$\ln k = 2.88 - 4030/RT$	(288-500°C)
phthalide	$\ln k = 0.19 - 1380/RT$	(256-455°C)
PA	$\ln k = 18.57 - 29700/RT$	(440-570°C)

Sasaki (1972 studied the mechanism of o-xylene oxidation on V_2O_5 catalyst using differential thermal analysis and x-ray diffraction.[99] He concluded that the reaction was initiated by chemisorption of o-xylene on the catalyst, oxidation occurred by reduction of the catalyst surface, and that the catalyst surface was reoxidized. The use of Mo, W, and Sn oxides as promoters of V_2O_5 showed little effect on the oxidation reaction, a reaction which yielded ca. 50% of PA.

Slavinskaya et al (1972) oxidized o-xylene and other aromatics[100] using a V-Mo phosphate catalyst at 400-430°C in a recycle reactor at a space velocity of 23,000 $hr.^{-1}$ Overall conversion rates for the several hydrocarbons were approximately equal. They concluded that the rate determining step was chemisorption of oxygen for reoxidation of the reduced catalyst. Alanova et al (1972) reported that complete oxidation of o-xylene in excess air proceeded on a Pt/Ni-Cr catalyst at temperatures above 300°C.[101] The rate of carbon dioxide formation was 0.8 order in o-xylene at 300-320°C but was first order at 380°C. The rate was zero order in oxygen.

Juusola et al (1972) used a tubular flow reactor for kinetic parameter determination of the rate of oxidation of o-xylene.[102] Commercial V_2O_5/K_2SO_4 on silica catalyst, with a surface area of 70 m^2/gm, was used. A type 304 stainless steel reactor tube interferingly catalyzed the reaction at temperatures above 315°C, so experimental work was conducted over the range 270-300°C. Conversions were limited to 7%, in order to operate as a differential reactor. Data were statistically fitted with a steady state adsorption model based on oxygen adsorption on the catalyst surface, and reaction by o-xylene impingement from the vapor phase.

$r_R = \frac{(k_o C_o)(k_R C_R)}{(k_o C_o) + n(k_R C_R)}$, where n was 2.23-2.41, the stoichiometric number of oxygen moles for average products.

$\ell n\ k_o = 21.76 - 36300/RT$

$\ell n\ k_R = 6.34 - 15200/RT$

These specific rate constants and activation energies at 270-300°C are in substantial disagreement with their 1970 data at 290-310°C with the same catalyst, conditions and hardware.[93]

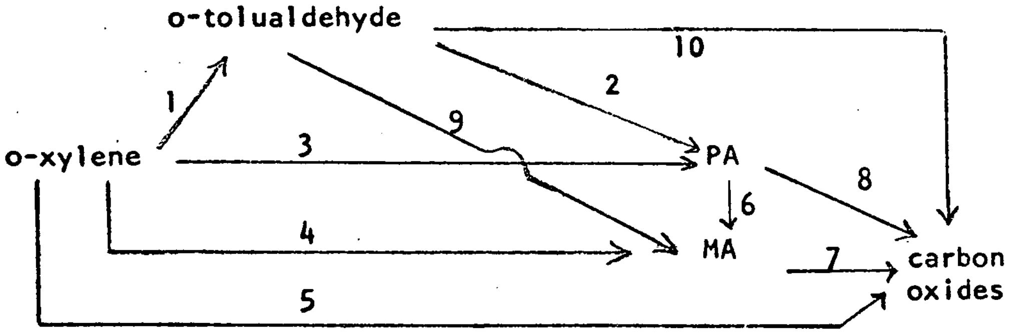
Calderbank and Caldwell (1972) reported data on 1 mole % o-xylene oxidation[103] in a single tube pilot reactor. The reactor had an inner diameter of 2.5 cm, and packed length of 2 meters.[96] Catalyst was commercial V_2O_5 on SiC. Temperature profiles showed that the reaction was nearly complete a short distance from the inlet. Selectivity to PA was

58-60% being independent of temperature (370-418°C) and the flowrate (0.84-1.26 ft^3/min of air). Activation energies for the production of PA and combustion of o-xylene were the same. Combustion of PA was negligible.

Sharipov et al (1972) reported that they had oxidized o-xylene to 87-90% pure PA with an overall yield of 93-95%.[104] This would be equivalent to a 70-74 mole % yield of PA. V_2O_5 containing 0.8% Nb_2O_5 was used at 425-430°C at space velocity 2500 $hr.^{-1}$ and air/xylene ratio of 30-35.

Haber et al (1973) measured the reduction rate of a series of industrial V_2O_5 catalysts for the oxidation of o-xylene to PA.[105] Catalyst reduction by hydrogen was diffusion limited. Catalytic activity of these catalysts for PA formation was measured by a pulse technique. No apparent correlation existed between a catalyst's reduction parameters and its selectivity for forming PA.

Lyubarskii et al (1973) reported their investigations of o-xylene at seq. oxidations on a high temperature, unpromoted V_2O_5 catalyst.[106] Using a glass, external recycle tubular reactor at a flow rate of 800 liters/hr., they measured kinetics of air oxidation of 0.1-0.8 mole % o-tolualdehyde at 400-460°C. Their o-xylene oxidation scheme contains major elements in agreement with those of most other investigators:



They noted that PA oxidation was inhibited by o-xylene at one tenth the PA concentration, and that PA strongly inhibited MA oxidation. Therefore, those further degradation paths were effectively closed. Most significant elements of o-tolualdehyde oxidation are to PA, to carbon oxides, and to MA. Rate of o-tolualdehyde disappearance was found to be independent of oxygen concentration in the range of 11-20 mole %, and independent of water and carbon dioxide concentrations.

Assuming that o-tolualdehyde disappearance was similarly affected by the interaction of PA and MA products, a rate equation along any one reaction path (based on Elovich adsorption at catalyst sites specific to that path) would vary according to:

$$r_i = \frac{k_i\ (b_{Ti}\ C_T)}{1 + (b_{Ti}C_T) + (b_{PAi}C_{PA}) + (b_{MAi}C_{MA})}\text{, where i is}$$

the reaction path considered, subscripted b is the adsorption coefficient of a component on sites specific to path i. This rate equation displays varying order in o-tolualdehyde concentration and retardation by PA and MA in the system. Oxidations to the various products are considered to take place at different types of catalyst sites. Adsorption coefficients may vary among the several species adsorbed at the different kinds of sites. The above equation may be simplified since concentration of o-tolualdehyde, C_T, was greater than C_{PA} and C_{MA}. Lyubarskii also assumed that $b_T C_T \gg b_{PA} C_{PA}$ and $b_{MA} C_{MA}$, therefore the last two denominator terms could be deleted, giving this simplified form:

$$r_i = \frac{k_i b_{Ti} C_T}{1 + b_{Ti} C_T}$$

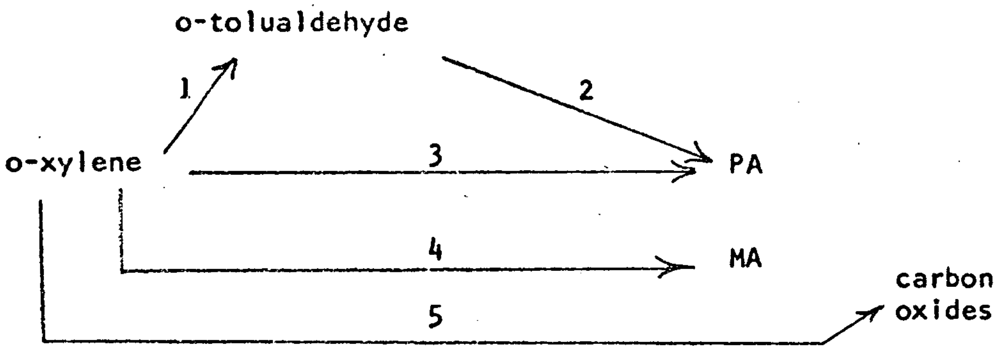
Experimental data were satisfactorily fitted along paths 2, 9, and 10 of the o-xylene reaction scheme. Rate constants are given by:

$$\ln k_2 = 4.68 - 16200/RT$$

$$\ln k_9 = 3.85 - 18700/RT$$

$$\ln k_{10} = 14.35 - 32000/RT$$

Kinetics of the oxidation of o-xylene were similarly determined. Arguments were advanced justifying the deletion of degradative paths 6,7,8,9 and 10 that involve o-tolualdehyde, PA and MA combustion. The remaining simplified scheme consisted of:



Since carbon dioxide did not inhibit the reactions, a general rate equation along any of the paths in the simplified reaction scheme is:

$$r_{ij} = \frac{k_i C_{ij}}{1 + A_i C_x + B_i C_T + C_i C_{PA} + D_i C_M}$$

where i = path of the reaction scheme,
and j = component

Experimental data were best fitted by the following rate constants:

$$\ln k_1 = 15.9 - 19600/RT$$

$$\ln k_2 = 9.85 - 10300/RT$$

$$\ln k_3 = 21.9 - 26000/RT$$

$$\ln k_4 = 24.2 - 31500/RT$$

$$\ln k_5 = 22.9 - 27200/RT$$

An immediate question arises: why must $\ln k_2$ derived from direct o-tolualdehyde oxidation differ so widely in magnitude and activation energy from $\ell n\ k_2$ shown above for the same reaction in the o-xylene scheme? Tishchenko and coworkers (1973) made systemmatic identification of byproducts existent in PA produced by air oxidation of o-xylene.[107] Industrial catalysts K-235, K-63B and KFK gave different product distributions due to their differing selectivities. Products identified, after hydration of anhydrides, were benzoic acid, o-toluic acid, maleic and succinic acids, monomethylmaleic acid, dimethylmaleic acid, phthalide, o-methoxy benzoic acid, phthalic acid, benzene tricarboxylic acids, and benzene tetracarboxylic acids.

Products using K-235 under mild oxidation conditions were dimethyl-MA, o-tolualdehyde, phthalide, dimethyl-PA and PA. Lactone of 2´-methylol-diphenyl-2-carboxylic acid, lactone of 2-methylol-3´-methyldiphenyl-2-carboxylic acid, lactone of 2´-methylol-3,3´-diphenyl-2-carboxylic acid, 9,10-anthraquinone, monomethyl anthraquinone, dimethyl anthraquinone, and three unidentified products were formed.

Ichinokawa et al (1973) taught methods of preparing porous V_2O_5 catalysts using TiO_2 mixed with sulfur to yield a porous support.[108] After forming and sintering this support, it was impregnated with $VOSO_4$-K_2SO_4 solution, dried and fired to yield a porous catalyst containing 13.5% wt. V_2O_5. This catalyst, after SO_2 activation, and with continuing small amounts of SO_2 in the o-xylene air feedstream, yielded 72 mole % PA at 390°C and a space velocity of 4000 $hr.^{-1}$

Suvarov et al (1973) taught that improved V_2O_5-TiO_2 catalysts could be produced by tableting and sintering.[112] These catalysts were abrasion resistant and effective for the oxidation of o-xylene to PA. Air containing 0.5 mole % o-xylene, passed over catalyst in a molybdenum glass reactor tube at 390°C, yielded 64.5 mole % PA at high space velocity. Racz and coworkers (1973) reported that the air oxidation of o-xylene occurred in a silimanite (Al_2O_3-SiO_2) lined flow reactor.[113] No reaction occurred at 400°C, but combustion did occur at 500°C.

Ono et al (1973) taught the use of seven component V_2O_5 catalysts for oxidation of o-xylene to PA.[109] Different catalysts, placed at inlet and outlet ends of the tubular reactor, gave improved selectivity to PA. Andreikov and Rusyanova (1973) reported that their recycle reactor investigations of o-xylene and o-tolualdehyde oxidations on industrial catalysts showed three main parallel reaction paths.[111] These paths were: (1) via sequential side chain oxidations through o-tolualdehyde, o-toluic acid, and phthalide to PA; (2) via direct oxidation of both methyl groups to PA; (3) complete combustion via formation of unstable quinones.

The oxidations of intermediate products were inhibited by o-xylene, while o-xylene oxidation was inhibited only by o-tolualdehyde.

In a second paper Andreikov et al (1973) reported further studies[110] on the oxidation of o-xylene to PA at 340-420°C. They used a variety of vanadium oxides with differing initial oxidation states, and analyzed the surface oxide structure of the used catalysts. Each oxide showed different selectivities to PA and to o-tolualdehyde. This was interpreted as meaning different products were formed at different active centers.

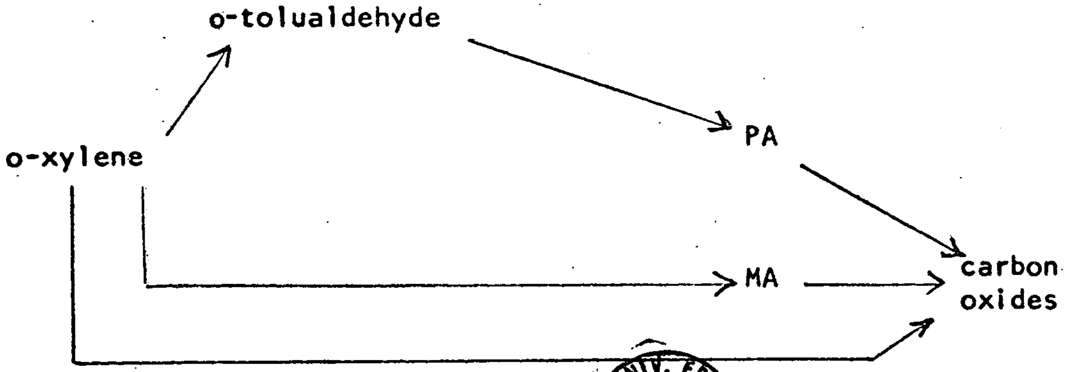
Fluid Bed o-Xylene Oxidation

Rollman (1952) reported a 60% molar yield of PA when 2-2.5 mole % o-xylene was oxidized on V_2O_5 in a fluid bed at 480-550°C.[114]

Bhattacharyya and Krishnamuthy (1959, 1963) investigated the air oxidation of o-xylene on a fluidized bed of fused V_2O_5 at 490°C. At 1 mole % o-xylene feed and at space velocity 10,000 hr.,$^{-1}$ maximum conversion to PA was 67.8%, and to o-tolualdehyde was 3.56%. Carbon dioxide, traces of quinone, and some MA were formed. Product distributions varied from catalyst to catalyst and differed from those obtained in static beds of the same type catalyst. Similar oxidation of m-xylene and of p-xylene failed to yield significant quantities of isophthalic and of terephthalic acids.[115,116]

Costa-Novella and Escardino-Benlloch (1962, 1963) presented, in a series of three papers,[117] their data on the air oxidation of 1-2 mole % o-xylene. A fluidized bed of $V_2O_5/K_2SO_4/SiO_2$ catalyst was used at 310-370°C. They found that they needed to reactivate their catalyst every 12-14 hours by heating it to 400°C in a stream of air.

Maximum combined yield of PA and MA was 67 mol % at 310°C. Additional products were o-tolualdehyde, carbon oxides and water. They adopted a reaction scheme.



First order kinetics were assumed, independent of oxygen concentration, throughout the data analyses. Rate laws for disappearance of reactants were of the form $r_R = k P_R$. Derived rate constants,[98] for the several steps of their reaction scheme, in moles/Kgm. hr. atm. were:

o-xylene to o-tolualdehyde: $\ln k = 10.94 - 9200/RT$
o-xylene to carbon oxides: $\ln k = 20.49 - 22900/RT$
o-xylene to MA: $\ln k = 6.78 - 5400/RT$
o-tolualdehyde to PA: $\ln k = 13.50 - 11350/RT$
o-tolualdehyde to carbon oxides: $\ln k = 17.74 - 18600/RT$
PA to carbon oxides: $\ln k = 20.93 - 25000/RT$
MA to carbon oxides: $\ln k = 17.56 - 18000/RT$

Carra and Beltrame (1964)(1965) air oxidized 0.25-1. mole % o-xylene using V_2O_5 on silica in a fluidized bed at 410 and 460°C. They considered that the reaction consisted of o-xylene oxidation to products, followed by products combustion to carbon dioxide. Derived kinetics were 0.5 order for o-xylene disappearance:[118] $r_x = k P_x^{0.5}$ where rate constant k with units of moles/gm. hr. atm.$^{0.5}$ was expressed by: $\ln k = 30.00 - 14800/RT$. Analogous oxidation of p-xylene at 420-510°C yielded MA, p-tolualdehyde, p-toluic acid, and p-benzoquinone.[119]
No terephthalic acid was formed. They concluded that o-xylene was 5-6 times more reactive than p-xylene to air oxidation.

Satterfield and Loftus (1965) reported their investigations of vapor-liquid oxidation of o-xylene in foaming melts of V_2O_5 - K_2SO_4 and V_2O_5 - $K_2S_2O_7$ mixtures.[120] A V_2O_5 - $K_2S_2O_7$ eutectic mixture containing 14 wt. % V_2O_5, 60% K_2SO_4 and 26% SO_3 was molten above 270°C. O-xylene at 1.1 mole % in air was bubbled through V_2O_5 - K_2SO_4 melt at 500°C. Residence time was estimated at 2 sec. in the bubbles, and 15 sec. in the foam. About 40% conversion of o-xylene occurred, and yielded o-tolualdehyde as the principal product. When o-xylene at 0.4-1.2 mole % in air was bubbled through the V_2O_5 - $K_2S_2O_7$ melt at 425-455°C, up to 50% conversion occurred. Principal products were o-tolualdehyde and carbon dioxide. Significant decomposition of $K_2S_2O_7$ occurred, giving troublesome quantities of SO_3 in the vapor phase, and it would be probable that some simultaneous sulfonation of aromatics occurred.

Aliev et al (1965) determined kinetics of oxidation of o-xylene to PA in a "boiling layer" or short fluid bed of KO-33 Russian commercial catalyst at 380-420°C.[121] They determined that o-xylene disappearance was independent of oxygen and occurred by three parallel routes: (1) first order in o-xylene to PA, independent of reaction products; (2) first order in o-xylene to carbon dioxide; (3) 0.5 order in o-xylene to MA. Rate constants for these reactions, in moles/gm. hr. atm.^{n}, were:

o-xylene to PA: $\ln k = 7.66 - 15300/RT$
o-xylene to carbon dioxide: $\ln k = 8.10 - 17200/RT$
o-xylene to MA: $\ln k = 1.10 - 14000/RT$

Abo et al (1967) oxidized o-xylene in a fluid bed reactor at 370-410°C using 0.3-0.8 mm particles of $V_2O_5/K_2SO_4/TiO_2$ catalyst.[122] Overall rate for o-xylene disappearance was first order in o-xylene, but reaction rate increased with particle size. Activation energy similarly increased from 4. to 10. Kcal/mole with increased particle size.

Imamverdiev et al (1973) developed a model for the oxidation of o-xylene to PA in a fluidized catalytic bed.[124] This was based on the kinetics of Aliev.[121]

Cheavens and Montgomery (1973) taught that they had succeeded in deactivating their fluid bed catalyst to prevent afterburning of PA using a titania supported catalyst.[123] Composition of their multicomponent catalyst, in wt. %, was 2.7 V_2O_5, 4.0 Sb_2O_3, 7.5 $Cs_2S_2O_7$, 15.6 $K_2S_2O_7$ and 70.2 TiO_2. A small SO_2 content is required in the feedstream to retain activity. The fluid bed was operated at 1.4 atm., 380°C and with a mean residence time of 8 seconds. A feedstream containing 2.6 mole % o-xylene in air was converted to 72 mole % PA, 6 mole % MA and small amounts of o-tolualdehyde at 97% conversion.

Fixed Bed Naphthalene Oxidation

Shortly after the air oxidation of o-xylene to PA on V_2O_5 was reported, the air oxidation of naphthalene to PA was developed.

Gibbs and Conover (1918) taught that PA, phthalic acid, benzoic acid and naphthoquinones were formed by the air oxidation of naphthalene[126] over V_2O_5 at 350-550°C, and preferably at 500°C. Similar results were reported over MoO_3.

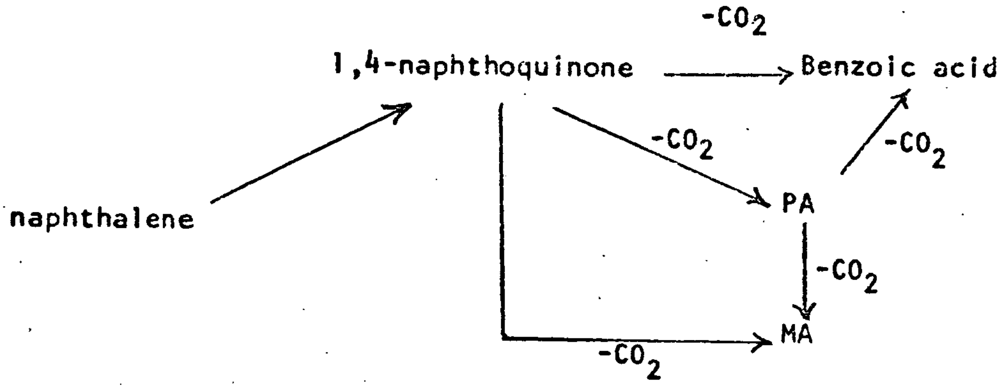
Wohl simultaneously developed naphthalene oxidation to PA on vanadia catalysts.[127]

Craver (1924) reported that naphthalene was readily air oxidized to PA on catalysts containing V_2O_5 and/or MoO_3.[163] He found that the addition of oxides of Na, Cu, Pb, Co, Al and Cd decreased the yield of PA and increased that of MA.

Maxted (1928) introduced tin vanadate as a low temperature catalyst for the oxidation of naphthalene and o-xylene to PA at 280-290°C.[63]

Marek and Hahn (1932) reviewed PA production by vapor phase air oxidation of coal tar naphthalene over catalysts containing vanadia.[125] Products were PA, naphthoquinones, MA, benzoic acid, carbon dioxide and water, with possible traces of ethylene and acrylic acid. During the period to 1930, operation at 330-400°C yielded maximum PA over fused or supported V_2O_5 catalysts. The accumulated reaction scheme involved 1,4-naphthoquinone as an intermediate, to the practical exclusion of 1,2-and 2,6-naphthoquinones, due to its much greater reactivity.

Marek and Hahn's reaction scheme was:



Industrial processes obtained 80 mole % yield of PA from 78° (95% pure) coal tar napthalene using V_2O_5 catalysts. V_2O_5 was found to be more active, less volatile and more selective to PA than MoO_3.

From 1935, German industrial processes began to be based upon a V_2O_5/K_2SO_4 silica gel catalyst which was active at low temperatures, and was selective for the oxidation of naphthalene to PA. This industrial work became public in a series of post World War II industrial reviews that have been summarized by Sittig.[128]

Marisic (1940) studied mixed catalysts,[129] and concluded that phospho-vanado-tungstate was better than a variety of phosphorus and molybdenum containing catalysts. This phospho-vanado-tungstate catalyst was comparable in activity with V_2O_5 for conversion of naphthalene to PA and MA, accompanied by traces of 1,4-naphthoquinone and benzoic acid.

Porter (1942) taught that the inclusion of small amounts of P_2O_5 moderate activity of V_2O_5 catalysts for naphthalene to PA.[130]

Brown and Fraser (1942) studied a series of molybdo-tungsto-silicic acid mixed catalysts[132] for the oxidation of naphthalene, 1,4-naphthoquinone and PA. They concluded that 1,4-naphthoquinone was not an important intermediate between naphthalene and PA, but speculated that one of the other naphthoquinones 1,2-or 2,6-might be involved. They observed that 1,4-naphthoquinone was combusted at three times the rate of naphthalene, and produced a much smaller yield of PA.

Sasayama (1943) used tin vanadate for the production of benzoic acid from naphthalene at 31% selectivity.[131]

Staatsmijnen in Limburg (1949) taught that V_2O_5 containing 5-15% wt. SnO_2 improved the selectivity of V_2O_5 for naphthalene oxidation to PA.[133] Maximum selectivity to PA was 79 mole %.

Schoen and Zoon (1949) reported that titanium vanadate catalysts yielded up to 90% selectivity for naphtalene to PA conversion.[134] Optimum titania content was about 67 mole %, while larger amounts of titania promoted complete combustion.

Calderbank (1952) concluded that 1,4-naphthoquinone was not an intermediate in the formation of PA from naphthalene.[135] Naphthoquinone and PA must be formed by simultaneous reactions. Using high naphthalene concentrations at 310-360°C on V_2O_5 catalyst, he obtained low conversions and concluded that PA formation was zero order in naphthalene, but controlled by oxygen adsorption. Rate of 1,4-naphthoquinone formation was more rapid than PA formation.

Ioffe and Sherman (1954) reported extensive kinetic studies[136] of naphthalene oxidation on V_2O_5 - K_2SO_4 catalyst at 260-400°C. Products, at contact times 0.05-0.5 sec., were PA, MA, 1,4-naphthoquinone, carbon dioxide and water. Rate of naphthalene disappearance was expressed by

$$r_N = \frac{k_1 C_o}{1 + k_2 C_p^2}$$

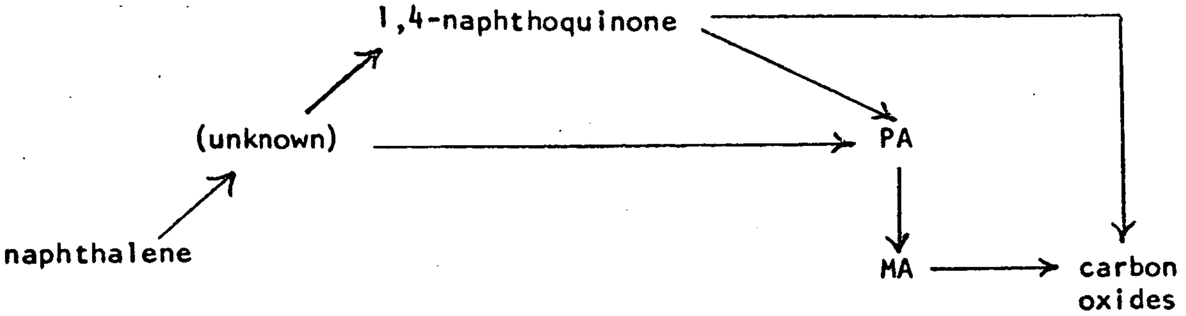
over a range of naphthalene concentrations, where C_o is oxygen concentration and C_p is products concentration. This rate equation indicated that the rate determining factors were desorption of products and oxidation of the catalyst surface. This was the first indication that product inhibition plays an essential role in the kinetics of naphthalene oxidation. Temperature dependence of the rate constants was fitted by:

$$\ell n\ k_1 = 22.36 - 27400/RT$$

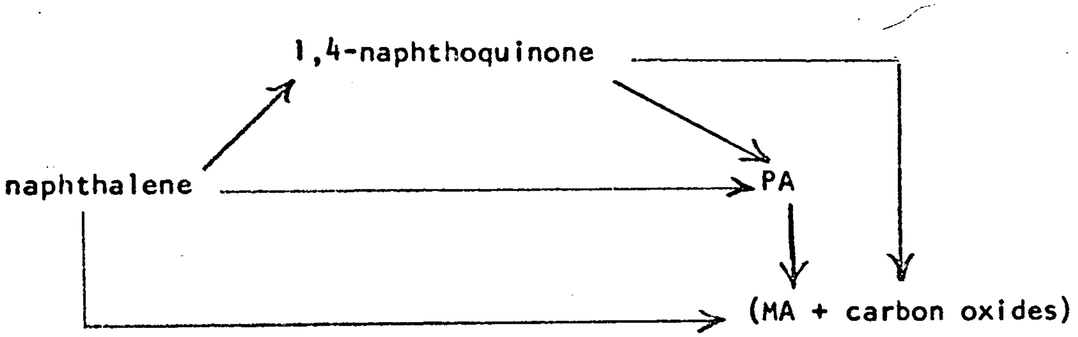
$$\ell n\ (k_2 - 9 \times 10^6) = 28.32 - 47500/RT$$

Non-Arrhenius behavior of k_2 suggests a progressive decrease in apparent activation energy with temperature.

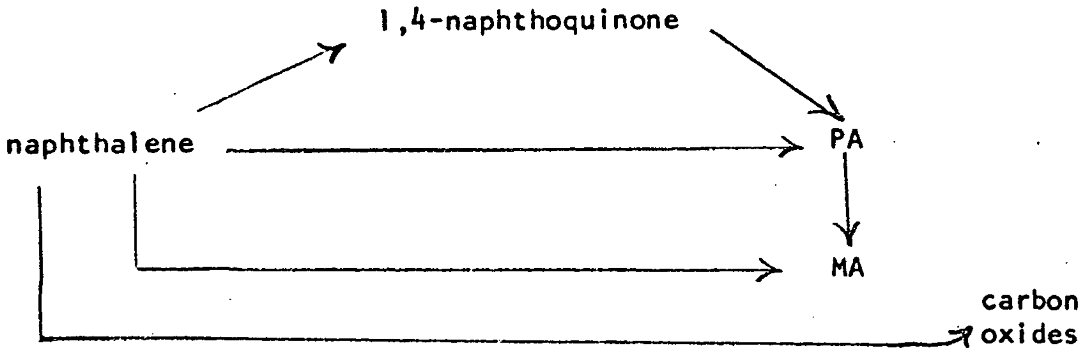
Ioffe and Sherman (1955) reported their kinetic studies of the oxidation of 1,4-naphthoquinone, PA and MA on a V_2O_5-K_2SO_4 catalyst.[164] They showed that naphthoquinone could not be the principal intermediate between naphthalene and PA, because PA yield from naphthoquinone was only 20-25%. Activation energies for reactant disappearance were 11500 cal/mole naphthoquinone, 26000 cal/mole PA, and 10500 cal/mole MA. They proposed a reaction scheme containing an unknown, short lived oxygenated intermediate:



D'Alessandro and Frakas(1956) presented fixed bed data for naphthalene oxidation[137] on fused V_2O_5, supported V_2O_5 and supported V_2O_5 - K_2SO_4. A stainless steel reactor was used at 340-475°C. Product compositions at various contact times and temperatures were measured. They concluded that no significant differences existed among catalysts. Reaction order was one for naphthalene disappearance at very low concentrations. They believed that their data were kinetically controlled, and free of mass transfer limitations. Proposed reaction scheme for naphthalene disappearance involved three parallel routes:



Ushakova, Korneichuk and Roiter (1957) oxidized naphthalene in a recycle reactor over crystalline V_2O_5 to avoid internal diffusion effects.[138] They developed a reaction scheme which showed that naphthalene directly formed four products:



Order of naphalene dependence and activation energies for the four parallel paths are:

(1) naph. to 1,4-NQ:	2nd order	32700 cal/mole
(2) naph. to CO_2:	1st order	37200 cal/mole
(3) naph. to MA :	0.5 order	31600 cal/mole
(4) naph. to PA:	1st order	34700 cal/mole

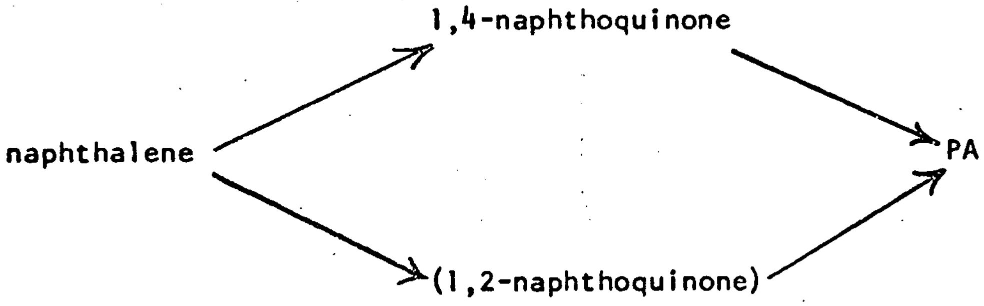
They noted that increased naphthoquinone concentration did not affect the rate of PA formation, but decreased the rate of carbon oxides formation, and increased the rate of MA formation. They postulated existence of an unknown intermediate product that interfered with combustion to carbon dioxide.

Kornelchuk et al (1958) reported that naphthalene inhibits PA combustion on lower vanadium oxides existent at the inlet of an industrial 380-400°C reactor.[139]

Vol'fson and coworkers (1960) compared V_2O_5 and V_2O_5-K_2SO_4 - SiO_2 catalysts.[140] They found substantial difference existed in reactant reaction orders for the various steps of the successive, parallel reaction scheme:

reaction step	V_2O_5	V_2O_5-K_2SO_4
naph. to PA	1	0
naph. to MA	0.5	1
naph. to 1,4-NQ	2	1
naph. to carbon oxides	1	-
1,4-NQ disappearance	1	1
MA disappearance	1	1

Shelstad et al (1960) used V_2O_5 - K_2SO_4 catalyst for naphthalene oxidation at 300-335°C.[141] Among the usual products, they found a small concentration of 1,2-naphoquinone. The 1,2-NQ concentration decreased as PA concentration increased. This led them to conclude that both 1,2- and 1,4-NQ were intermediates in the reaction scheme:



Their kinetic data for naphthalene disappearance were best fitted by first order in oxygen and variable zero to first order in naphthalene. Therefore, the Hinshelwood[82] equation was used. This equation has the form:

$$r_R = \frac{(k_oC_o)(k_RC_R)}{(k_oC_o) + n(k_RC_R)}$$, where n is the stoichiometric number of oxygen moles per mole of reactant.

This type of rate equation is based upon steady state adsorption of oxygen molecules, without dissociation on the catalyst surface, and upon reaction occurring as reactant impinges upon the catalyst surface from the vapor phase.

Korneichuk et al (1960) reported PA yields of 76-78% mole % from naphthalene using V_2O_5 - K_2SO_4-silica gel catalyst at 370-390°C.[142] This compares with less than 70 mole % from a partially reduced commercial V_2O_5 catalyst.

Stukanovshaya and Roiter (1960) used V_2O_5 containing lattice O^{18} for naphthalene oxidation.[143] Isotopic concentration of the catalyst remained constant; this conclusively showed that alternate redox of the catalyst was not involved in naphthalene oxidation at 398°C.

Roiter and coworkers (1961) used a flow circulation (external recycle) reactor to study naphthalene oxidation[144] on V_2O_5 - K_2SO_4 catalyst at 330-360°C. They determined that the rate of PA formation was zero order in naphthalene and first order in oxygen. The rate of naphthalene oxidation was also zero order in naphthalene and first order in oxygen, but was inhibited by the naphthoquinone intermediate in a complex manner. The rate law for naphalene oxidation was:

$$r_n = \frac{a\ C_o}{(C_{NQ})^{0.6}(1+bC_{NQ})}$$

Grossianu and Kohn (1961) studied the effects of various additive and support materials[145] for naphthalene oxidation to PA on V_2O_5. An aluminum metal support gave higher selectivity to PA than any of the other support materials investigated. This was interpreted as the result of a lower catalyst surface temperature due to the high thermal conductivity of aluminum.

Peterson (1962) smoothed and reanalyzed[146] the kinetic data of Ioffe and Sherman[136] for naphthalene oxidation. He determined best fit parameters using nonlinear estimation. The original investigators had concluded that the overall reaction order in naphthalene decreased with temperature. Peterson found that the data could be statistically better fitted by a first order in naphthalene dependence if a concurrent downward estimate of activation energy was made. Such a downward estimate could be plausibly explained by internal pore diffusion.

Odrin et al (1968) showed that the rate of air oxidation of naphthalene on V_2O_5 catalyst greatly exceeds both the rate of V_2O_5 reduction by naphthalene, and the rate of V_2O_4 reoxidation by air.[147] They further concluded, from IR studies, that the stationary composition of the catalyst is a function of temperature and concentration of substance being oxidized, resulting in catalyst reduction and the formation of surface compounds.

Aleksandrov and coworkers (1972) reported a dual effect of SO_2 on the activity of V_2O_5/K_2SO_4 on silica gel for the air oxidation of naphthalene.[148,149] At concentrations below 0.08% in the naphthalene-air mixture, SO_2 promotes catalyst activity; above 0.14%, the catalyst is reversibly poisoned, resulting in reduced activity and selectivity to PA.

Kratochvil (1973) reported 9,10-dihydroxynaphacenequinone as a minor product among the tarry condensation materials resulting from naphthalene oxidation.[150]

Rus'yanova and Zhilina (1973) reported that thionaphthalene, at 0.4% of naphthalene being oxidized to PA, stabilized a vanadium complex catalyst (presumably V_2O_5 - K_2SO_4).[151] At 1.25% wt. of thionaphthalene, the PA yield was maximized as the 1,4-naphthoquinone yield was minimized.

Ishida et al (1973) taught that a $V_2O_5/TiO_2/K_2SO_4/Li_2SO_4$ catalyst produced 95-102 wt % PA and less than 0.2% 1,4-naphthoquinone from the air oxidation of naphthalene.[152] The oxidation was conducted at 470°C at a space velocity of 6000 $hr.^{-1}$

Fukui and coworkers (1973) taught that the air oxidation of naphthalene could yield 30-40% of 1,4-naphthoquinone over a supported $V_2O_5/K_2SO_4/K_2S_2O_7$ catalyst at 380°C and 1500 hr^{-1} space velocity.[153]

Fluid Bed Naphthalene Oxidation

Following construction and operation of the Sherwin-Williams fluid bed process for the oxidation of naphthalene to PA in 1945, several groups of research workers focused their attention on the process.

Beach and Connolly (1949) taught that 1 mole % naphthalene could be air oxidized in the presence of 40 mole % steam at 460°C. A fluidized bed of V_2O_5 on sintered silica gel catalyst yielded 77 mole % PA at 0.1 sec. mean contact time.[157]

Mars and van Krevelen (1954) presented data on the air oxidation of naphthalene, and several other aromatics, in a fluidized bed.[158] Kinetics of naphthalene disappearance were measured at one gas velocity and mass of V_2O_5/K_2SO_4/silica gel catalyst at 300-337°C. The fluidized bed was chosen for its isothermal characteristics; it was treated as a plug flow, integral reactor. Assuming kinetics that were first order in naphthalene and first order in oxygen, they adopted a cyclic redox mechanism of the Eley-Rideal type, wherein naphthalene was oxidized by catalyst reduction and the catalyst was reoxidized by air. This mechanism yielded the steady state redox model, which gives a rate equation for naphthalene disappearance:

$r_R = \frac{(k_o C_o)(k_R C_R)}{(k_o C_o) + n(k_R C_R)}$, where n is the stoichiometric number of oxygen molecules involved. On manipulation this yields:

$r_R = \frac{k_R C_R}{1 + K_1 C_R}$, where K_1 is $\frac{nk_R}{C_o}$. This equation is identical in form with that of Hinshelwood.[82]

Franklin, Pinchbeck and Popper (1956) reported results of an investigation by United Coke and Chemicals Co. on development of an optimized $V_2O_5/K_2SO_4/SiO_2$ catalyst for fluid bed air oxidation of naphthalene to PA.[159] Their results indicated that rate was proportional to oxygen concentration, and that the rate of oxygen adsorption upon the catalyst surface was controlling. Products were the same as obtained in the fixed bed processes: PA, MA, 1,4-naphthoquinone and carbon oxides.

Pinchbeck (1957) interpreted data of the previous paper,[159] and found that kinetics of naphthalene disappearance were 0.8-0.9 order in naphthalene.[160] Surface kinetics were controlling below 400°C.

Mars (1958) presented further data on the rate of air oxidation of naphthalene on V_2O_5/K_2SO_4/silica gel catalyst in a fluid bed over the temperature range of 250-500°C. He concluded that the rate of naphthalene disappearance was mainly dependent on catalyst reoxidation at low temperatures, and dependent on naphthalene reduction of the catalyst at the higher temperatures.[161]

Dixon and Longfield (1960) reviewed literature data through 1956 and presented the data of Booth and Fugate (proprietary, American Cyanamid Co.) for the air oxidation of naphthalene to PA in a fluidized bed of $V_2O_5/K_2S_2O_7/SiO_2$ catalyst. At 1% naphthalene in air, the kinetics were 0.5-1.0 order in naphthalene, and 0.7-1.0 in oxygen. The oxidation scheme was consistent with findings of other investigators in fixed bed studies.[78]

Tsipenyuk and coworkers (1973) reported advantages for a pressure increase in fluid bed reactors for oxidation of naphthalene to PA on V_2O_5-K_2SO_4-silica get catalyst. Pressure increase to 2 atm. reduced optimum operating temperature by 30°C, and raised catalyst bed efficiency.

Phthalic Anhydride Oxidation

Craver (1924) oxidized PA, at 12 mole % in air, over V_2O_5 at 425°C, with a contact time of 0.4 second.[163] His experiments showed that 53% of PA underwent complete combustion and conversion to MA. Benzoic acid was also formed.

Marisic (1940) observed that Ni, Cr, and Fe oxides promoted the oxidation of PA.[129] For naphthalene oxidation to PA, mixed oxide catalysts containing P, Mo, W and Si were more selective to PA than either V_2O_5 or WO_3.

Brown and Fraser (1942) air oxidized PA over 3-molybdo-9-tungsto-silicic acid at 490°C. Measured products were MA and carbon oxides.[132] Conversion of PA was increased with time, as space velocity was reduced. They tentatively concluded that MA produced during naphthalene oxidations had originated from PA. They observed that PA and MA were burned at approximately the same rate, and that high carbon dioxide concentrations suppressed the air oxidation of PA to MA.

Ioffe and Sherman (1955) oxidized PA and MA over V_2O_5/K_2SO_4 on silica gel catalyst.[164] They used a tubular reactor in a lead bath over the temperature range 350-480°C. First order rate constants for MA oxidation were 15-20 times greater than for PA oxidation, in the temperature range 350-400°C. Arrhenius activation energies for PA and MA were, respectively: 26000 and 10500 cal/mole. They proposed a sequential reaction scheme from PA to MA and from MA to carbon oxides.

D'Alessandro and Farkas (1956) during naphthalene oxidation studies on fused V_2O_5 catalyst, derived first order rate constants for the several steps of their reaction sequence.[104] They reported a relative rate constant for PA formation direct from naphthalene that was 10 to 20 times greater than the rate constant for oxidation of PA to MA and carbon oxides.

Ushakova et al (1957) reported that lower vanadium oxides readily oxidize PA.[165] Naphthalene concentrations inhibit PA oxidation, and simultaneously reduce V_2O_5 to lower oxides. Thus, an industrial reactor operates with some lower vanadium oxides, but does not burn more of the PA produced, because of naphthalene inhibition. They further found that PA was easily oxidized on Cu, brass, Al and glass; oxidation rate increased as the metals were oxidized.

In a second paper Ushakova and coworkers[138] used a coursely crystalline V_2O_5 catalyst to avoid the effects of internal pore diffusion during naphthalene et seq. oxidations. They found that MA directly originates from the oxidation of naphthalene and from PA.

Korneichuk et al (1958) substantiated Ushakova's report[165] that naphthalene suppresses oxidation of PA. They recommended use of the shortest reactor contact time consistent with acceptable conversion at 380-400°C.[139]

Burney and Hoff (1960) reported that PA stability was shown by the fact that four times the contact time was needed for PA oxidation to MA, than was needed for oxidation of naphthalene to MA.[55]

Booth and Fugate (1960) studied the oxidation of PA to MA and carbon oxides using a fluidized bed of V_2O_5 - $K_2S_2O_7$ on silica catalyst at 325-375°C.[166] Disappearance rate of PA was somewhat less than first order with respect to PA, and was 0.5-0.8 order in oxygen. Activation energy for PA oxidation was 29 Kcal/mole.

Vol'fson and coworkers (1960) studied kinetics of PA oxidation on V_2O_5 in a glass recycle reactor at 422-462°C.[167] They concluded that PA disappearance was first order for PA, but was hindered by reaction products, and that complete PA combustion to carbon oxides was independent of PA concentration. They proposed the following rate laws to account for their findings:

PA disappearance: $r = \frac{k_1 \; C_{PA}}{C_{\text{Products}}}$, and

PA combustion to carbon oxides: $r = k_2$.

Numerical values of the rate constants were given by:

$$\ell n \; k_1 = 25.49 - 58120/RT$$

$$\ell n \; k_2 = 12.41 - 40920/RT$$

These investigators postulated that the catalyst has centers of varying activity. Complete combustion takes place on the most active centers, leaving oxidation to take place homogeneously or at the less active centers. Hughes and Adams (1960) found that PA was 15% oxidized at 575°C in an empty steel reactor, while an empty borosilicate glass reactor was inert.[83] PA was oxidized on a fused V_2O_5 on SiC catalyst at 497-575°C, with a contact time of 0.1 sec. The rate of PA oxidation was independent of oxygen concentration above 10 mole %. Below 10 mole % oxygen, anomalous effects due to catalyst reduction were observed. Measured product was MA. Carbon oxides were also formed. Postulated mechanism involved a model based on unimolecular surface reaction. This model involved steady state PA adsorption, redox on the surface producing products and reduced catalyst, product desorption, and very rapid catalyst reoxidation. Form of the resultant rate equation reduced to that of Hinshelwood.[82] Hinshelwood treatment was based on steady state oxygen adsorption on the catalyst surface, and reaction occurred by reactant impingement from the vapor phase. Both models reduce to the same mathematical form:

$r_R = \frac{a \, P_R}{1+bP_R}$, where a and b are temperature-dependent parameters.

When an exponential form of rate equation, $r_R = k \, P_R^n$, was applied to the

Hughes and Adams data, the order n with respect to PA was found to increase from 0.36 to 0.53 with temperature.

Yield of MA increased linearly with PA partial pressure, and decreased with temperature.

DeMaria and coworkers (1961) presented more Booth and Fugate (American Cyanamid, proprietary) data for the oxidation of PA on a fluid bed of V_2O_5 - K_2SO_4 on silica catalyst.[168] Mean contact times of 4-15 sec. were used at 375-400°C. Oxygen dependence of the rate constant was 0.8 power, over the range of 10 to 20 mole % oxygen, and PA dependence was 1.0 or less. Mixing in the fluidized bed was characterized as perhaps closer to a plug flow reactor than to a completely mixed reactor.

Costa-Novella and Escardino-Benlloch (1963), in their work with o-xylene oxidation in a fluid bed of $V_2O_5/K_2SO_4/SiO_2$ at 310-370°C, derived first order rate equations for their reaction scheme.[117] All MA was assumed to originate directly from o-xylene, and products of PA oxidation were assumed to be carbon oxides. Rate constants, first order in reactant, were expressed by:

$$\text{PA to carbon oxides:} \quad \ln k = 20.93 - 25000/RT$$

$$\text{MA to carbon oxides:} \quad \ln k = 17.56 - 18000/RT$$

Carra and Beltrame (1964) reported that PA and MA products of o-xylene oxidation were burned to carbon oxides[118] on a fluidized bed of V_2O_5 on SiO_2 at 410 and 460°C. Mean contact time was 5 sec. Combustion of PA and MA combined was represented by a rate equation that was first order in the sum of PA plus MA. The combined combustion reaction had an apparent activation energy of 31.6 Kcal/mole.

Bernardini and Ramacci (1966) found that PA was 8-13% oxidized in an empty stainless steel tubular reactor at 500°C and 0.14 sec. contact time.[85]

Under the same conditions, 1% of the PA was oxidized in an empty glass reactor.

On V_2O_5 catalyst, in the glass reactor, 70 to 80% of PA fed was oxidized at 500°C and 0.07 sec. contact time. These investigators proposed that the oxidation of PA is inhibited by the presence of o-xylene or intermediate products.

Vrbaski and Matthews (1966) reported o-tolualdehyde et seq. oxidations on fused V_2O_5 in a flow reactor.[87] They adopted, as part of their reaction scheme, the steps PA to MA, and MA to carbon oxides. They proposed that part of the MA and carbon oxides observed was formed from all of the precursors of PA.

Froment (1967) presented a triangular o-xylene, PA, and carbon oxides reaction scheme as basis for a two dimensional model for tubular reactor design.[88] The PA to carbon oxides rate equation was assumed pseudo first order in PA, and had a rate constant expressed by: $\ln k = 20.86 - 31400/RT$.

This was considered representative of industrial experience in 360°C tubular reactors, using $V_2O_5/K_2S_2O_7$ catalyst and 1 mole % o-xylene in air, at near atmospheric pressure.

Pollak (1967) developed a three component catalyst containing V_2O_5-alkalai metal salt inhibitor - transition metal oxide promoter, for o-xylene oxidation to PA.[89] This catalyst was used to oxidize PA to MA, carbon oxides and traces of benzoic acid. PA was twice as stable as MA towards oxidation at 375-500°C.

Blanchard and Vanhove (1971) prepared PA with a carbon-14 label in the anhydride ring.[95] This PA was oxidized at 450°C on V_2O_5 to give 10% conversion to inactive MA, and to give carbon oxides with some activity.

This showed that part of the carbon oxides originated from the anhydride ring, and all of the MA came from the benzene ring.

Calderbank and Caldwell (1972) reported negligible combustion of PA formed by air oxidation of o-xylene with V_2O_5 on SiC at 370-418°C, in a single tube pilot plant reactor.[103]

Ellis (1972) searched for a tail gas component, from a long tubular reactor oxidizing o-xylene on V_2O_5, that was believed to inhibit PA oxidation.[98] None was found. The PA-containing stream from this reactor, at high xylene conversion, was 50% oxidized on glass beads in a stainless steel tube at 500°C and 2 sec. contact time.

Lyubarskii et al (1973) conducted experiments at 480°C on V_2O_5 in an external recycle reactor to study the influence of o-xylene on the oxidation rate of PA.[106] Without o-xylene, PA was 40% oxidized. With a PA to o-xylene molar ratio of 8, complete stability of PA was observed. A similar strong inhibition of MA oxidation by PA presence was demonstrated. It was postulated that o-xylene similarly inhibits MA oxidation.

In a second paper Lyubarskii et al[106] cited previous PA oxidation data of Roiter et al (1963).[169] These data showed apparent activation energies of 41 Kcal/mole for PA to carbon oxides, and 58 Kcal/mole for PA to MA. Lyubarskii and coworkers studied the air oxidation of PA on V_2O_5 at 440-500°C. They used concentrations of 0.06-0.24 mole % PA in air. Oxidation of PA at 500°C was not detected, but 4% was oxidized at 580°C in an empty quartz reactor. Catalyzed oxidation of PA on V_2O_5 in the recycle reactor was reported as proceeding by two parallel paths to MA, and to extensive oxidation products.

A zero order reaction relative to oxygen was found over the range of 10-21 mole % oxygen. The reaction kinetics were unaffected by water vapor or carbon dioxide concentrations. Kinetics of the PA to MA path were represented by:

$$w_1 = \frac{k_1\ b_{PA}C_{PA}}{1+b_{PA}C_{PA}}\ ,\ \text{where } \ell n\ k_1 = 17.2 - 41700/RT \text{ and}$$

b is an adsorption coefficient.

Kinetics of the PA to extensive oxidation products path were zero order in PA, and are represented by:

$$w_2 = k_2,\ \text{where } \ell n\ k_2 = 15.95 - 37200/RT.$$

Sharipov et al (1973) studied the relative oxidation stability of PA and its methyl derivatives on V_2O_5 at 350-550°C and reported that decreased stability of the methyl derivatives was apparently due to an alteration of symmetry.[170]

Maleic Anhydride Oxidation

Hammar (1952) used V_2O_5-M_oO_3 on aluminum in a tubular reactor to air oxidize MA to carbon oxides.[171] At 375-400°C, MA oxidation was first order in MA, and had an activation energy of 28 ± 4 Kcal/mole.

Holsen (1954) oxidized low concentrations of MA at 325-400°C using V_2O_5 on Al_2O_3. Products were carbon oxides. An activation energy of 8-14 Kcal/mole was indicated.[172]

Steger (1960) conducted air oxidation of MA to carbon oxides on a fixed bed of V_2O_5-MoO_3-Ag_2O-Al_2O_3 on SiC catalyst at 400-500°C. Kinetics were zero order in oxygen concentration, and about 0.5 order in MA. The activation energy was 16 Kcal/mole.[173]

Vol'fson et al (1960) reported differences in reaction orders involved in naphthalene et seq. oxidations between V_2O_5 and a V_2O_5 - K_2SO_4 on SiO_2 catalyst. Oxidation of MA was found to be first order in MA on both catalysts.[140]

Ioffe and Lyubarskii (1962) studied the kinetics of benzene oxidation to MA in a glass recycle reactor at 380-440°C, using a V_2O_5 - MoO_3 on Al_2O_3 catalyst.[174] They concluded that MA inhibits benzene oxidation. Oxidation of MA was first order in MA, and independent of oxygen concentrations above 10 mole %. Rate constant for combustion of MA was given as $\ln k_2 = 7.38 - 12650/RT$. Rate of combustion of MA was an order of magnitude smaller than rate of benzene oxidation to MA.

Costa-Novella and Escardino-Benlloch (1963), in their study of o-xylene oxidation to PA on V_2O_5, derived a rate law that was first order in MA, for the MA to carbon oxides reaction.[117] The rate constant was expressed by: $\ln k = 17.56 - 18000/RT$.

Ioffe and Lyubarskii (1963) measured the kinetics of air oxidation of MA using V_2O_5 - MoO_3 - P_2O_5 on Al_2O_3 catalyst at 360-460°C. They found that the kinetics, over a wide range of MA concentrations, were first order in MA and zero order in oxygen.[175] Rates were unaffected by carbon oxides and water vapor concentrations. The rate constant was expressed by $\ln k = 7.27 - 12500/RT$. No appreciable homogeneous reaction was observed at 460°C. They suggested that this oxidation is one of the rare cases where catalyst redox and lattice oxygen participate in the reaction. They noted that benzene oxidation to MA was strongly inhibited by MA.

Pollak (1967) investigated MA oxidation on a three component V_2O_5 catalyst at 400-500°C. He concluded that relative stabilities to air oxidation of PA, MA, and benzoic acid were in the ratio of 3:2:1 in his non-isothermal, pilot plant, single tube flow reactor.[89]

Schaefer (1967) reported that he had oxidized MA on a series of reduced vanadia catalysts.[176] No differences in activity were found over the composition range V_2O_4 - V_2O_5.

Kirk-Othmer (1968) stated that the products of benzene oxidation to MA were MA, maleic acid, carbon oxides, water and unreacted benzene.[177]

Ahmad et al (1970) studied the oxidation of 1 mole % MA in air over V_2O_5 - MoO_3 and V_2O_5 - Cr_2O_3 on silica catalysts at 300-500°C.[178]

Prachensky (1972) studied the homogeneous oxidation of up to 0.5 mole % MA in dry air at 350-450°C with contact times to 5 seconds.[179] MA disappearance followed a first order rate law at 425°C. Temperature dependence of the rate constant was given by $\ln k = 12.91 - 21400/RT$.

Brown and Trimm (1972) reported extensive over-oxidation of MA at 415°C, in an empty 316 stainless steel tubular reactor, yielding carbon dioxide. Benzene presence did not affect the over-oxidation. No oxidation occurred in an empty glass reactor. Oxidation of MA was reported to be small on a vanadia-molybdena catalyst in the glass reactor.[180] The same catalyst contained in a stainless steel reactor yielded 95% conversion of MA to carbon dioxide and water, at contact times of about 0.4 sec. These data demonstrate the high catalytic activity of stainless steel.

Lyubarskii et al (1973) studied the kinetics of air oxidation of MA on V_2O_5 catalyst in a glass recycle reactor at 380-500°C.[106] The rate of MA oxidation was found to be first order in MA, and independent of concentration of oxygen, carbon dioxide and water vapor, in agreement with their earlier work.[175] It was found that PA presence inhibits the rate of MA oxidation.

The appropriate rate equation is: $r_{MA} = \frac{k\, C_{MA}}{1+b_{PA}\, C_{PA}}$, where r_{MA} = rate in moles/gm. hr., concentrations C are moles/liter and b_{PA} is a temperature dependent adsorption coefficient. Temperature dependence of the rate constant was given by $\ell n\, k = 8.493 - 11400/RT$. Homogeneous oxidation of MA was not observed at 500°C. Products of the catalytic oxidation were carbon oxides and water.

4. Discussion of Literature Survey

After 50 years of industrial PA production, catalysts have been optimized for increased yield at the best compromise of high space velocity and low reactor temperature. Applied research, done in laboratories of the process licensors, yields little basic information in the patent and trade literature. Basic research, performed in other laboratories, has been directed towards determining the reaction scheme and the reaction kinetics involved in PA production.

A. Reaction Schemes

Evolutionary versions of reaction schemes for PA production have contained the same intermediates and products. The assembly and relative importance of principal reaction steps in reaction schemes has shown little uniformity. Research workers have used catalysts with different selectivities, have worked under diverse reaction conditions, have measured various products and have differed in the interpretation of their data.

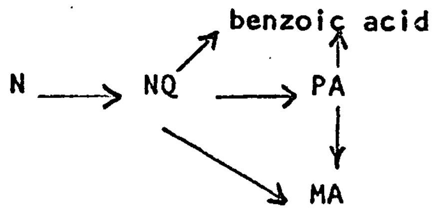
Figure 2 shows reaction schemes for the oxidation of naphthalene(N) to 1,4-naphthoquinone (NQ), PA, MA and carbon oxides (COX). Investigators have agreed that PA is formed directly from naphthalene and via naphthoquinone, and that MA originates from PA. There is disagreement on the source of carbon oxides, for they were shown as originating from naphthalene, from naphthoquinone, from both, or from neither. Some investigators have shown carbon oxides coming from MA, and others have considered that route inconsequential. There is disagreement whether MA is formed directly from naphthalene, but all agree that PA is a source of MA.

Although the naphthalene scheme remains unresolved, there has been little activity in the past decade. Limited naphthalene availability, and

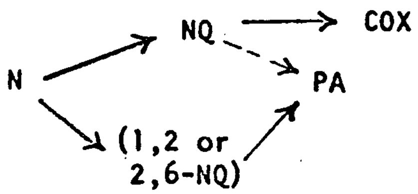
Figure 2

Reaction Schemes: Naphthalene Oxidation

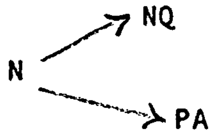
Marek and Hahn[125] (1932)



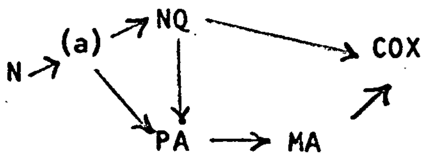
Brown and Fraser[132] (1942)



Calderbank[135] (1952)

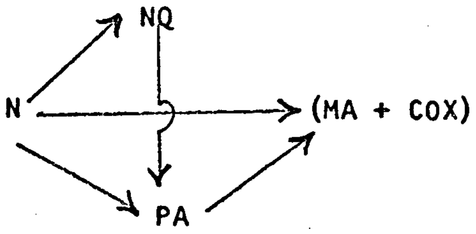


Ioffe and Sherman[164] (1955)

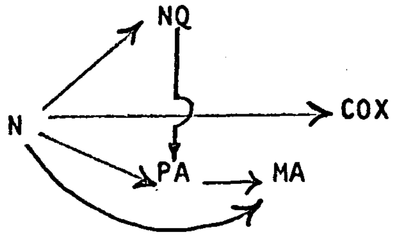


a unknown

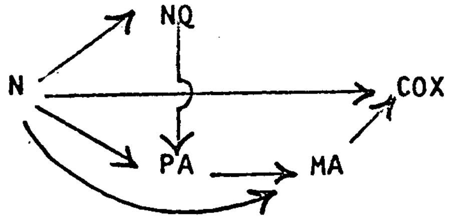
D'Alessandro and Farkas[137] (1956)



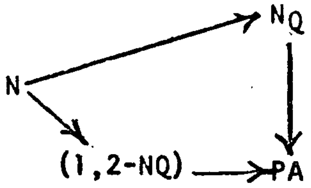
Ushakova et al[138] (1957)



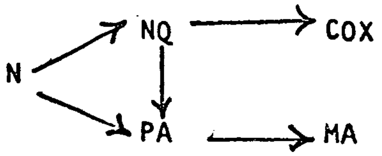
Vol'fson et al[140] (1960)



Shelstad et al[141] (1960)



Peterson[146] (1962)



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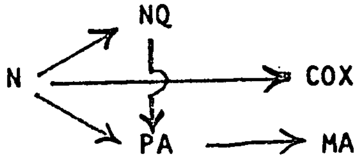


increased PA demand have directed efforts toward study of the oxidation of o-xylene.

Reaction schemes for o-xylene oxidation are compiled in figures 3 and 4. These figures show o-xylene (x), o-tolualdehyde (T), o-toluic acid (TA), o-methylbenzyl alcohol (OMBA), phthalide (P), PA, MA and carbon oxides (COX). The major route from o-xylene to PA has been subject to different interpretations. Three paths to PA have been used, either alone or in parallel: (1) directly from o-xylene to PA (in 10 schemes), (2) via o-tolualdehyde bypassing phthalide (in 8 schemes), and (3) via o-tolualdehyde through phthalide (in 7 schemes). Many investigators have considered the route from phthalide to PA a minor one, due to phthalide combustion. Eight schemes have eliminated the disappearance of PA from their reaction schemes, in order to simplify them. Nine schemes show PA to MA and/or carbon oxides.

The source of MA has been subject to disagreement among investigators. MA has been shown as originating from one or more sources: o-xylene, PA and intermediates. Some workers have considered MA to be a minor by-product.

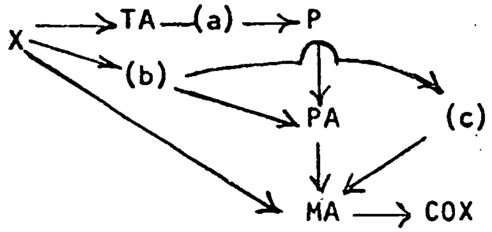
Reports are divergent on the several sources of carbon oxides. All agree that o-xylene was one of those sources. Differences in research emphasis have led to reports that carbon oxides originate: (1) solely from o-xylene, (2) also from PA or MA, and (3) also from PA or MA and intermediates.

There is no one accepted reaction scheme from o-xylene to PA. The latest schemes should be the best ones, because they are a summation of prior work, and are based upon later analytical methods. There is wide divergence between the recent schemes of Lyubarskii and of Andreikov,

Figure 3

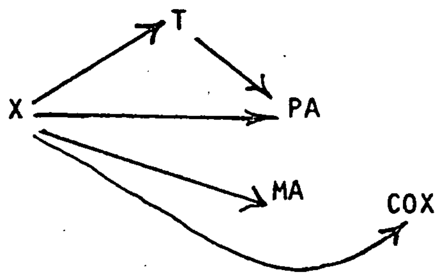
Reaction Schemes: o-Xylene Oxidation

Levine[72] (1955)

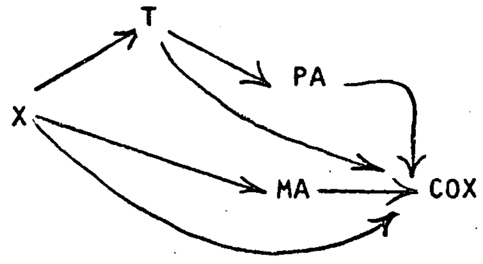


a o-hydroxymethylbenzoic acid
b phthalic acid
c benzene to benzoic acid

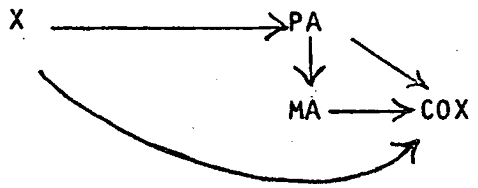
Simard et al[73] (1955)



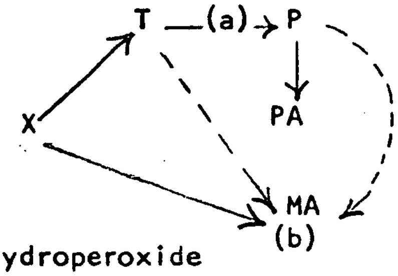
Costa-Novella and Escardino-Benlloch[117] (1963)



Carra and Beltrame[118] (1964)

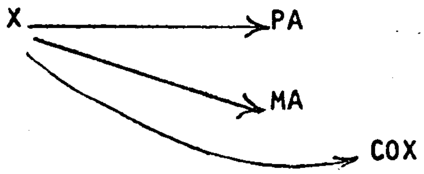


Pichler and Obenaus[84] (1965)

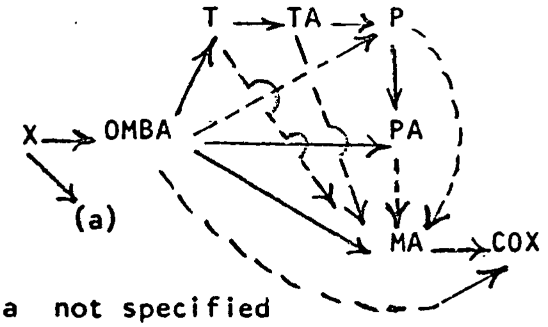


a hydroperoxide
b citraconic anhydride

Aliev et al[121] (1965)

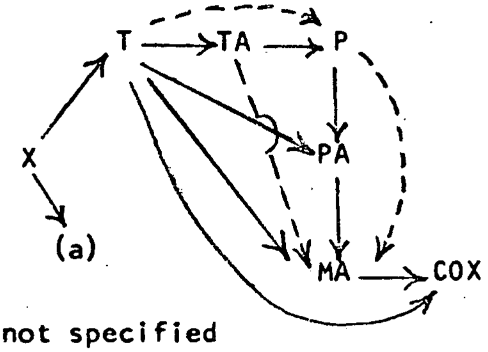


Vrbaski and Matthews[80] (1965)



a not specified

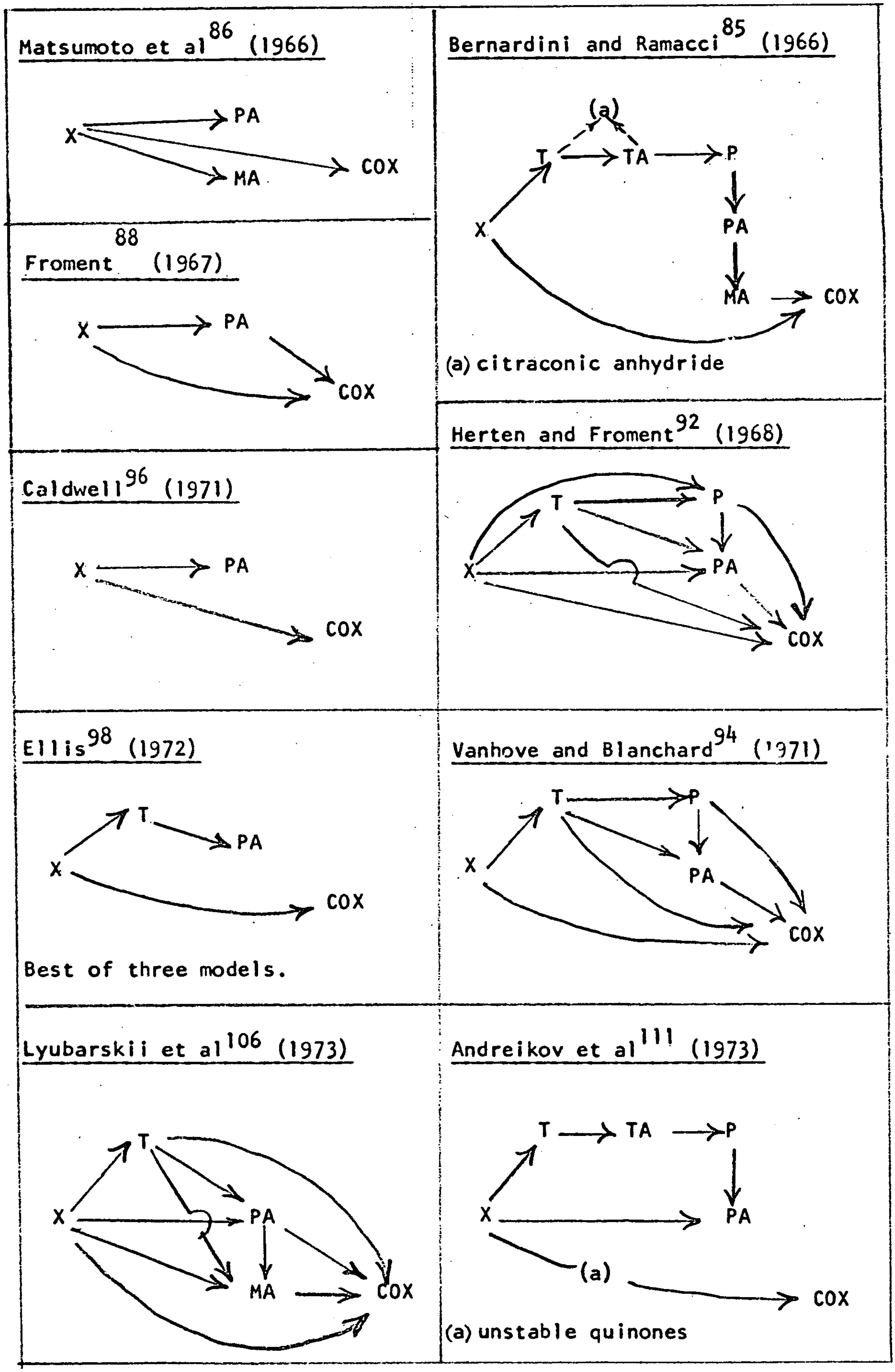
Vrbaski and Matthews[87] (1966)



a not specified

Figure 4

Reaction Schemes: o-Xylene Oxidation



Matsumoto et al[86] (1966)

Bernardini and Ramacci[85] (1966)

(a) citraconic anhydride

Froment[88] (1967)

Herten and Froment[92] (1968)

Caldwell[96] (1971)

Ellis[98] (1972)

Best of three models.

Vanhove and Blanchard[94] (1971)

Lyubarskii et al[106] (1973)

Andreikov et al[111] (1973)

(a) unstable quinones

shown at the bottom of figure 4. A synthesis of the several reaction schemes would be expected to contain all of the important reaction steps, and also to contain some relatively minor steps. Maximum yields from o-xylene to PA are 75-77 mole %. The reaction schemes suggest that combustion reactions accompany the desired sidechain oxidations. These combustion reactions are most likely to be: (1) aromatic ring rupture of o-xylene and intermediates to carbon oxides and/or MA, and (2) decarboxylation and ring rupture of PA to form MA and carbon oxides.

Productive areas that require further investigation to clarify the overall reaction scheme are: (1) to determine whether any MA is formed directly from o-xylene, and (2) to elucidate the reaction scheme involved in the combustion of PA. A defined PA combustion sequence would clarify the terminal portion of the overall reaction from o-xylene to PA and byproducts. Relative importance of this terminal portion of the scheme would be evident from a study of the kinetics of PA disappearance.

B. Kinetics

Kinetics of PA oxidation have been studied by four groups of workers. Ioffe and Sherman[164] used a non-isothermal steel tubular reactor at 0.4-0.8 second contact time. Costa-Novella and Escardino-Benlloch[117] used a fluid bed at a mean contact time of several seconds. Hughes and Adams[83] used a non-isothermal rectangular glass box reactor at 0.1 second. Lyuborskii and coworkers[106] used a gradientless, glass, external recycle tubular reactor.

Figure 5 is an Arrhenius plot showing the existent rate data on PA oxidation to all products. Data points represent rate per gram of catalyst at a 0.5 mole % PA concentration. None of the data was taken over a very broad temperature range. Data of Hughes and Adams was obtained

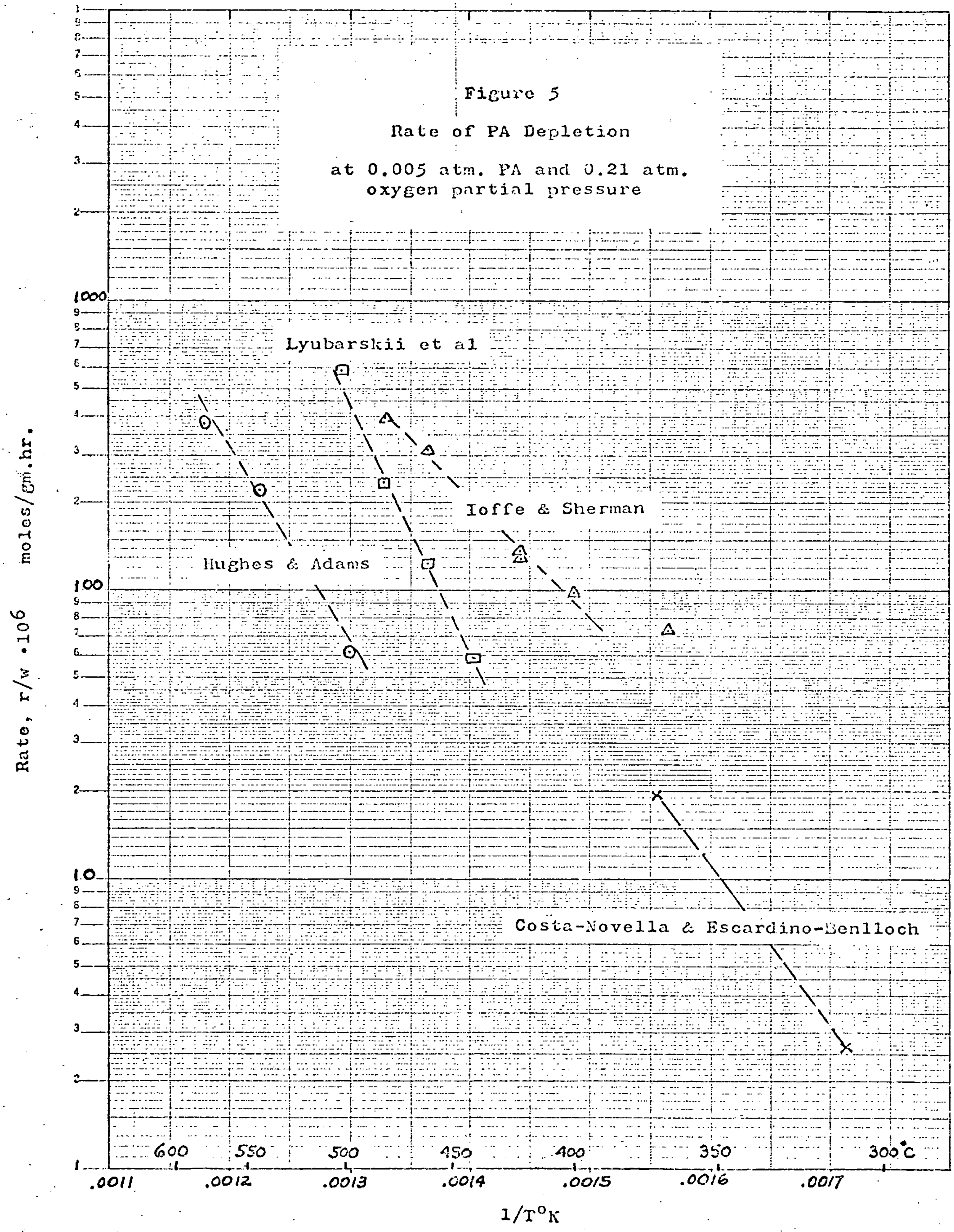


Figure 5

Rate of PA Depletion

at 0.005 atm. PA and 0.21 atm. oxygen partial pressure using a V_2O_5 on SiC catalyst, while the other data were measured using V_2O_5 - K_2SO_4 on silica catalysts. Since increased catalyst activity would elevate the lines connecting data points, the Hughes and Adams V_2O_5 catalyst appears to have been a decade lower in activity than the others.

It would be desireable to obtain one set of data over an extended temperature range, using the same catalyst.

Figure 6 shows the recycle reactor data of Lyubarskii[106] and the integral reactor data of Hughes and Adams.[83] This figure shows that the rate of PA oxidation to all products is concentration dependent, and follows an adsorption type rate law:

$$r = \frac{k\ bP}{1 + bP},$$

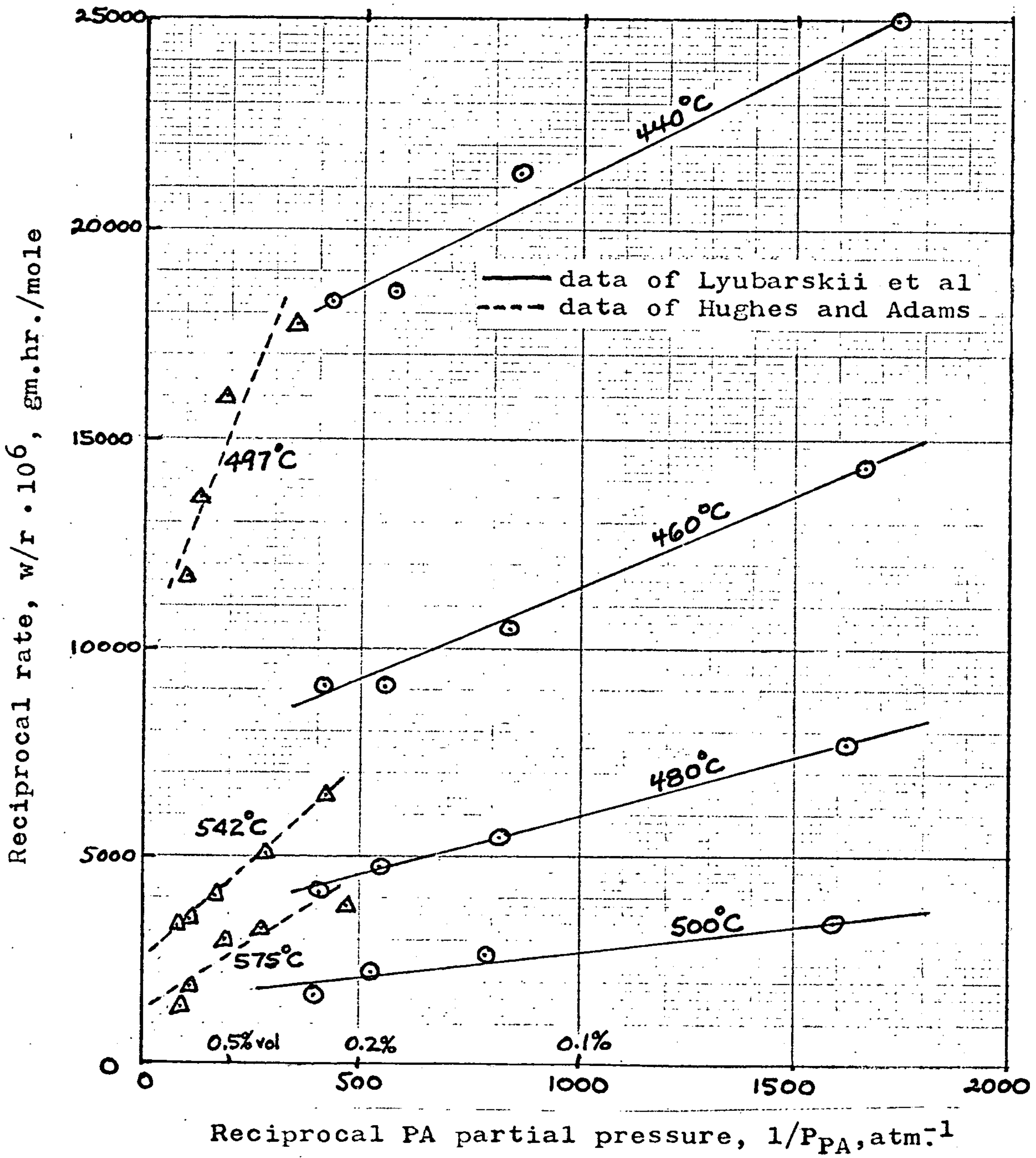
where k is the rate constant, b is an adsorption coefficient for PA, and P is the PA partial pressure. By rearrangement this rate law yields a linear equation in reciprocal rate vs reciprocal partial pressure of reactant: $\frac{1}{r} = \left(\frac{1}{kb}\right)\left(\frac{1}{P}\right) + \left(\frac{1}{k}\right)$. Intercept yields reciprocal rate constant $\left(\frac{1}{k}\right)$ and slope gives the parameter $\left(\frac{1}{kb}\right)$; adsorption coefficient b may be obtained from those parameters.

Hughes and Adams[83] used a similar rate law, $r = \frac{a\ P}{1 + b\ P}$, where a in this equation equals kb of the previous equation. Integral rate data may, as a first approximation, be applied to the differential rate equation. If partial pressure of PA is below 1% of total pressure, the log mean partial pressure of PA may very nearly represent PA partial pressure existent in an integral reactor. This permits the two sets of data to be compared on an equivalent basis.

Hughes and Adams covered the higher PA concentration range from 1.2 - 0.2 % PA while Lyubarskii et al covered a lower range from 0.24 - 0.06%

Figure 6

Determination of
Langmuir-Hinshelwood
Parameters



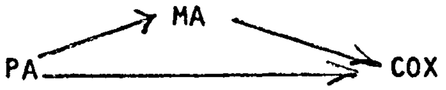
PA. Aside from the previously seen catalyst activity difference, slopes obtained from the two data sets are so different that the data appear mutually inconsistent. These are the only PA data that have been reduced on the basis of an adsorption type heterogenous rate law. Other data assumed, for simplicity, that a first order rate law applied.

It would be desireable to obtain one set of kinetic data, over the PA concentration range from 0.05 to 1.0% vol. These data should be obtained on one catalyst over at least a 100°C temperature range, in order to generate a large consistent data matrix. A plot similar to figure 6 should then show straight lines over the entire PA partial pressure range, if this form of rate equation is valid.

Uncertainties were revealed during the literature search on PA production. There appears to be insufficient information on the source of byproduct MA and on PA oxidation. Hypotheses that are to be tested are that:

(1) MA, obtained during oxidation of o-xylene, is derived from PA combustion, rather than from initial o-xylene attack,

(2) the PA oxidation scheme substantially follows two parallel paths from PA to carbon oxides as shown below, and



(3) kinetics of PA disappearance may be represented by a single adsorption type rate equation, over a range of temperature and PA concentrations encountered in PA production.

C. Experimental Methods

Kinetic measurements, for systems involving PA, have been made using plug flow reactors, fluid bed reactors and recycle reactors.

Tubular reactors have been operated as differential reactors at low conversions and low heat release. This has the advantage that concentration gradients are sufficiently small that data may be directly used in differential rate equations. Input-output analyses of reactant and product concentrations must have good sensitivity and precision in order to produce useful kinetics. Low heat release facilitates isothermal operation; this is necessary because rate constants are very temperature dependent. Low conversions mean that major product concentrations are low, and minor product concentrations are much lower. Tubular reactors may be operated as integral reactors at high conversion, with correspondingly high heat release. High conversions result in severe concentration gradients. These gradients require use of integrated rate equations. High heat release leads to non-isothermal operation, unless there is a high rate of heat transfer from the reaction zone. High heat transfer requires careful design to provide high heat flux from catalyst and products to surroundings.

Fluid bed reactors have an advantage that temperature is reasonably uniform throughout the entire fluidized reactor volume. Data has been treated as originating from a plug flow integral reactor.[117,158] Backmixing and bubble passage through the bed cast severe reservations on validity of the plug flow approximation. Some very long and very short times exist in the residence time distribution, due to backmixing and bubble passage. Fluid bed reactors do have a very low ratio of structural material surface to catalyst mass. If structural materials are catalytic to the reaction being investigated, the fluid bed may be advantageous.

Recycle reactors operate as backmix reactors, where an incoming reactant stream is mixed with a system stream passing over the catalyst.[181] A product stream is withdrawn from the system stream. Recycle provides circulation of the system stream over a catalyst surface, or through a short fixed catalyst bed. Small conversions per pass over the catalyst give gradientless performance. Since system temperature and concentration are uniform at the steady state, the rate data may be used directly in differential rate equations. A very high ratio of structural surface area to catalyst mass can be troublesome, unless the structural surface is inert at the reaction conditions.

One common factor in reactor choice lies in the required non-catalytic nature of reactor structural materials. Table 5 shows the reported activity of reactor materials for oxidation of o-xylene, PA and MA.

Table 5

Catalytic activity of structural materials

non catalytic	catalytic
borosilicate glass[85,180,52,83]	Ni, Cr and Fe oxides[129]
Mo glass[112]	Cu, brass[165]
stainless steel[52,93]	stainless steel[118,85,180,98,10,2]
aluminum[91]	steel[52,83]
quartz[52]	glass[165,93]
	quartz[106]
	silimanite $(Al_2O_3 \cdot SiO_2)$[113]
	aluminum[83,165]

There is no common agreement among investigation on catalytic activity of structural materials. Activity of materials varies with temperature. Borosilicate glass has been preferred for small research reactors. There is contradiction on the catalytic activity of aluminum and stainless steels.

Based upon information obtained in the literature search, plan of the research program was developed as follows:

1. Determine a structural material sufficiently inert to permit an isothermal reactor to be operated at moderate to high conversions. If a sufficiently inert material is found, kinetic data could be obtained on catalyst up to 600°C without significant amounts of parallel reaction occurring on the reactor materials present. The ratio of heated reactor surface to catalyst mass would be a consideration in choice of reactor type. If the structural material had high thermal conductivity, a small tubular integral reactor could be designed to approach isothermal operation, with reasonably high conversion.
2. Measure product distributions over a temperature range to give evidence of the reaction sequence involved in oxidation of o-xylene to products. Catalysts of different selectivity would be expected to show different products growth and decay curves. Comparison of several curves would be expected to show whether MA was produced during initial attack on o-xylene or later in the oxidation sequence. Occurrence of previously unrecognized intermediate products should be most evident if growth and decay curves involve reasonably

high product concentrations, and were obtained at short contact times.

3. Measure the effect of concentration on PA oxidation rate with one catalyst over concentration and temperature ranges broader than the combined ranges covered by the data of Hughes and Adams and the data of Lyubarskii. Confirm that the form of the Langmuir-Hinshelwood rate equation used by those investigators applies over the extended range of variables.
4. Investigate the PA oxidation reaction scheme by measuring product distributions obtained from PA and from MA.

5. Apparatus

A. Choice of Reactor

A tubular reactor configuration was selected because it could be designed to approach isothermal operation, could give a low structural surface to catalyst ratio, and could produce finite conversions at contact times related to industrial practice. A low structural surface area was desired to minimize catalysis by reactor surfaces during high temperature operation. Relatively small reactor bore was necessary to insure thermal contact between each catalyst particle and the reactor wall, for radial heat transfer. Reactor wall material should be catalytically inert for the reaction, and should have high termal conductivity, for longitudinal heat transfer.

B. Experimental Apparatus

The experimental apparatus consisted of feed, reactor and analytical sections. The feed section saturated a small primary air-stream with reactant to be oxidized, and diluted that primary stream with a secondary air stream to produce the desired reactant partial pressure. Performance of the feed section, for delivering a constant composition, was monitored by a continuous quantitative combustor system that measured feedstream carbon content. The reactor section contained the tubular reactor in a well circulated and controlled air oven. The reactor wall at the catalyst location could be maintained at the desired reaction temperature. The analytical section routinely analyzed the reactor exit stream by chromatography. Tail gas, after condensation, was analyzed by non-dispersive IR for carbon oxides

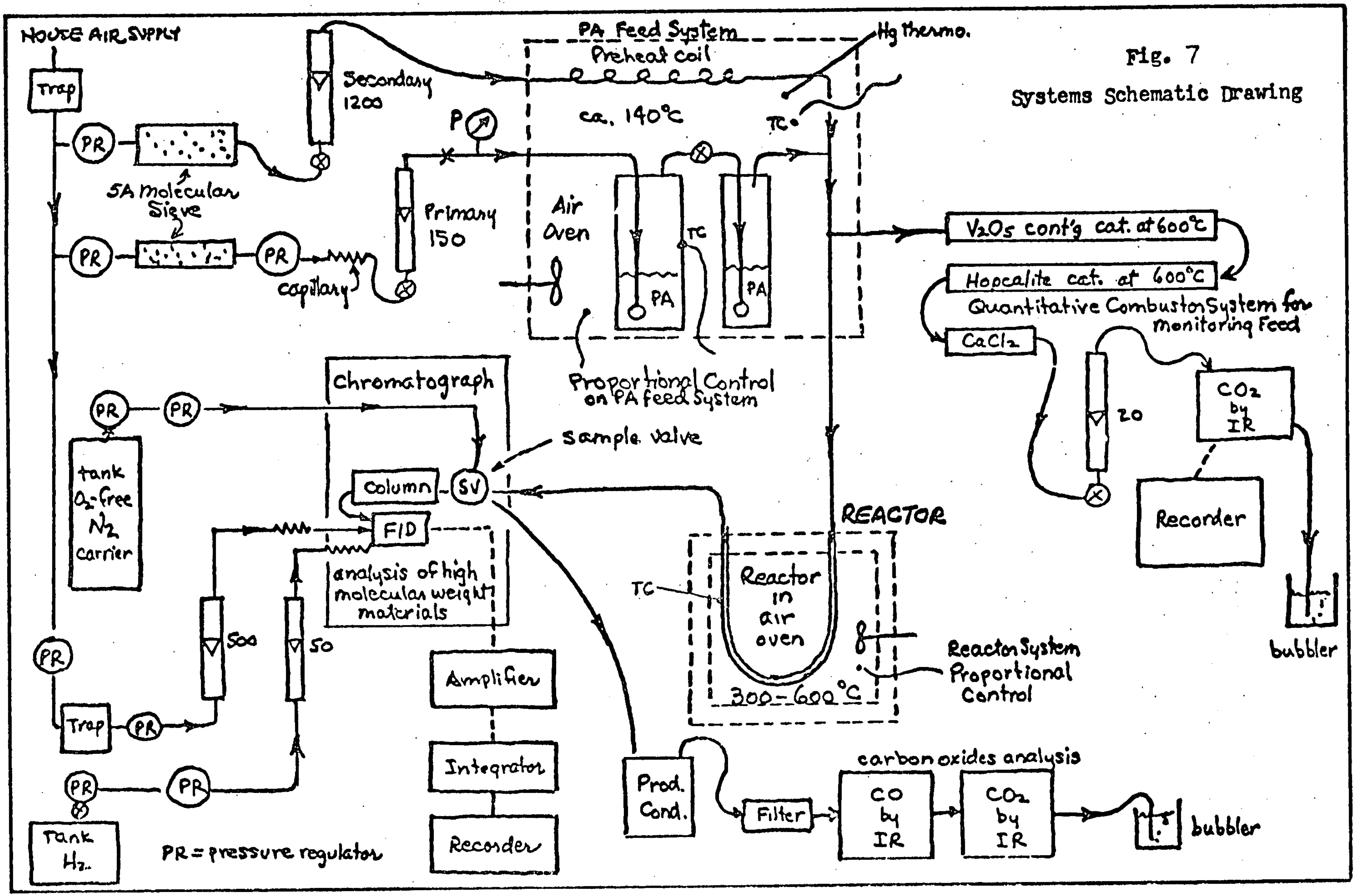


Fig. 7

Systems Schematic Drawing

content. A systems schematic drawing in figure 7 shows the feed, reactor and analytical sections of the apparatus.

C. Feed Section

Methods for continuously delivering a feedstream of constant composition are: (1) vapor pressure controlled bubblers and solid saturators, and (2) controlled delivery of liquid to a preheated gas stream. The PA melting point is 131°C. Heats of sublimation and vaporization, and vapor pressures of PA are given in the appendix. A feedstream, containing 0-1 mole % PA at 1 atm. total pressure, can be generated by using the required 0-7.6 mm PA vapor pressure of solid PA. Higher partial pressures are available from molten PA.

Simple thermodynamic calculations show that vapor pressure variation with PA temperature, in the region of interest around the triple point, is 4.0%/°C from the liquid, and 6.4%/°C from the solid. Transfer of heat of vaporization to liquid, and heat of sublimation to solid phase, are required for an isothermal saturator. The required heat transfer is feasible for properly designed liquid bubblers, but much more difficult for packed beds of solid particles, cooled on the surface by their own sublimation. Packed beds tend to become sticky at 10-20°C below their melting point; they compact and generate problems of increased pressure drop.

Despite obvious limitations, liquid bubblers were used. This required adequate heat transfer, excellent temperature control, slow flows and sufficient sintered plate area in bubblers to achieve necessary mass transfer for saturation. Two bubbler type saturators were used sequentially at low flowrate. One was a large, high heat capacity copper tank for primary stream partial saturation; the other was a glass bubbler to achieve final approach to saturation. These saturated the air at primary flowrates below 200 cc/min., but it was necessary to install proportional control on the saturator oven, and to analyze the reactor feedstream to maintain control, due to changing levels in the bubblers during long term operation.

Primary and secondary air flows were controlled by using pressure drop across fixed capillary devices. These devices were flattened and constricted tubing, packed beds of filter material, or lengths of small-bore tubing. Flows were monitored by calibrated rotameters.

D. Reactor Section

The reactor section consisted of a simple U tube or coil, containing a short preheat zone and catalyst at the downstream end. The reactor was contained in a small, high temperature, controlled air oven. Reactor wall temperature was measured by attached thermocouple at the catalyst section. On occasion, a very small thermocouple probe (ca. 0.2mm wires) was inserted to determine catalyst surface temperature at the downstream end of the bed.

Reactors, designated A-L, were constructed from appropriate tubing, bent in either U, or 1-1/2 or 2-1/2 turn coil configurations. These shapes were used to conveniently fit into the top-opening oven. Joints to external piping were made outside the high temperature zone. Materials, configurations and pertinent dimensions are shown in figures 8 and 9.

Heated lines, connections and joints were held at temperatures

Fig. 8 Tubular Reactor Configurations

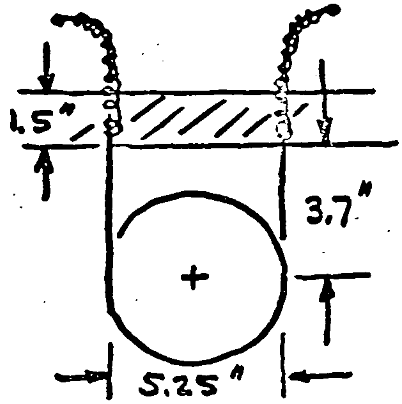
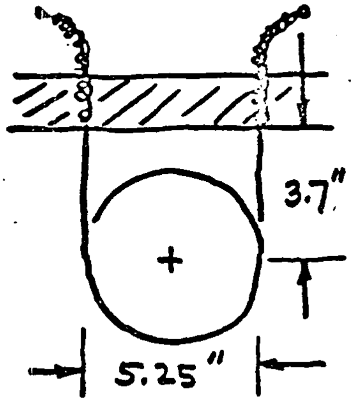
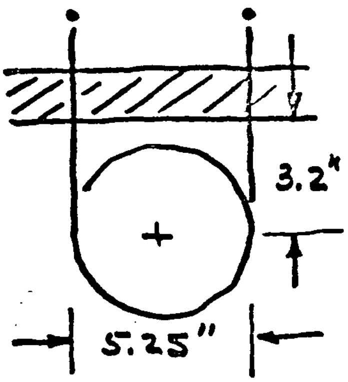
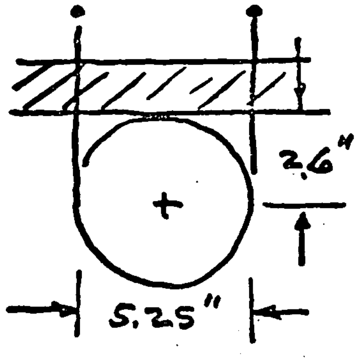
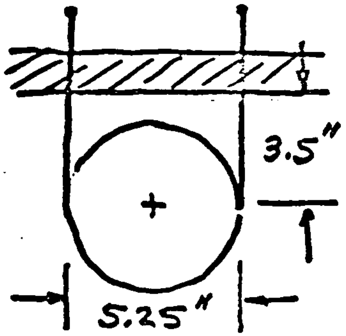
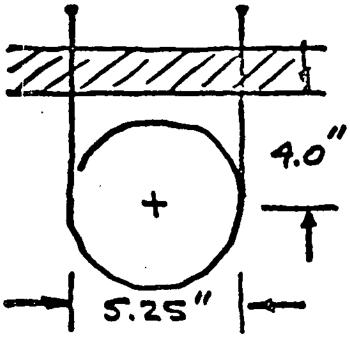
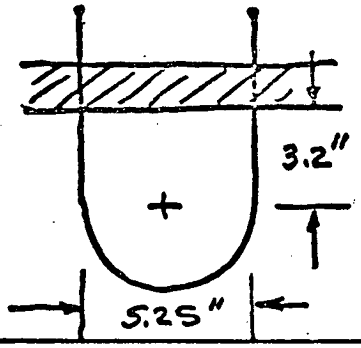
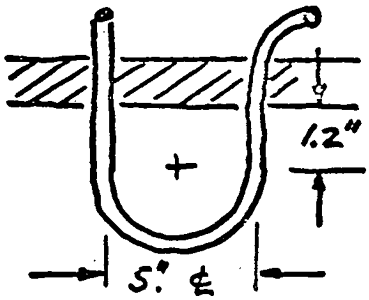
REACTOR A  	Small bore stainless steel tubing, type EN-58B, .0625" (1.6 mm) i.d., ca. 2. mm o.d. $2\frac{1}{2}$ turn coil + 8" at each end. Brazed connections to larger tubing and fittings; Cu wire clad for heat transfer at inlet and exit sections. Heated volume V_r = 2.44 cc, heated length L = 123. cm, and heated surface area S = 61. cm^2.
REACTOR B  	Small bore stainless steel tubing type EN-58B, AISI 321, .125" (3.2 mm) i.d., ca. 4 mm o.d. $2\frac{1}{2}$ turn coil + 8" at each end. Brazed connections. Cu clad as above. Heated volume V_r = 9.76 cc, heated length L = 123. cm, and heated surface area S = 123. cm^2.
REACTOR C  	Pyrex (borosilicate) glass laboratory tubing, 3. mm i.d. CIBA Araldite joints at ends to metal fittings. $2\frac{1}{2}$ turn coil + 7" at each end = 55." long. Heated volume V_r = 8.46 cc, heated length L = 120. cm, and heated surface area S = 112. cm^2.
REACTOR D  	Aluminium tubing, type 2S $99.^{+}\%$ purity, 0.25" (6.4 mm) o.d., .19" (4.7 mm) i.d. Annealed at 500°C. Brazed joints to fittings. $2\frac{1}{2}$ turn coil, total length 43.5". Heated volume V_r = 20.8 cc, heated length L = 117. cm, and heated surface area S = 175. cm^2.

Fig. 9 Tubular Reactor Configurations

REACTOR E  	Pyrex (borosilicate) glass laboratory tubing, 5. mm i.d. CIBA Araldite joints to metal fittings. $2\frac{1}{2}$ turn coil + 8" each end. Heated volume V_r = 23.5 cc, heated length L = 120. cm and heated surface area S = 188. cm^2.
REACTORS F & G  	Aluminium tubing, type 2S 99.$^+$% purity, 0.38" (9.5 mm) o.d., 7.8 mm i.d. Annealed at 500°C. Brazed joints to fittings. $1\frac{1}{2}$ turn coil + 7" at each end, total length 34.5". Heated volume V_r = 36.3 cc, heated length L = 76. cm, and heated surface area S = 187. cm^2.
REACTOR H  	Same 2S Aluminium as above. Simple U-tube, total length 19.6". Heated volume V_r = 17.7 cc heated length L = 37. cm, and heated surface area S = 91. cm^2.
REACTORS I, J & K	Same dimensions and configuration as Reactor H, but material is EC-grade 99.5$^+$% purity Aluminium tubing.
REACTOR L  	Earliest configuration, stainless steel tubing, type EN-58B, .63" (16. mm) o.d., .50" (12.7 mm) i.d. Simple U-tube, bent at red heat. Stainless steel compression fittings at ends. Heated volume V_r = 58. cc, heated length L = 46. cm, and heated surface S = 184. cm^2.
<u>Reactor M,</u> EN-58B Stainless Steel CSTR, as constructed and described by Brisk et al.[181]	

above 150°C, to exceed dew and melting points of vapors in the system. Joints were either metal compression fittings or brazed metal-metal connection. Interconnecting lines in the several systems were made of annealed 99.+% aluminum. Aluminum was needed for axial and circumferential heat transfer to avoid hotspots in lines heated with thermocord tracing and guarded with asbestos tape. This requirement was necessitated by malperformance of stainless steel lines due to poor thermal conductivity, catalytic nature of stainless steel in this system, and development of hotspots.

E. Product Section

Much of the analytical effort was based upon gas phase chromatography, with direct gas sampling of the hot reactor streams. The method was made reasonably reliable for aromatics, C_4-plus components and some lower molecular weight polar compounds. Successful usage was dependent upon proper isothermal column performance, control of the operational parameters, and attention to sample valve malfunction.

(1) Gas chromatography. Column packing materials were screened to find one that would give the desired isothermal resolution of the products of o-xylene et seq. oxidation. Hewlett-Packard supplied 10% (Union Carbide W-98 series, vinyl methyl silicone rubber) W-982 on AW-DMCS treated Chromosorb W as a bulk column filling (catalog no. 80-170591). This packing was used for construction of 3 meter analytical columns. Annealed aluminum tubes of 4.7 mm i.d. were filled with packing and retained by glass wool plugs to within 3. cm of the ends. Ends were

terminated with standard brass threaded fittings, very carefully brazed to the aluminum tube.

The analytical column gave excellent resolution of aromatic and polar compounds encountered. Gas samples up to 5 cc could be used. System limitation was overloading the flame ionization detector (FID) by narrow high peaks of individual components; this was readily handled by reduced sample volume. The column was operated isothermally at 150°C, with oxygen-free nitrogen as carrier gas at 14.5 psig. Carrier flow was held constant by a gas pressure and flow controller at ca. 50 cc (amb.)/min.

Hydrogen flowrate to FID burner was 50 cc (amb.)/min; it was controlled by pressure drop across a capillary, and monitored by a small rotameter. The general laboratory compressed air supply was filtered, and subjected to two stage pressure reduction, then it was cleaned by passage through molecular sieve 5X and fed, via capillary flow constrictor and monitoring rotameter, to the FID at 500 cc (amb.)/min. Although operated in the so-called "flat region," FID sensitivity varied with hydrogen flowrate. FID overload, or high concentration deviation from linearity caused by narrow high peaks, was a function of burner air supply. To achieve stability of the system, the electronic components, FID and nitrogen carrier gas flow were left on continuously.

Using the above column and operating conditions, a series of standard retention times was established for reactants and products. These times are: MA (122 sec.), o-xylene (145 sec.), o-tolualdehyde (256 sec.), benzoic acid (422 sec.), o-toluic acid (490 sec.), PA (650 sec.) and phthalide (770 sec.).

(2) On-line, hot product IR adsorption spectra. A heated 150°C gas cell, of 2.5 cm i.d. and 20. cm path length, was constructed for use with Hilger & Watts dual beam Infrascan equipment. This cell was connected to the reactor exit, for full product flow through the cell, using traced and lagged aluminum tubing at 150°C. The heated cell had rapidly exchangeable NaCl optical windows 4mm thick by 2.5cm diameter. This equipment permitted unequivocal identification of some reaction products by their IR adsorption spectra. Several reference spectra are appended.

(3) Continuous carbon analysis by quantitative combustor. A small fraction, 20. cc (amb.)/min, of reactor feed stream was continuously oxidized to CO_2 and H_2O. Carbon content was quantified by on-line IR analysis for carbon dioxide, with readout on a chart recorder. Purpose was reactor feed analysis, and elimination of reactor feed system variation.

The quantitative combustor system consisted of two sequential catalytic reactors, each made of thick wall copper tubing (11. mm i.d., 15. mm o.d. and 43. cm long) traced with thermocord and heavily lagged with thick asbestos to retain heat and exclude air from the outside surfaces. Combustion tubes were operated at 600°C, with residence time of 24. sec. in each tube. The first tube was filled with a 3-6 mesh vanadia-iron catalyst, and the second contained 2 mm particle size Hopcalite (60% MnO_2 and 40% CuO). All copper surfaces readily oxidized to CuO. Completeness of combustion was verified by gas chromatography, by CO_2 and by zero CO exit gas analyses. Flow through the system was regulated by needle valve and rotameter on the cooled products side following water removal by $CaCl_2$, and prior to gas entry into the IR CO_2 analysis instrument.

6. Experimental

A. Experimental data

Experimental data were taken to define feed, flowrate, reactor and catalyst conditions, and products composition. Data for reactor feed and flowrate are ambient temperature and system pressure, primary and secondary air flowrates, saturation temperature, and measured feedstream composition by chromatographic and combustion analysis. Data for reactor and catalyst are mass and volume of catalyst, reactor void volume in the catalyst zone, total reactor surface area in the heated zone, reactor wall temperature, and, on some occasions, catalyst temperature at the bed outlet. Data for products composition were obtained by chromatographic analysis of the hot product stream, and by non-dispersive IR determination of % volume carbon oxides in the tail gases. Under standardized chromatograph conditions, retention times identified products, and peak areas were converted to product partial pressures using calibration charts for PA and MA.

These experimental data were reduced to yield reaction data for each series shown in the appendix. Data for one reactor temperature in Series 38 is duplicated below:

Series 38 Reactor: F, Catalyst: CCI-C103, $W = 14.10$ gm (5.93 cc), $L = 34$ cm, $V_r = 10.1$ cc, $\Delta P \leq 1$ psig, feed: PA, 13.3 cm^2 Al/gm cat.

The above statement indicates that reactor F was used. (Further detail on reactor F configuration and material is given in previous figure 9). Catalyst bed consisted of 14.10 grams of CCI-C103, which had a liquid displacement volume of 5.93 cc. The catalyst bed occupied the outlet 34 cm of the reactor tube and left 10.1 cc of void space in the packed bed. The inlet portion of the reactor tube length constituted a feed preheat section. System pressure drop, measured ahead of the saturator, was less than 1 psig. Feedstock was PA, and the ratio of heated aluminum reactor surface to catalyst mass was small, 13.3 cm^2/gm.

Reduced data for one temperature of the 300-600°C range studied in that series is shown below:

T°C	q liters/min.	P_i atm.	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ moles/gm.hr.	$r_t \cdot 10^6$ moles/gm.hr.
450	.478	.0055	.130	0.38	0.115	21.4	24.5

Reactor wall temperature, T°C, was measured. At the highest heat flux, generated by the greatest conversion of the most concentrated feedstock, catalyst temperature was only 5°C greater. Temperature T°C is used as the mean catalyst temperature existent in the bed.

Volumetric flowrate, q, is liters/min., measured at ambient temperature and reactor pressure. Summation of primary and secondary flowrates yields q. Contact time may be calculated from reactor void volume in the catalyst bed, V_r, and volumetric flowrate corrected to reactor temperature:

$$\text{contact time} = \frac{V_r}{q}\,\frac{T_{\text{ambient}}}{T_{\text{reactor}}} = \left(\frac{10.1}{478}\right)\left(\frac{293}{723}\right)(60) = 0.51 \text{ sec.}$$

Feedstream PA partial pressure, P_i, is given in atm. This is calculated from saturator vapor pressure and the secondary/primary air dilution ratio. Calculated P_i was confirmed by combustion analysis, and crosschecked against chromatograph calibration curve.

X_t is the fraction of feed converted to total products; it is obtained directly from measurements of reactor input-output feed ratio. Fraction of unconverted feed, $1-X_t$, equals P_o/P_i, the feed outlet to inlet partial pressure ratio.

Percents of carbon oxides are measured composition of the tail gas. Ambient CO_2 is subtracted from % CO_2 reported. The fraction of feed converted to carbon oxides, X_c, may be calculated using feed composition.

For C_8 feed:
$$X_c = \frac{\left(P_{CO_2} + P_{CO}\right)}{8\ P_i} = \frac{(0.0038 + 0.00115)}{8(0.0055)} = 0.113.$$

Rates r_t and r_c are for conversion of feed to total products, and to carbon oxides. Units are moles/gm.hr.

Reaction rate, $r_t = \frac{F}{W} X_t$, where $\frac{F}{W}$ is the feed rate in moles/gm.hr., and X_t is fraction of feed converted to total products. Feed rate $\frac{F}{W}$ is derived from volume flow rate, (q), feedstream mole fraction $\frac{P_i}{P_{total}}$, using the ideal gas law at the temperature and pressure of flowrate measurement:

$$\frac{F}{W} = \frac{60}{W} q \left(\frac{P_i}{P_{total}}\right)\left(\frac{n}{V} = \frac{P_{total}}{RT}\right).$$

Thus the feed rate, $\frac{F}{W} = \frac{60(0.478)(0.0055)}{14.10\ \ (0.0821)(293)} = 465. \times 10^{-6}$ moles/gm.hr.

Reaction rate to total products, $r_t = (465 \times 10^{-6})(0.130) = 60.5 \times 10^{-6}$ moles/gm.hr.

Reaction rate to carbon oxides r_c may be similarly calculated using X_c:

$$r_c = (465 \times 10^{-6})(0.113) = 52.5 \times 10^{-6} \text{ moles/gm.hr.}$$

It is evident, in this case, that carbon oxides constitute 52.5/60.5, or 87% of the products of PA.

B. Experimental Procedure

The steps used in obtaining data for one reaction series are given below. Elapsed time per series was one day, except in those cases where 16 hour operation at 500°C was added to evaluate catalyst stability.

(1) The series was begun with catalyst in an air oxidized state, after having been in the reactor overnight at 500°C in a small secondary air flow of 100 cc/min. The reactor oven was set to give a reactor wall temperature of 300°C. Secondary air was increased to the operating flow of 424 cc/min., measured at ambient temperature and pressure. All aluminum feed and product lines, including sample valve and chromatograph lines, had been held at 150°C. The chromatograph was stable, having been held continuously at 150°C with carrier gas on, and flame detector lit.

(2) The saturator oven, preheat lines and saturators had been on continuously and were stable at 170°C, as determined by thermocouples. PA vapor pressure at this temperature is 37 mm or 0.0487 atm.

(3) Chromatograph and associated electronics were shown to be stable by yielding standard peak area for a 1 mole % propylene in nitrogen reference gas injected with a separate gas sample valve in the system.

(4) Calibration of non-dispersive IR analysis equipment for CO and

for CO_2 was checked, using tanks of 1% CO_2 in nitrogen and 0.25% CO in nitrogen references gases.

(5) The quantitative combustor was brought up to its operating temperature of 600°C.

(6) When all equipment was stable at their operating temperatures, the primary air to the saturators was started at 54 cc/min. (ambient). This yields a dilution ratio of 8.85, giving a PA feedstream partial pressure of 0.0055 atm.

(7) System backpressure was measured upstream of the saturator. Normally this pressure is below 0.5 psig at the flowrates used. Since tailgases exhaust to the atmosphere, reactor pressure is taken as 1.0 atm.

(8) After 15 minutes, when steady state had been achieved, the feed composition was determined by measuring % CO_2 (above 0.04% in air) generated by a small sidestream of reactor feed passed through the quantitative combustor. Chromatograph measurements were made of the 300°C reactor outlet stream composition. Elution time for PA was 650 seconds. Three analyses were made; these yielded consistent PA peak areas that were converted to PA partial pressure using a calibration chart. With the reactor at 300°C, there was no CO or CO_2 produced, and there were no chromatograph peaks other than PA. The reactor outlet stream was the same as the inlet stream, because no reaction occurred at 300°C.

(9) The above steps were used to bring the system onstream. Further work consisted of raising reactor temperature by 50°C increments,

achieving steady state at each temperature, and making product analyses at each reactor temperature. Feedstock composition was held constant during the run series.

(10) Product compositions became stable upon reaching steady state at each reactor temperature. Three chromatographic analyses were made of the reactor output, and three determinations of carbon oxides were similarly made.

(11) After measurements had been made at the highest temperature, 600°C, the reactor oven was set to give a 300°C reactor temperature again. Cooldown to steady state took one-half hour. Carbon oxides in the tailgas dropped to zero again, and reactor outlet equalled feedstream composition. This redundant run at 300°C served to confirm that feedstream and analytical equipment were performing as they had at the beginning of the series.

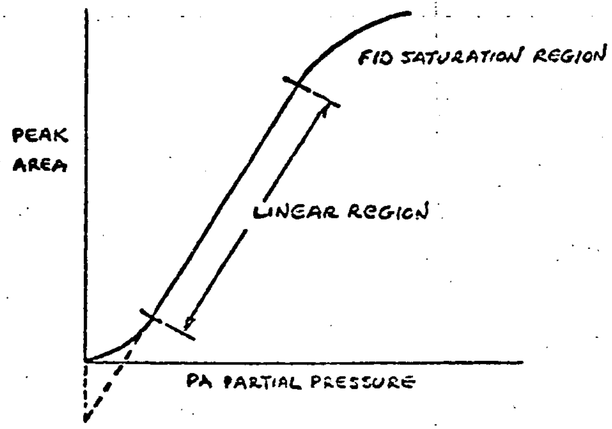
(12) System shutdown consisted of turning off primary air flow to the saturators, and power to the reactor oven. The chromatograph, heat to the sample lines and a small flow of secondary air were left on to purge the system.

C. Operational Problems

Three major areas influenced accuracy, but not overall validity of data from the chromatographic product analyses. These areas are: (1) chromatograph non-linearity due to FID response characteristics, (2) sample valve problems, and (3) adsorption and desorption of PA from polymeric deposits that result from minor products of PA oxidation.

Chromatograph non-linearity

In all systems worked with, the FID and associated electronic responses yielded comparably shaped curves of peak area vs. concentration.



Recurring negative intercept of the linear region imposes limitation on numerical accuracy of input-output ratio determinations. Calibration curves were necessary to remedy this.

Sample valve problems

Perkin-Elmer sample valves available were troublesome. They required constant attention, adjustment and acetone cleanout. Polymeric products from PA oxidation contributed much of the problem.

Adsorption-desorption of PA from polymeric products

Very troublesome deposits of polymeric materials were laid down, in all system piping downstream from the reactor, during the long term experimental periods. Piping had to be held above 150°C to prevent deposition of PA from the vapor phase; at those temperatures, reactive minor products formed tar deposits in lines, sample valve, and sample loop. These deposits were partially soluble in acetone. Adsorption-desorption of PA in such deposits in lines required extended periods to achieve steady state. Acetone and mechanical cleanouts were frequently made, and the single loop sample valve switching time was held constant at 30 seconds throughout the experimental work in order to obtain repeatable PA determinations.

7. Results

A. Catalysis by Reactor Materials

Preliminary experiments were conducted to determine appropriate reactor materials for design of an isothermal reactor for PA oxidation. Relatively non-catalytic structural surfaces were needed in the high temperature reaction zone.

Series 1 oxidized a low concentration of PA on Alundum SA-201 spheres contained in a 12.7 mm inner diameter stainless steel tubular reactor. These materials had been previously used, as catalyst diluent and as reactor tube. From 30 to 100% PA oxidation occurred at 425°C and above. Velocities through the catalyst bed were low, 1.5-1.7 ft/sec., and contact times were long, 0.7-0.8 sec.

Series 2 oxidized the PA product stream from a single tube pilot reactor operated by Ellis.[98] This feedstream contained about 0.5% vol. PA derived from 1 % vol. o-xylene feed in air. The secondary oxidation experiments of this series were conducted, using glass beads in a stainless steel reactor. Temperatures of 425 and 500°C, and contact times of 0.05-0.5 second were used. Secondary combustion of PA to carbon dioxide was 31% at the most severe condition. Combustion to other products was not measured. Subsequent experiments by Ellis showed that stainless steel on top of his catalyst bed reduced selectivity to PA. Conversion of o-xylene to PA dropped from ca. 65 mole % to ca. 40 mole %, due to post-combustion.

Series 3 confirmed that stainless steel filling in a stainless steel reactor was very catalytic for PA oxidation to carbon dioxide at contact times of 0.14 sec. at temperatures above 425°C.

Series 4 and 5 oxidized PA in an empty 1.6 mm inner diameter stainless steel reactor tube. This small bore was selected to suppress homogeneous reaction. Surface quenches free radicals present in homogeneous oxidation reactions. High flowrates yielded linear velocities of 50-120 ft/sec. and contact times of 0.035-0.080 second. At a 0.7 mole % PA feed flowrate of 2370 x 10^{-6} moles/10 cm^2 of SS per hour, 34% of the PA was combusted at 500°C. With about one fifth the PA concentration, and correspondingly reduced feed flowrate of 517 x 10^{-6} moles/10 cm^2 SS hr., all of the PA was combusted. These experiments confirmed the highly catalytic nature of stainless steel at elevated temperatures. They substantially elimated opportunity for PA homogeneous oxidation. Reduction of PA partial pressure by a factor of five did not produce a corresponding reduction in oxidation rate. This showed that PA oxidation kinetics on stainless steel were not simple first order.

Series 6 and 7 used the same stainless steel spinning basket internal recycle reactor that had been used by Watt[97] for the oxidation of o-xylene to PA. In series 6, the basket was filled with the small stainless steel cylinders that had filled the tubular reactor in Series 3. In series 7, the basket contained V_2O_5 on SiC catalyst (CCI-C103) from the same batch used by Watt. Feed was 0.15 mole % PA in air during both series. The flowrate yielded mean residence times of 0.8-0.9 sec., over the temperature range 330-490°C. Carbon dioxide measurements showed that about 30% of the PA charged was combusted at 490°C in both series. Results were inconclusive with respect to the V_2O_5 catalyst. The high catalytic activity and surface area of the stainless steel reactor, 32 cm^2/gm catalyst, masked the effect of catalyst contained in the basket.

Series 8 was the last set of experiments conducted in stainless steel tubular reactors. This series was conducted in an empty reactor at 390-500°C. The linear flowrate was 30 ft/sec., equivalent to 0.13 sec. contact time. Feedstock was 0.14 mole % PA in air; this yielded a mass flowrate of 494×10^{-6} moles/10 cm^2 SS per hr. Results of this set of kinetic data showed pseudo first order rate constants per 10 cm^2 of stainless steel that were much larger than similar rate constants later measured per gm of V_2O_5 catalyst.

Series 9 evaluated surface of a small bore borosilicate glass tubular reactor for its catalytic activity towards PA oxidation. The relative inertness of this glass was demonstrated at 500°C, and at 0.1 and 0.6 sec. contact times.

Series 10 showed the inertness of an empty reactor, made from 4.75 mm inner diameter aluminum tubing. The type 2-S aluminum used was 99+% pure. Pseudo first order rate constants per 10 cm^2 were comparable with, but slightly higher than were obtained with borosilicate glass in the prior series.

Series 11-18 were a group of non-isothermal experiments conducted in a 5 mm bore borosilicate glass reactor to screen a variety of materials for their activity towards PA oxidation at 380-500°C wall temperature. The volume flowrate of 0.535 liter/min. yielded contact times of 0.10-0.13 second. Linear velocities, through the void space of the packed beds of materials, were 5-8 ft/sec. Two PA partial pressures were used to permit estimation of the order of reaction on the tested materials.

Series 11 and 12 were data sets to evaluate the activity of oxidized mild steel. The two series differed by reversal of bed configuration. In series 11, 24 cm. of steel filling was followed by 96 cm.

of empty heated reactor tube. In series 12 the reactor was reversed, giving a 96 cm. empty preheat section followed by the same 24 cm. filled section. Results of the two series were similar, all PA was combusted at 460-480°C. The mild steel was so active that the reversal aspect of the experiments was inconclusive. The iron component of stainless steel was much more catalytically active than austenitic stainless steel.

Series 13 was conducted to test activity of the chromium and nickel components of stainless steel. Nichrome alloy at 20% Cr and 80% Ni was used. It proved to be less catalytic than mild steel, but more catalytic than the stainless steel previously tested.

Series 14 used small particle commercial V_2O_5 on SiC catalyst (CCI-C103). This catalyst was the same as used by Watt[97] in a fluidized bed. It had been prepared from the commercial 6-8 mesh material by size reduction in a ball mill, followed by screening to 1-1.4 mm particle size. One gram showed comparable activity with about 3 cm^2 of stainless steel for PA oxidation. At the low PA flowrate of 605×10^{-6} moles/gm hr., an embedded thermocouple showed at 38°C rise above 500°C wall temperature. This temperature was measured at 68% conversion of the 0.14% PA feedstream. This series demonstrated the known futility of attempting to obtain isothermal operation at reasonable conversions, in a reactor with the poor thermal conductivity of glass, and without all catalyst particles contacting the reactor wall.

Series 15 measured the activity of small soft glass beads as a possible catalyst diluent. Catalytic activity of the beads for PA oxidation was more than a decade higher than borosilicate glass.

Series 16 screened Duraluminum as a reactor material. As anticipated from its copper content, it was much more active than 99+% aluminum for oxidation of PA.

Series 17 examined SA-203 Alundum. This material was a porous catalyst carrier. It consisted of alpha-alumina and mullite ($Al_2O_3 \cdot SiO_2$). This Alundum had very limited activity towards PA oxidation. Being porous, and having an unknown surface area, rate data were reported on a weight basis.

Series 18 was conducted to evaluate activity of austenitic stainless steel relative to the Cr, Ni and Fe components measured in previous series 11, 12 and 13. Results were lower, with this 18-8 austenitic stainless steel than were observed with the small bore tubing of series 4 and 5. This particular stainless steel sample was cut from reactor L used in series 1-3.

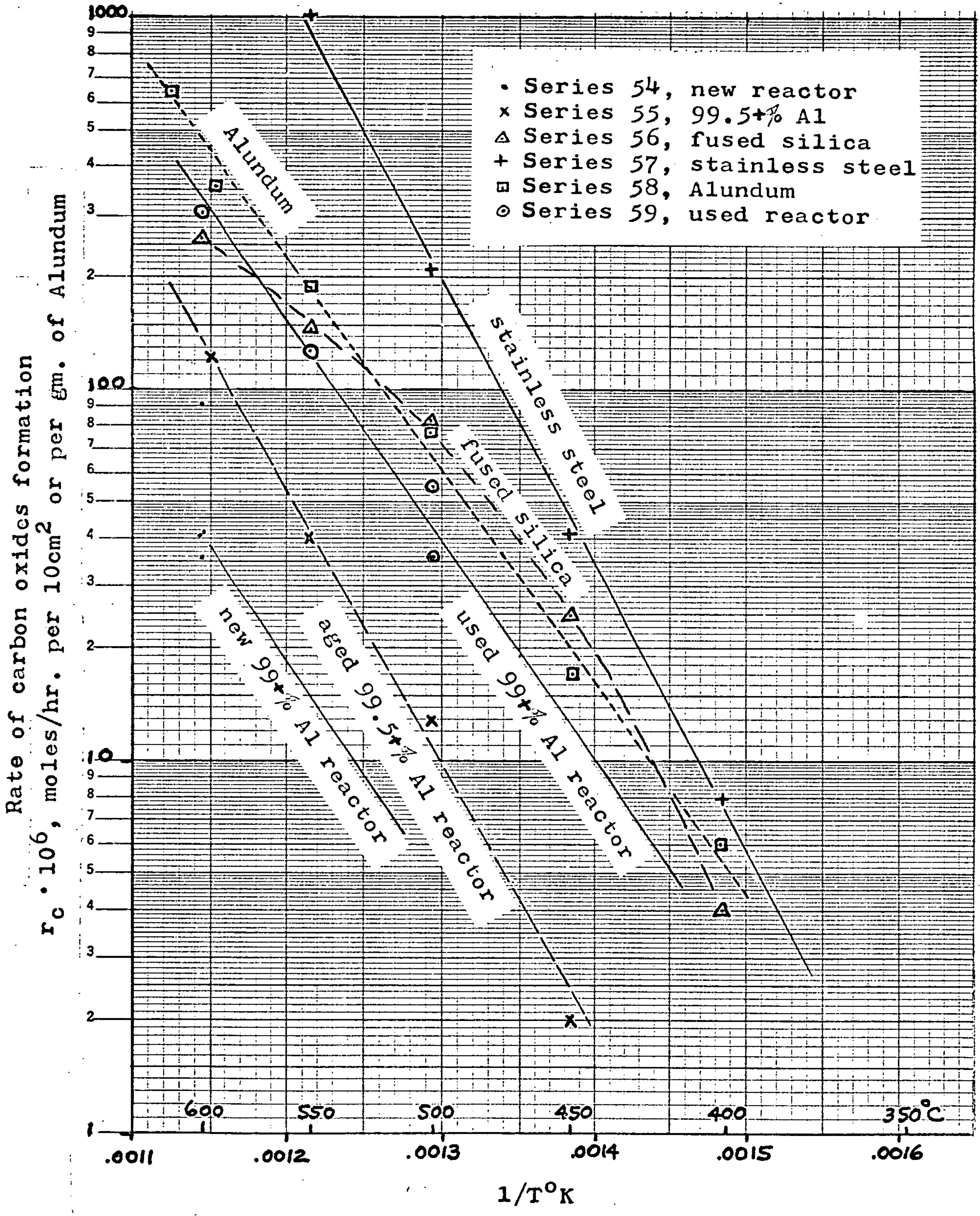
Series 19 evaluated prototype tubular reactor D for later kinetic studies of PA oxidation on V_2O_5 catalyst. This reactor consisted of a 2-S (99+%) aluminum tube filled throughout its heated length with 1.8 mm irregular spheres of EC grade (99.5+%) aluminum. Since the reactor tube had already been evaluated empty in series 10, this series measured catalytic activity of the aluminum spheres. These spheres were later used as a thermally conductive catalyst diluent, in order to achieve isothermal reactor operation. Results, at one inlet PA partial pressure, indicated that this high purity aluminum was the least active of the metals tested, but it was not as inert as borosilicate glass. The very high thermal conductivity of aluminum was deemed to outweigh the lesser catalytic activity of relatively non-conductive borosilicate glass. Series 19 was run for sixteen hours at 500°C to condition the metal surfaces, in case there was an ageing effect. No significant change was detected with time.

Later series 50-53 were data taken to determine extent of ageing in an empty tubular reactor made of 99+% aluminum. These experiments were conducted in the new reactor, in the reactor after one and four weeks of operation, and finally in the brushed out reactor. The temperature range of operation was 300-600°C. Feed composition was held near 0.45 mole % PA in air. Flowrate was varied by a factor of five. Comparison, by means of rate constants that were pseudo first order with respect to PA, showed that catalytic activity of the aluminum surface doubled after three weeks of operation. Physical cleanout with a brush was partially effective in reducing the activity increase.

In series 54-59, the activity of $99.5^{+}\%$ aluminum, fused silica, stainless steel and Alundum spheres were compared over the temperature range 300-600°C. Data for these materials were bracketed between before and after blanks on the new and used $99^{+}\%$ aluminum reactor. Rates of PA conversion to carbon oxides were measured. PA inlet partial pressure was held constant, and volume flowrates were varied by a factor of five in some cases. Results of these series, uncorrected for reactor PA partial pressure, are shown in figure 10. Rates for PA conversion to carbon oxides, r_c, are shown on the basis of 10 cm^2 of smooth surfaces, and one gm. of porous Alundum. Apparent activation energies were about 35 Kcal/mole, except for stainless steel which was higher.

Figure 10

Oxidation of PA
on Structural Materials
(at ca. 0.47 mole% PA in air)



Other later series 63 and 64 evaluated the catalytic activity of individual 99.5+% aluminum reactors as blanks for studies involving the contained catalysts. Surface activity of this high purity aluminum tubing was very low at all temperatures to 600°C. Data from these preliminary studies has been reduced, to a series of pseudo first order rate constants for the various catalytic surfaces. Rate constants for metals of 450°C and their associated Arrhenius activation energies are shown in table 6.

Pseudo first order rate constants, k_t, were determined using the measured rates of conversion of PA to all products, and using the logarithmic mean PA partial pressure existent in the tubular reactors. Rate constants are inversely related to PA partial pressure. These should have been constant at one temperature for a true first order reaction. Thus, the data are useful only for comparison purposes. The ferrous metals yielded activation energies of 55 Kcal/mole and above. These high activation energies indicate that catalytic activity rises extremely rapidly with temperature. Rate constants and activation energies for aluminum materials are much lower. The highest purity aluminum had the lowest rate constant of any of the metals screened.

Table 7 shows pseudo first order rate constants and activation energies for non-metals. Borosilicate glass has a very low rate constant per 10 cm^2. Alundum is porous, and has an estimated surface area of the order of 10^4 cm^2/gm. The Alundum composition may be more inert than borosilicate glass on a smooth surface area basis, but porous Alundum is not inert towards PA oxidation.

TABLE 6

Catalytic Activity of Metals

Metal	Series No.	P_i atm.	k_t at 450°C (note 1)	E_t (note 2)
Oxidized mild steel	11	.0014	(.2)	-
	12	.0014	.4	85.
	12	.0070	.02	85.
Stainless steel	4	.0014	.3	55.
	4	.0014	.2	60.
	5	.0072	.04	55.
	5	.0016	.3	60.
	8	.0014	.3	55.
	18	.0014	.01	55.
	18	.0070	.004	55.
	57	.0047	.007	-
20 Cr-80 Ni	13	.0070	(.001)	-
	13	.0014	.07	55.
Dural	16	.0014	.06	(35.)
Aluminium 99. + %	10	.0014	(.002)	-
	10	.0014	.002	(35.)
	50	.0045	.005	35.
	50	.0044	.007	-
	51	.0041	.01	35.
	52	.0048	(.004)	-
	53	.0046	.003	-
Aluminium 99.5 + %	19	.0013	.002	35
	55	.0048	.001	35
	63	.0045	(.0001)	-
	64	.0049	(.0001)	-

Notes: P_i = inlet PA partial pressure

(1) gm moles/(10cm^2)(hr)(atm)

(2) Kcal/gm mole

TABLE 7

Catalytic Activity of Non-metals

Material	Series No.	P_i atm.	k_t at 450°C (note 1)	E_t (note 2)
Soft glass	15 15	.0014 .0070	.01 .004	) 33.)
Borosilicate glass	9 9	.0014 .0064	) (.0005))	(30.)
Fused silica	56	.0047	.01	30.
Alundum SA-203	17	.0014	.001/gm	33.
Alundum SA-201	58	.0049	(.01/gm)	(32.)

Notes: (1) gm moles/(10 cm^2)(hr)(atm), except for Alundum

(2) Kcal/gm mole

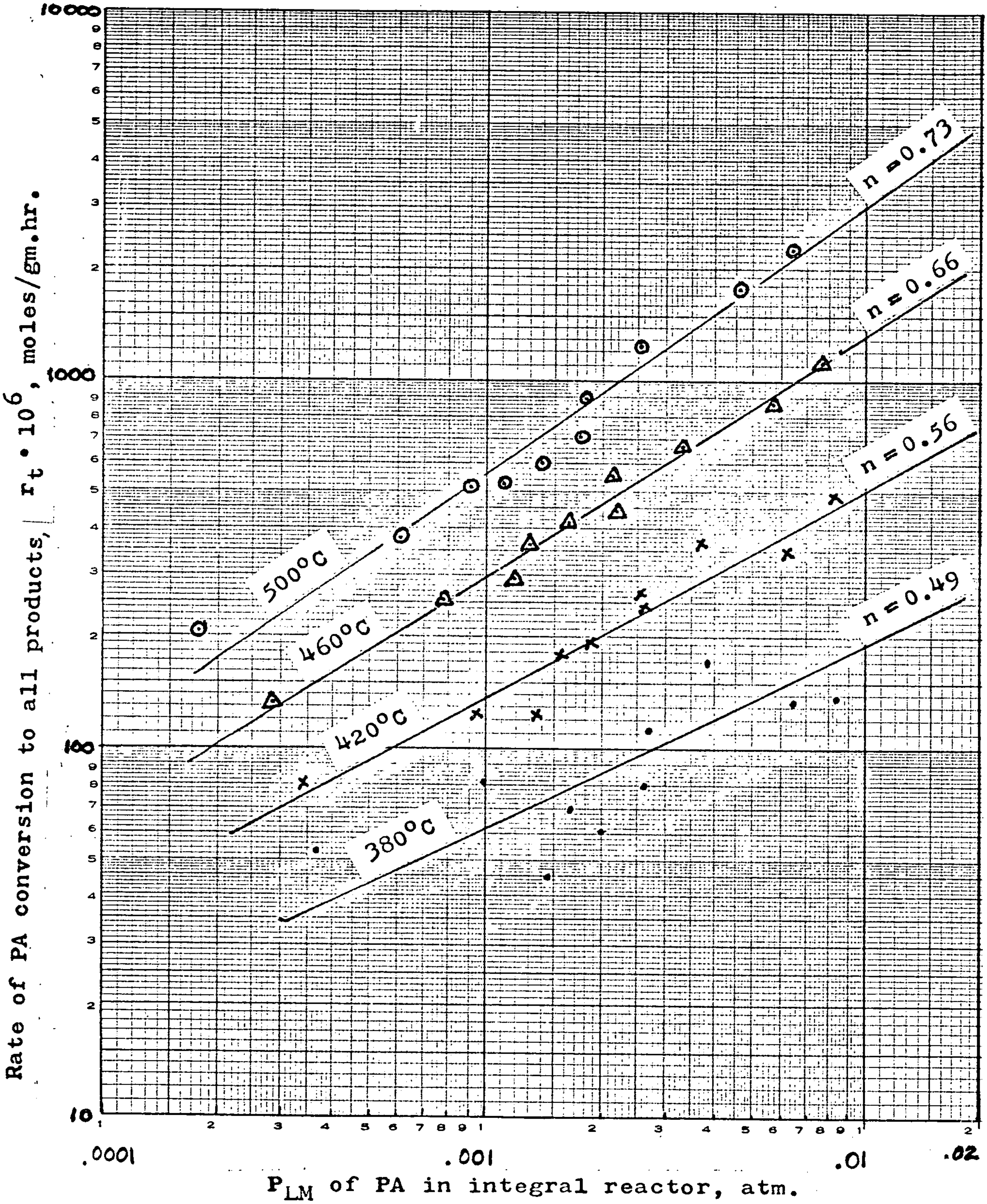
B. Kinetics of PA Oxidation

Series 20-29 generated data for determining the form of rate equation involved in the air oxidation of PA on aluminum-diluted, small particle V_2O_5 on SiC catalyst. One volumetric flowrate, with varied PA inlet partial pressures from 0.00043 to 0.0087 atm., yielded PA feed flowrates that varied by a factor of 20. The 117 cm aluminum tubular integral reactor and 99.5+% aluminum diluent were the same as had been used, without the added V_2O_5 catalyst, in previous series 19. Reactor temperatures were varied from 300-500°C for each PA feed flowrate. No detectable PA oxidation occurred at 300°C. Measurable rates were obtained at 380°C upward. Conversions of PA to all products and to carbon dioxide were measured. MA was the major product observed chromatographically. These measurements yielded a data set that consisted of ten inlet PA partial pressures, each at four temperatures. The last two inlet conditions were very near the first two; this served as a data check, and to show that catalytic activity of the system was stable over the long operating period. The method to achieve isothermal operation was to use a long, aluminum-diluted catalyst bed to distribute the heat release longitudinally and to conduct heat radially to the conductive reactor wall. Measured temperature in the catalyst bed was 2°C above reactor wall temperature at the highest reactor heat release. Highest heat release occurred at 47% conversion of the highest PA feed rate using 0.87 mole % PA at 500°C. Contact times, decreasing with reactor temperature, were 0.40-0.47 sec.

Consistency of the data is shown in figure 11. Rate of PA conversion to all products is plotted against logarithmic mean PA partial

Figure 11

Rate of PA Conversion
vs. PA partial pressure



pressure existent in the reactor. Slope of lines connecting data points at each temperature is indicative of reaction order with respect to PA in an exponential type rate equation. Although this plot shows some data scatter at 380° due to lesser analytical accuracy at low conversions, overall homogeneity of the data matrix is apparent. Figure 11 shows that the data may be adequately represented over the entire temperature and PA partial pressure range by a two parameter exponential form of rate equation: $r_t = k\, P_{LM}^{n}$ where n is the order of reaction with respect to PA. Parameters k and n may be expressed, over the experimental range by: $\ln k = 32.21 - 32000/RT$, where T is °K and

$$n = 0.0020\ T - 0.82$$

The experimental data were plotted to determine whether they could be adequately represented by a Langmuir-Hinshelwood heterogenous rate law of the form: $r_t = \frac{k_1 P}{1+k_2P}$, where P is the partial pressure of PA in the reactor. A plot of reciprocal rate versus reciprocal reactor partial pressure indirectly yields parameters k_1 and k_2. Figure 12 shows this plot. Slope of the least squares of deviations line for each temperature yields reciprocal k_1; intercept yields k_2/k_1. Parameters, over the temperature and partial pressure range shown, are expressed by:

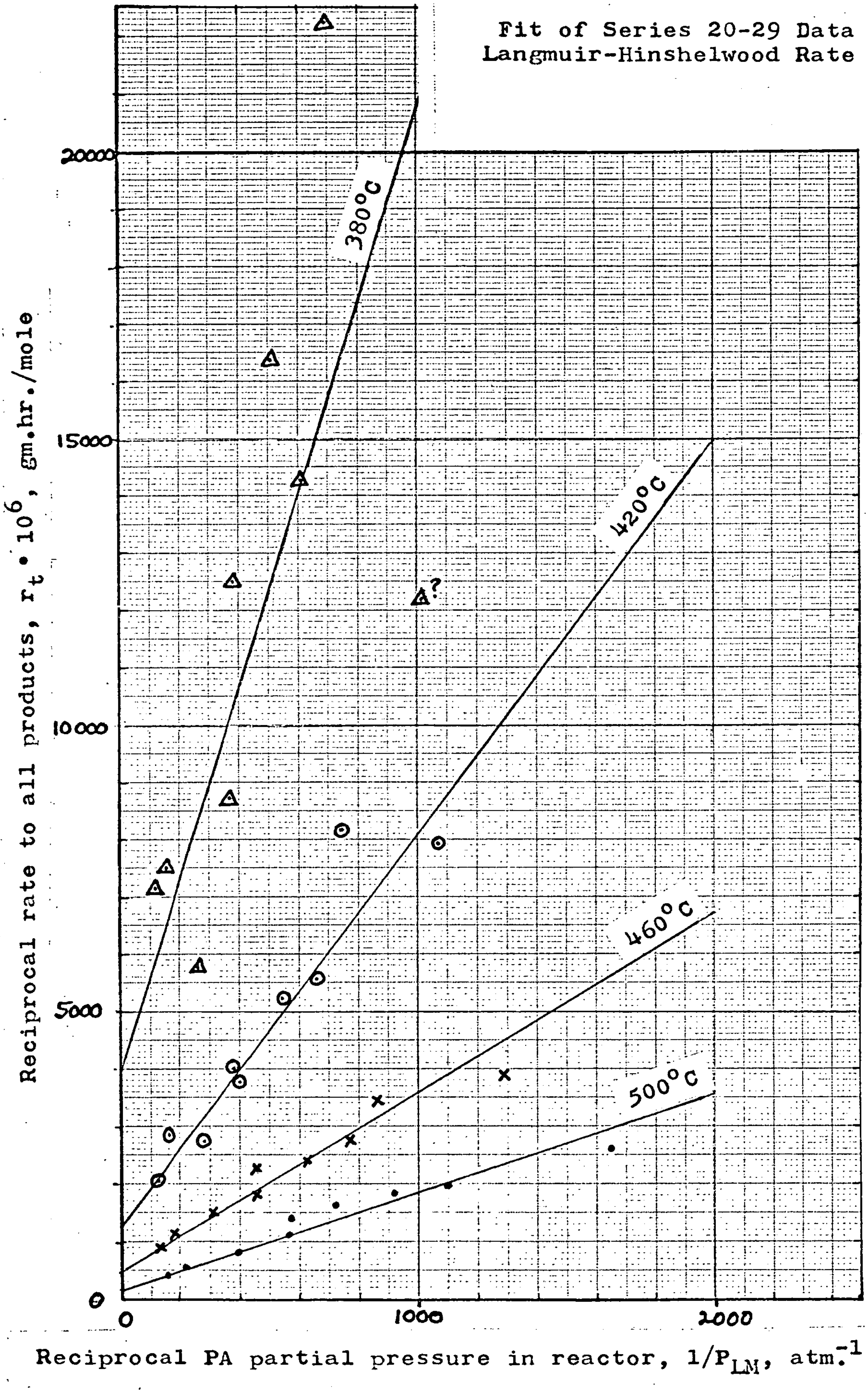
$$\ln k_1 = 11.73 - 18800/RT, \text{ and}$$

$$k_2 = 990 - 1.15T, \quad \text{where T is °K.}$$

Data of series 26, at the lowest partial pressure of PA, lie off the plot to the right, and fall below the lines fitting the remainder of the data.

Figure 12

Fit of Series 20-29 Data to Langmuir-Hinshelwood Rate Law



These data were also tested to determine compliance with an Elovich (Roginskii-Zeldowitsch) rate equation of the form: $r_t = k_1 \exp(-k_2P)$. This form of rate equation should yield a straight line when $\ln R$ is plotted against reactor partial pressure, P_{LM}. Since $\ln R$ vs $\ln P_{LM}$ yielded a straight line in fig 11, $\ln R$ vs P_{LM} could only yield a curved line that indicates non-compliance with that Elovich equation.

Several series of kinetic experiments were conducted on three undiluted V_2O_5 catalysts, in short aluminum tubular reactors, over the temperature range 300-600°C. These catalysts were CCI-C103 produced by Catalysts and Chemicals Inc., von Heyden Kontakt-S and experimental catalyst III. Experimental catalyst III consisted of V_2O_5 on an Alundum substrate.

Series 38 measured the kinetics of PA oxidation on 6-8 mesh V_2O_5 on SiC (CCI-C103). One feed flowrate at 0.0055 atm. partial pressure of PA was used over the temperature range 300-600°C. Conversions of PA increased with temperature to 44%.

Series 66 measured similar kinetics on the same catalyst at two feed flowrates using 0.005 atm inlet partial pressure of PA. These data were obtained in a short 99.5+% aluminum tubular reactor that had been run empty in series 63 as a blank. The empty reactor was inert over the temperature range. Conversions to 15% were obtained on catalyst at 600°C at 0.10 sec, contact time.

Series 65 used experimental catalyst III in an identical reactor at one flowrate and the same inlet PA partial pressure. Series 64 was a blank run on the empty reactor under the same conditions. Due to lesser catalyst activity, 7% conversion occurred at 600°C.

Series 60 used another identical high purity aluminum reactor containing von Heyden Kontakt-S catalyst. This catalyst had been previously activated with 1% vol SO_2 in air, per manufacturer's instructions, for one-half hour at 380°C in a separate reactor. This operation formed SO_3 in situ and established the active catalyst condition. Kinetic data were measured in less than 8 operating hours without any sulfur compounds in the PA feedstock. Some deactivation occurred at 600°C due to SO_3 loss, after the kinetic measurements had been made. Series 59 and 61 were before and after blanks run with the same empty reactor. The empty reactor was inert at 600°C during series 59; it was contaminated with catalyst residue in series 61. Kontakt-S was evaluated at one PA inlet partial pressure and one flowrate. This catalyst did not oxidize PA below 400°C, but it showed high activity with increased temperature.

Series 67 repeated the above kinetic measurements of PA oxidation on Kontakt-S. A new aluminum reactor was tested empty in series 62, then loaded with a new charge of freshly activated catalyst for the measurements of series 67. One inlet PA partial pressure and one flowrate were used at 300-600°C. Results were substantially the same as found in previous series 60.

Data obtained for the three V_2O_5 - containing catalysts are summarized on the Arrhenius plot figure 13. In this figure, rate of PA conversion to total products is plotted against reciprocal temperature. Due to the different PA partial pressures existent in the reactor at different temperatures, even though the inlet PA partial pressures were comparable, the data have been reduced to constant 0.005 atm PA

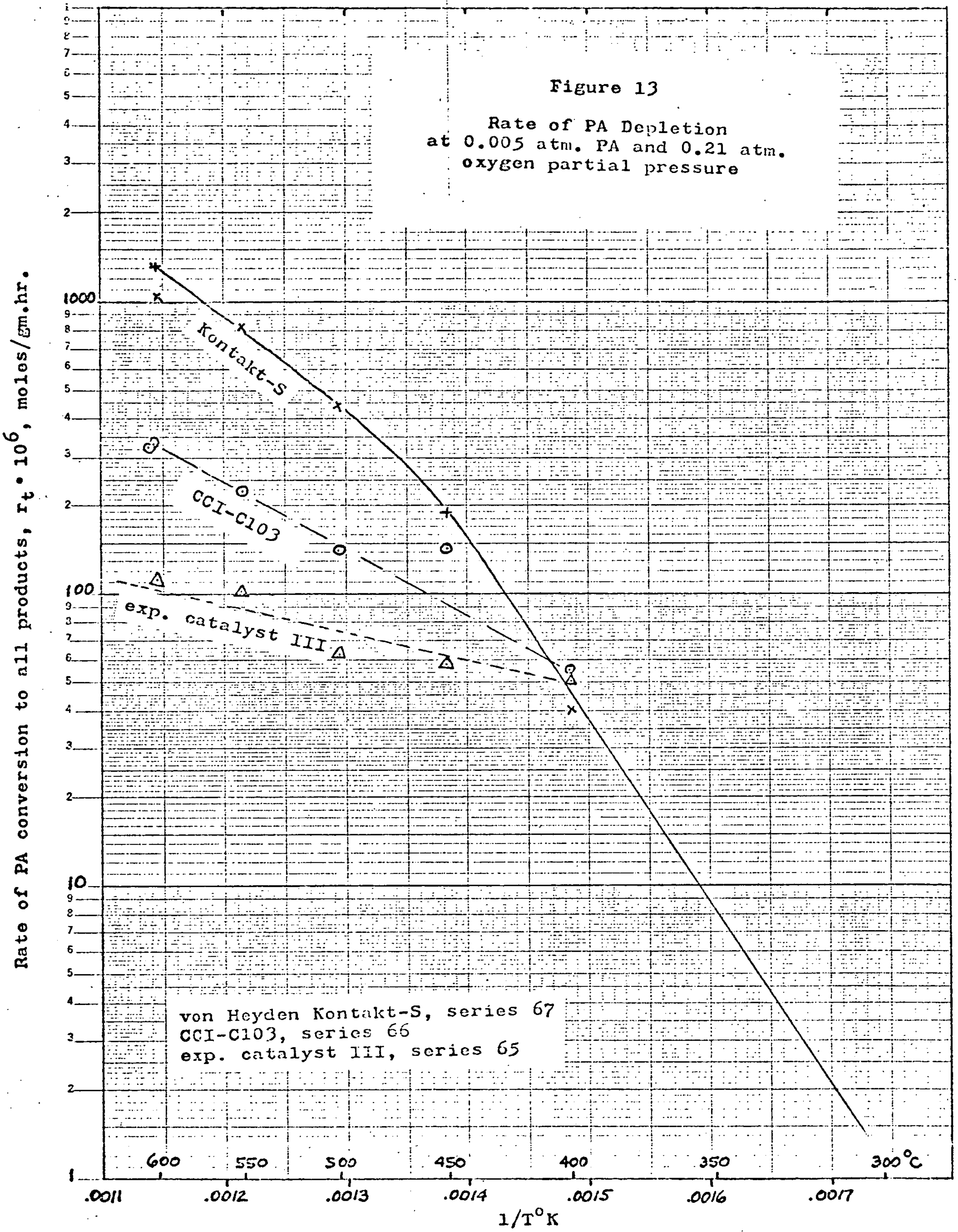


Figure 13

Rate of PA Depletion at 0.005 atm. PA and 0.21 atm. oxygen partial pressure reactor partial pressure by using an exponential rate equation with the exponents previously determined: $n = 0.0020T - 0.82$. Rate at $P_{LM} = 0.005$ equals measured rate at actual reactor P_{LM} multiplied by $(0.005/P_{LM})^n$. Data of figure 13 are shown in this way for comparison with previous figure 5. Previous figure 5 presented literature data for rate at 0.005 atm PA on other catalysts containing V_2O_5. Data on three catalysts shown in figure 13 were obtained in identical high purity aluminum tubular reactors. Each empty reactor yielded between 1-2% conversion at 600°C. Feedstream flowrate, inlet composition, catalyst mass and bed length were held constant for comparison of the three catalysts. Each catalyst particle was in thermal contact with the aluminum reactor wall. Maximum temperature rise measured in the catalyst bed was 5°C. The catalysts behaved similarly up to 400°C, and were quite inactive for PA oxidation. An apparent activation energy of 28.6 Kcal/mole was applicable to all 3 catalysts. Above 400°C the catalysts differed, with Kontakt-S the most active and the experimental catalyst the least active. Apparent activation energies above 400°C were related to catalyst activity.

C. Reaction Products from o-Xylene Oxidation

A group of five experimental V_2O_5 catalysts plus commercial CCI-C103 were used to oxidize o-xylene to products over the temperature range 300-600°C. The object of this experimental sequence was to determine whether MA was formed directly from o-xylene during initial oxidative attack, or whether MA was formed further along in the reaction sequence. Technique used was to conduct the oxidations on a group of different vanadia catalysts over the temperature range, and to examine birth and decay of individual intermediates in order to determine the earliest parent of MA. It was recognized that the series of catalysts with their different activities and selectivities would yield different product distribution diagrams.

Experimental catalysts I-V were prepared by adsorption of V_2O_5, V_2O_5-K_2SO_4 and V_2O_5-$K_2S_2O_7$ melts on porous Alundum substrate. These catalysts were stabilized by sintering at 800°C for several hours. Further catalyst details are appended.

Series 39 and 40 oxidized o-xylene on commercial V_2O_5 on SiC catalyst (CCI-C103). PA inlet partial pressure was .0096 atm., equivalent to 0.96 mole % in air. A volume flowrate of 0.5 liter/min. yielded contact time of about 0.5 second. Major products were o-tolualdehyde, o-toluic acid, PA, MA and carbon oxides. Catalyst activity was such that xylene depletion occurred at 450°C. Above this temperature, small amounts of a minor product, previously obscured by the xylene chromatograph peak, was evident. The ratio of CO_2/CO in the tail gas showed a transition from 4.5 to 2.5 between 400-450°C; it remained at the lower value at higher temperatures. The ratio, r_c/r_t, for o-xylene conversion to carbon oxides/conversion to total products showed a minimum of 0.42

at 450°C. That minimum was related to a PA product maximum.

Series 47 replicated the above series, but used a lesser amount of catalyst that approximately doubled the feed flowrate per gram of catalyst. This series was also conducted at higher chromatograph sensitivity for detection of minor products. The CO_2/CO ratio similarly dropped to 2.5 between 400-450°C. The ratio r_c/r_t showed a similar minimum of 0.4 at 450°C, the temperature of maximum PA production. Major products of o-xylene oxidation, in order of appearance as reactor temperature was increased, were: o-tolualdehyde, carbon oxides, PA, o-toluic acid, phthalide and MA. Minor products were designated according to their chromatograph retention times. These minor products, in order of appearance with reactor temperature, were the 60 sec., 201 sec., a 105 sec. intermediate, 87 sec. and the 180 sec. compounds. A minor product at 150 sec. was obscured by the o-xylene peak prior to xylene depletion. Product distribution diagrams for series 47 are shown in figure 14. In the upper figure chromatograph peak areas for o-xylene and major products are plotted against reactor temperature. Carbon oxides, as % vol in the tail gas, are shown as dashed lines on that upper figure. The lower portion of figure 14 shows peak areas of minor products versus reactor temperature. On this figure o-tolualdehyde and carbon oxides are observed at low temperature, but MA is not evident until after other products and PA were existent in the product stream.

Series 41 used relatively inactive experimental catalyst I. This catalyst was originally formulated with V_2O_5 and $K_2S_2O_7$; it was used to oxidize 0.96 mole % o-xylene in air at 300-600°C to generate another set of product distribution diagrams. Conversion of o-xylene

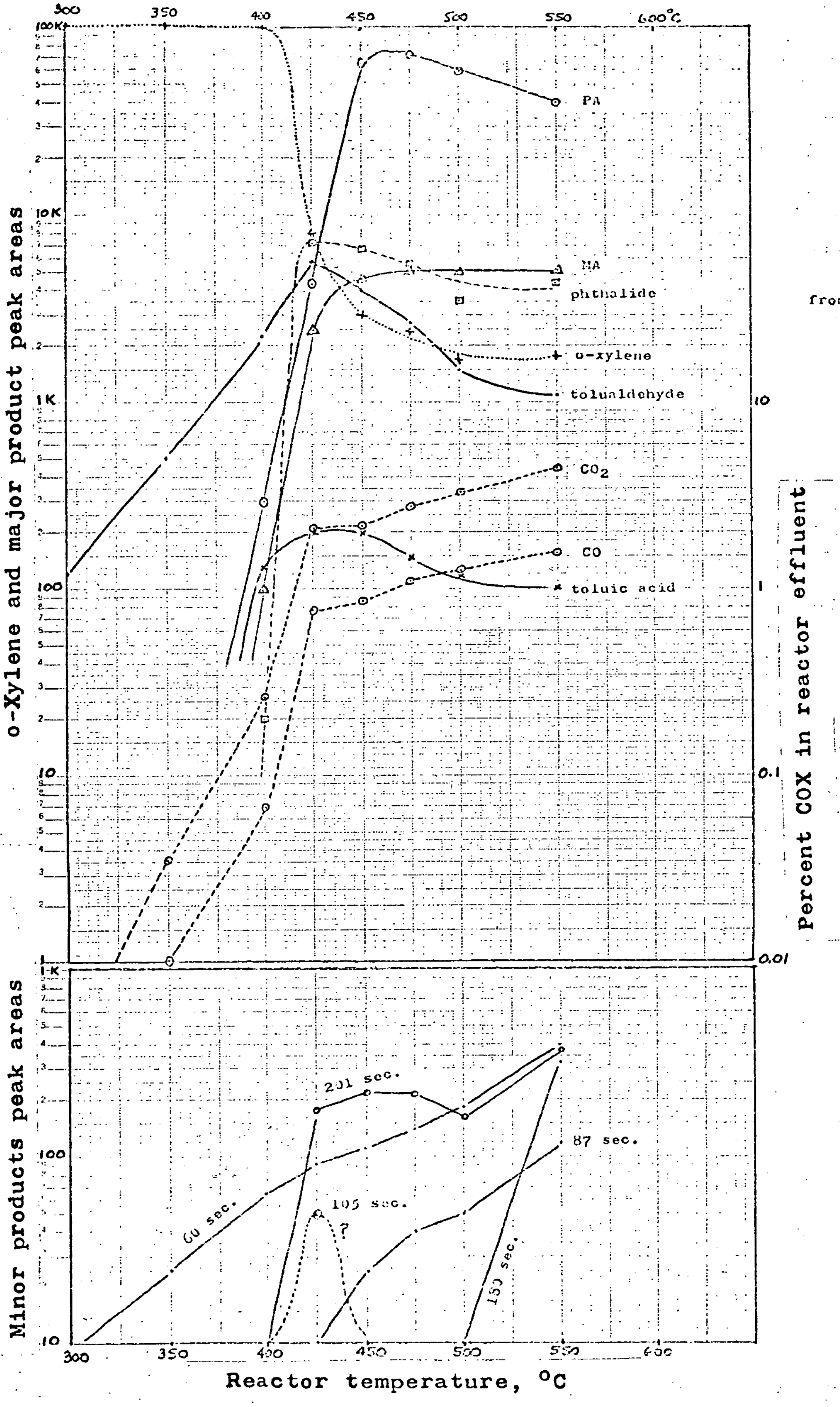


Figure 14

Products Distribution
from 0.96% o-xylene oxidation
on CCI-C103 catalyst

reached a maximum at 550° C; above that temperature some catalyst deactivation occurred. This catalyst produced o-tolualdehyde and carbon oxides at low temperature. Products in order of their appearance with reactor temperature were o-tolualdehyde and carbon oxides, PA, MA, phthalide and o-toluic acid. Minor products observed were the 201 sec., 60 sec. and 105 sec. compounds. None of these minor products were observed until after phthalide and o-toluic acid were present. Figure 15 shows the product distribution diagram for this series. On catalyst I, minimum r_c/r_t occurred at 500-550°C. This roughly corresponds to maximum production of o-tolualdehyde. Decrease in the CO_2/CO products ratio occurred with PA disappearance. MA appeared after o-tolualdehyde and PA, and before phthalide and o-toluic acid. Therefore, MA must be the product of o-tolualdehyde and/or PA.

Series 43 used experimental catalyst II for the oxidation of o-xylene under a similar set of reaction conditions. This catalyst contained V_2O_5-K_2SO_4, and had been shown to be the most active of the set of experimental catalysts for oxidizing PA. In this series, the ratio of rates of conversion to carbon oxides/conversion to all products, r_c/r_t, was reasonably constant at 0.65. It was a strongly oxidative catalyst, and showed deactivation with time above 575°C. Major products, in order of appearance with increased reactor temperature, were o-tolualdehyde, PA, phthalide, o-toluic acid and MA. Minor products, in order of appearance were the 201 sec., the 60 and 105 sec., and the 70 and 87 sec. compounds. These minor products increased in amount with reactor temperature.

Another sample of experimental catalyst II was used in series 48a

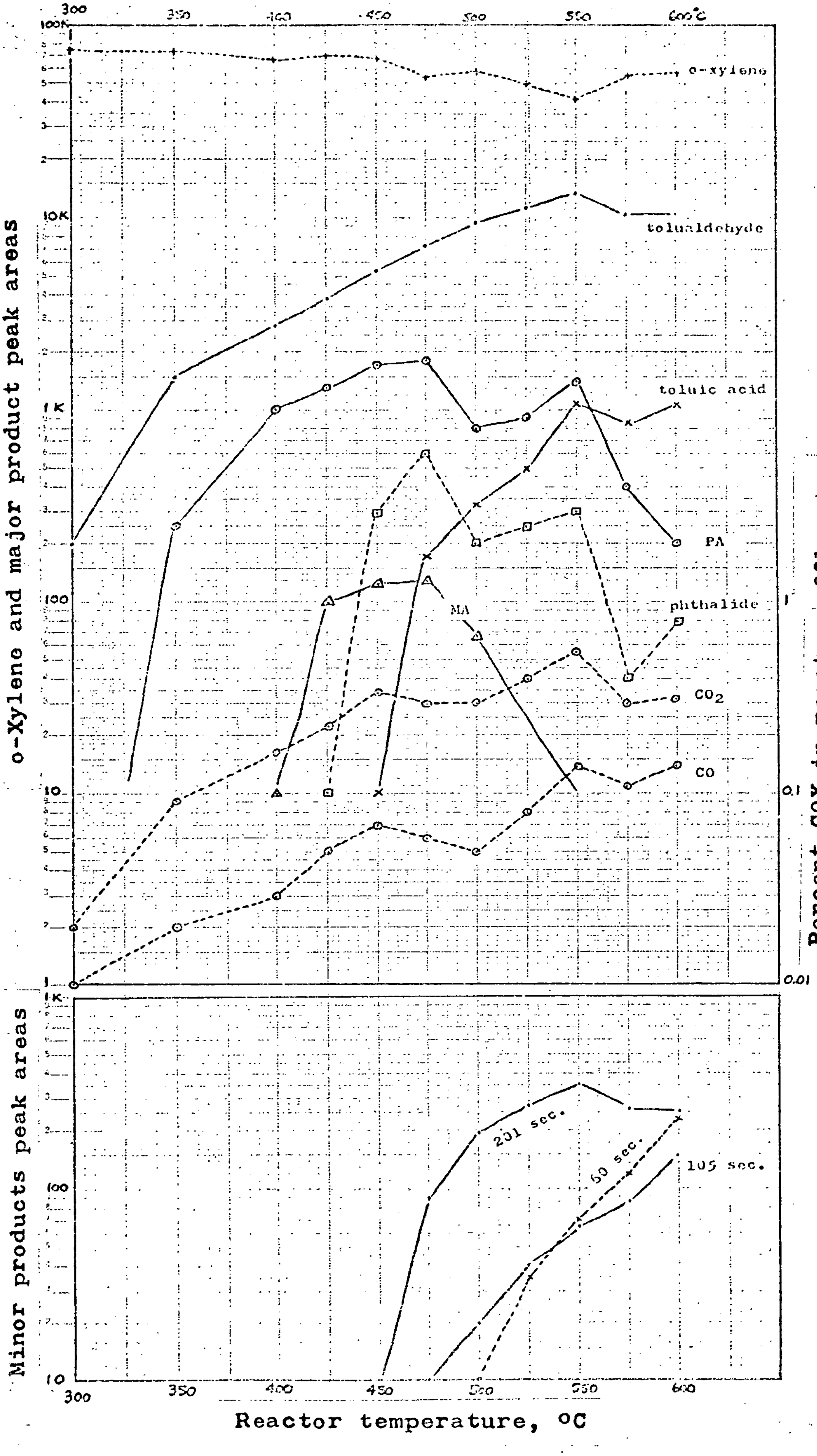


Figure 15

Products Distribution
from 0.96% o-xylene oxidation
on experimental catalyst I

to determine the minor products of o-xylene oxidation. Minor products found were the 60 sec., 70 sec., 105 sec., 180 sec., and 201 sec. compounds. The 201 second compound showed rise and fall with increased reactor temperature. Traces of benzoic acid (422 sec.) were evident at 600°C. Since this series was such a prolific producer of minor products during o-xylene oxidation, the series was rerun at doubled o-xylene concentration and doubled contact time in order to increase minor products concentrations. These data are shown in figure 16. The benzoic acid rise coincides with fall of o-toluic acid. MA concentration appears to follow PA up and down. The 201 second minor compound shows a decline that may be associated with o-xylene decrease. In addition to the usual major products and benzoic acid, six minor products are evident: 60 sec., 70 sec., 87 sec., 105 sec., 180 sec. and 201 sec. Existence of the previously observed 150 sec. compound was not shown here; because if it were present, it would have been masked in the chromatograph by unreacted o-xylene (145 sec.).

Experimental catalyst III was used in series 45 and 46 for the oxidation of o-xylene at 0.96 mole % in air. Major products of series 45, in order of appearance with increased reactor temperature, were o-tolualdehyde and carbon oxides, PA, phthalide, MA and o-toluic acid. Product distributions obtained during series 45 are shown in figure 17. Rise, fall and rise of o-tolualdehyde is accompanied by similar behavior of the o-toluic acid and phthalide daughter products. This is also evident for the 105 and 201 sec. minor products. MA area appears to mimic PA area, but at a lower concentration level. Minor products were the 60 sec., 105 sec., 180 sec. and 201 sec. compounds. No 422 sec. benzoic acid

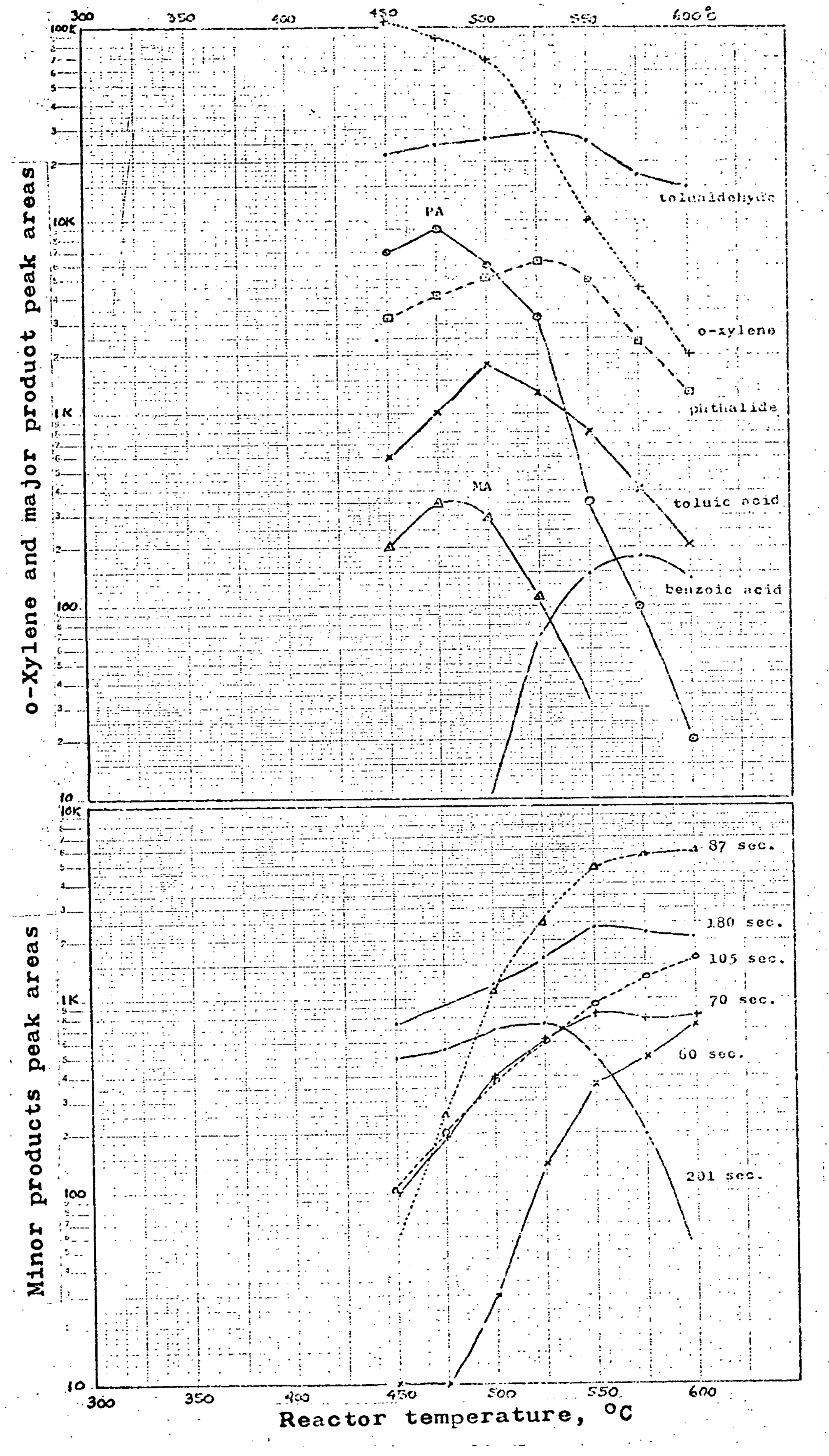


Figure 16

Products Distribution
from 0.06% o-xylene oxidation
on experimental catalyst II

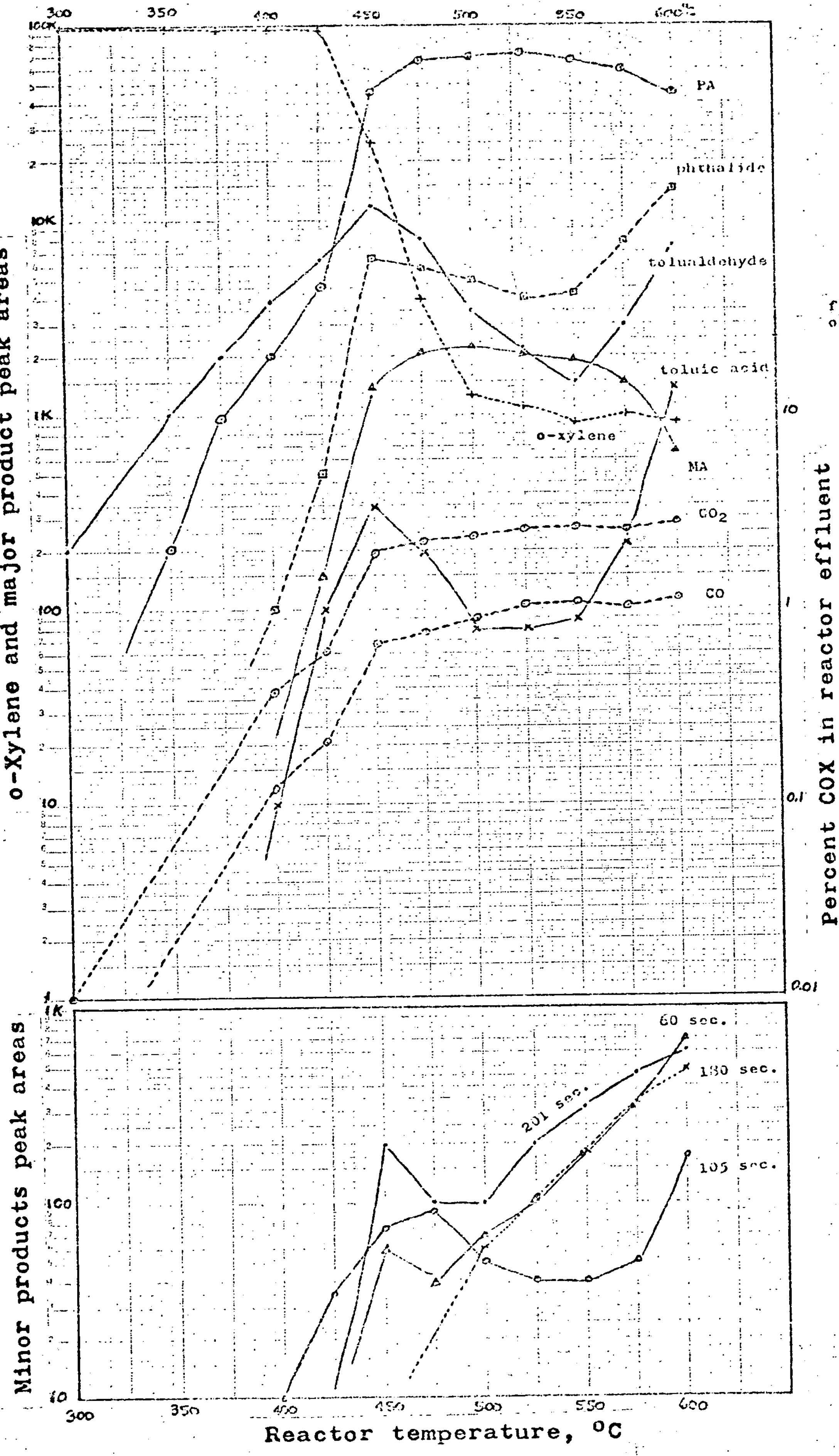


Figure 17

Products Distribution
from 0.96% o-xylene oxidati
on experimental catalyst II

was evident. Failure of the 145 sec. o-xylene area to decline at high reactor temperature may indicate existence of an underlying 150 sec. minor product. Series 46 was conducted in the same reactor, with the same catalyst and conditions used in prior series 45. Purpose was to confirm reproducibility of the product distribution diagram and equipment stability. Figure 18 shows this second product distribution diagram obtained from o-xylene oxidation on experimental catalyst III. In overall form figure 18 replicates figure 17. The rise, fall and rise of o-tolualdehyde, o-toluic acid and phthalide are again evident. PA follows o-tolualdehyde so closely that PA must be its direct product. Genesis of the 180 sec. compound at 450°C reactor temperature is not clear. All minor products previously seen are present, including the possibility that the 150 sec. compound underlies o-xylene at reactor temperatures above 500°C. Small amounts of the 87 sec. compound are present at 550°C and above.

Experimental catalyst IV was formulated with V_2O_5-$K_2S_2O_7$, but with half the $K_2S_2O_7$ used in catalyst I. Products of o-xylene oxidation on catalyst IV during series 42 are shown in figure 19. The usual major products exist, with PA directly related to o-tolualdehyde. Phthalide appeared at lower reactor temperature than o-toluic acid; this demonstrated that o-toluic acid was not an essential intermediate between o-tolualdehyde and phthalide. The 60, 105, 180 and 201 second minor products were present. No benzoic acid was evident until 600°C. Similar shapes of MA and the 60 sec. compound curves infer a relation between the two compounds.

Experimental catalyst V contained V_2O_5-K_2SO_4, with half the K_2SO_4 used in the active experimental catalyst II. Catalyst V was used

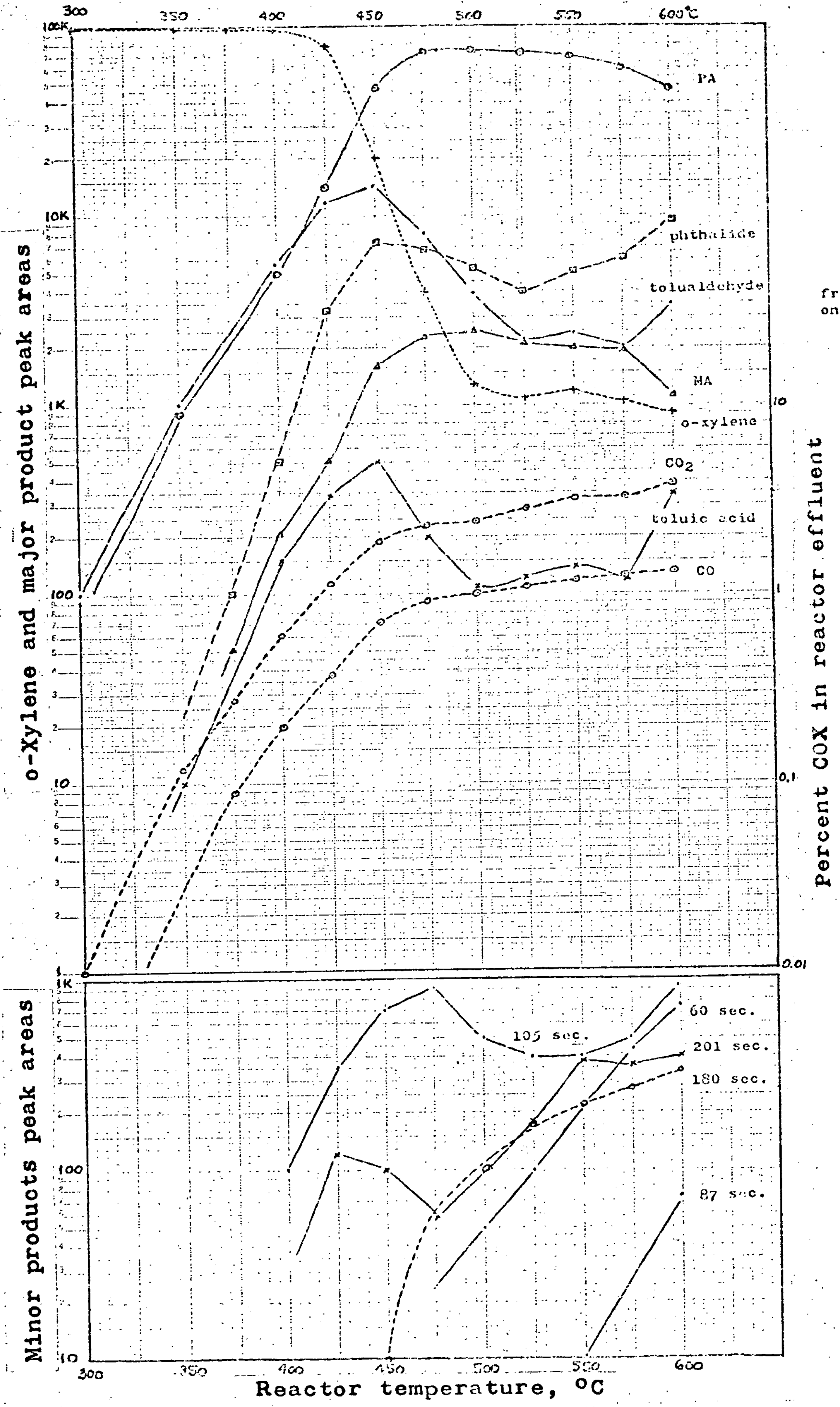


Figure 18

Products Distribution from 0.90% o-xylene oxidatio on experimental catalyst III

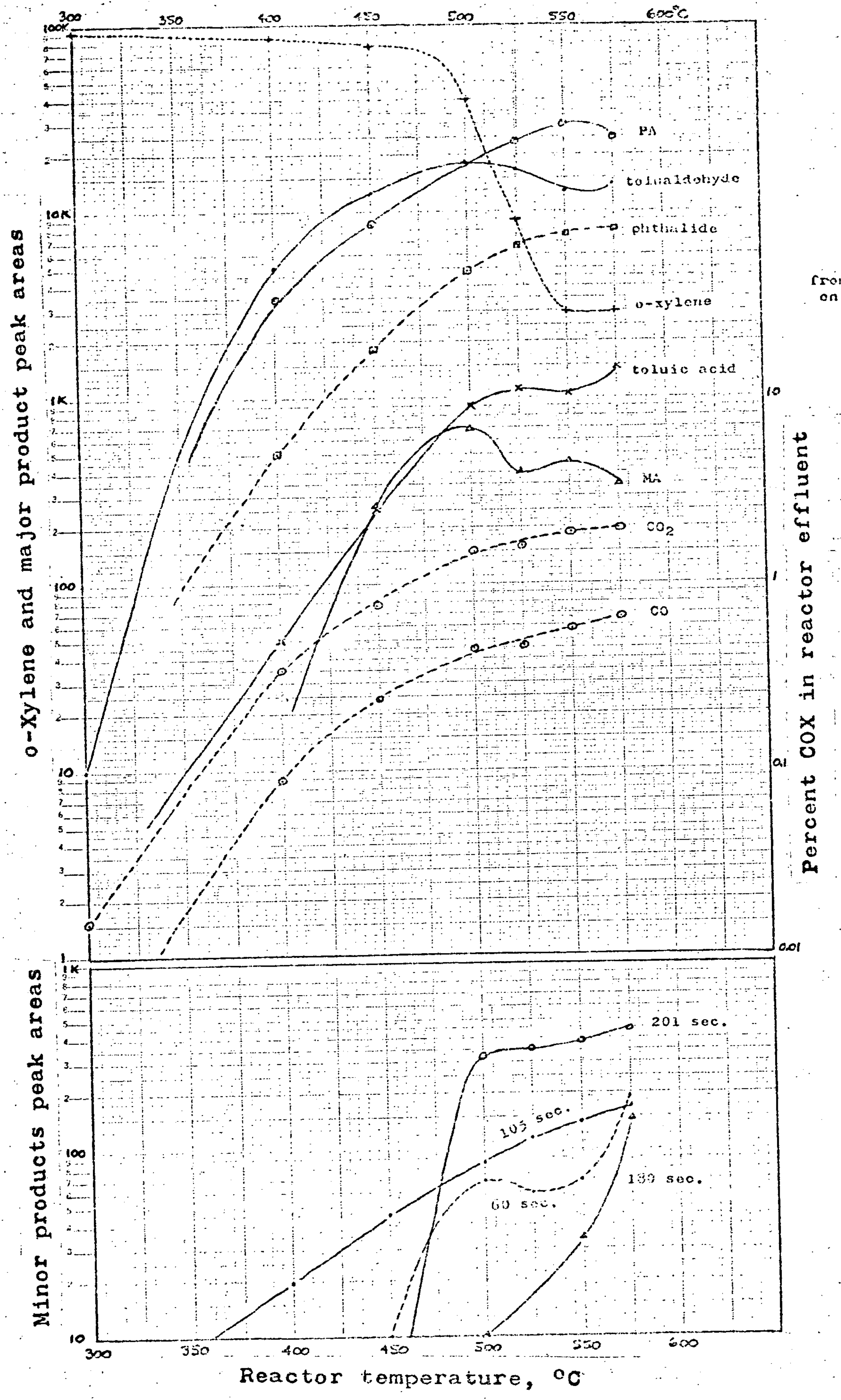


Figure 19

Products Distribution
from 0.95% o-xylene oxidatio
on experimental catalyst IV

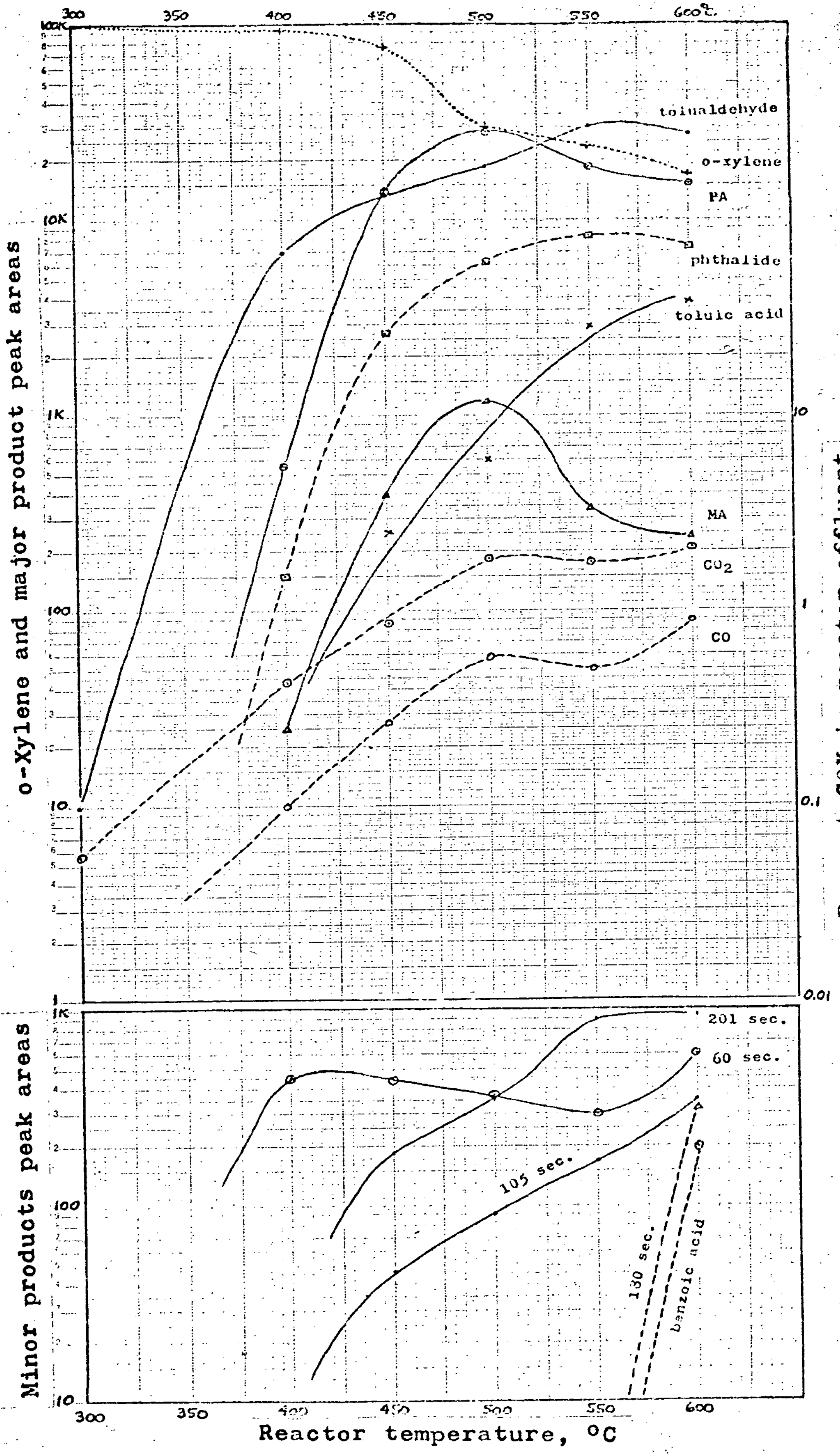


Figure 20

Products Distribution
from 0.96% o-xylene oxidatio
on experimental catalyst V

for the air oxidation of o-xylene in series 44. The products distribution diagram is shown in figure 20. Major products in order of appearance with reactor temperature increase are: o-tolualdehyde and carbon oxides, PA, phthalide, MA and toluic acid. Minor products were the 60 sec., 105 sec. and 201 sec. compounds. The 180 sec. compound and benzoic acid were evident only at 600°C reactor temperature.

D. Reaction Products from MA and PA Oxidation

Oxidation products of MA on experimental catalyst II were determined during series 49. This series used the same catalyst and volume flowrate as had been used for o-xylene oxidation. MA inlet concentration was 0.67 mole % in air to yield relatively large amounts of minor products in addition to carbon oxides and water. The 60 and 70 sec. compounds were formed below 400°C reactor temperature, Concentration of the 60 sec. compound increased with temperature. The 70 sec. compound declined with reactor temperature, yielding the 87 sec. compound. Thus, MA yields the 60 sec. compound directly, and the 87 sec. compound via the 70 sec. compound.

The products of PA oxidation were determined on several vanadia containing catalysts. Series 30-35 were a set of preliminary oxidations of PA, monitored by carbon oxides determinations, to determine that the five experimental catalysts were active for PA oxidation. The ratio of carbon dioxide to carbon monoxide was between 3 and 4. These series were conducted in the same reactor, at the same inlet PA partial pressure and volume flowrate, as was used for o-xylene oxidations. All experimental catalysts showed some activity for PA oxidation, but catalyst II, containing V_2O_5-K_2SO_4, was about twice as active as the others.

Series 36 used CCI-C103, the commercial V_2O_5 on SiC catalyst, to oxidize PA under the same conditions as were used in series 30-35. The purpose of series 36 was to make an activity comparison with the group of experimental catalysts. Activity of CCI-C103 was twice that of catalyst II, and four times the activity of the others. This series was conducted with high resolution Infrascan H-900 IR equipment on-line for analysis of the reactor exit stream. Compounds found with a 20 cm heated gas cell were CO_2, CO, H_2O, PA and traces of MA. All adsorption peaks were accounted for, except very small adsorptions at 962 and 1940 cm^{-1}. (The instrument reference for CO_2 peaks was 665, 718 and centered at 2320 cm^{-1}.). During the above on-line, hot-product analyses, the heated cell and traced aluminum feed line were maintained at 150°C, well above the m.p. and dew point of PA in the system. Series 37 was an extension of series 36 for 168 hours of operation. Products were monitored by non-dispersive IR instruments for CO_2 and CO analyses. The commercial CCI-C103 catalyst was stable, and there was no shift in tail-gas composition.

Series 38 was a set of kinetic measurements of PA oxidation on CCI-C103 over the temperature range 300-600°C. PA products on this catalyst were 80% carbon oxides, as shown by ratios, r_c/r_t, for rates of carbon oxides formation to rates of total products formation. At relatively low chromatograph sensitivity, only MA was recorded as an additional product. The ratio of CO_2/CO was about 3; this ratio was insensitive to temperature.

Products of PA oxidation on CCI-C103 were again measured during series 66. During this series, the ratio of rates to carbon oxides relative to rates to total products, r_c/r_t, was between 0.9-1.0. Thus, carbon oxides were the major PA products on this catalyst. The CO_2/CO ratio increased from 2.5 to 3.2 as reactor temperature was increased to 600°C. MA was formed in increasing amounts to 550°C reactor temperature. Above 550°C, MA declined and the 87 sec. compound was formed. A small amount of the 60 sec. compound was observed at 600°C. No benzoic acid was detected.

Experimental catalyst III, V_2O_5 on Alundum, had very low activity for PA oxidation during series 65. Maximum PA conversion of 7% occurred at 600°C, with 0.1 sec. contact time. The CO_2/CO ratio was 3-4, and r_c/r_t increased from 0.2 to 0.8 with reactor temperature. Low chromatograph sensitivity precluded meaningful products analyses.

Commercial von Heyden Kontakt-S catalyst was used to catalyze PA oxidation in series 60. Carbon oxides ratio, CO_2/CO varied from 5 to 8. At low chromatograph sensitivity, no MA and traces of the 87 sec. compound were detected. During series 67, another sample of von Heyden Kontakt-S was used for PA oxidation. Carbon oxides ratio increased with reactor temperature to 10 at 600°C. Rates ratio r_c/r_t was between 0.8-1.0. Concentration of MA peaked at 550°C reactor temperature, then declined with the appearance of traces of the 87 sec. compound.

The oxidation of PA occurred on aluminum surfaces at temperatures above 500°C in sufficient amounts to determine products. In series 51, a used 99+% aluminum reactor tube began to produce carbon oxides and traces of the 87 and 180 sec. compounds at 500°. At 600°C, some 87 sec. and much of the 180 sec. compounds were produced along with the 60 sec., 70 sec. and 150 sec. compounds. In addition, new compounds at 390 sec., 450 sec., and 610 sec. were observed. No MA was detected at any time, although its 87 sec. daughter product existed.

Series 59 measured PA oxidation on a used 99.5$^+$% aluminum reactor tube. Carbon oxides at a CO_2/CO ratio of 6-8 were produced at 500°C, and up. No MA was produced, although the 87 and 180 sec. compounds were produced in increasing amounts with reactor temperature increase. During this series, a portion of the tail gas, after ambient temperature condensation, was diverted through the quantitative combustor system. The purpose of this was to determine the amount of low molecular weight carbon compounds that may have escaped chromatograph detection. Results indicated that normal carbon oxides analyses accounted for 83-89% of the carbon contained in the tail gas. It is probable that some, if not all, of the additional low molecular weight compounds contributed to the early 87 sec. chromatograph peak. In series 61, the same used 99.5+% aluminum reactor tube was brushed out and rerun empty. The major products of PA oxidation were carbon oxides at a CO_2/CO ratio of 5-8. No MA was detected, but the 87 sec. compound appeared at 550°C. The 180 sec. compound was produced at 600°C reactor temperature.

Series 55a oxidized PA on the surfaces of an aluminum reactor filled with 99.5+% aluminum rings. At a contact time of 0.15 second, no MA was formed but the 180 sec. compound appeared at 500°C and increased with reactor temperature. At 550°C, and upward, the 87 sec.

compound and a new 450 sec. compound were observed. Small amounts of the 60 sec. compound were detected at 600°C. In series 55b, feed flowrate was reduced to increase the contact time by a factor of 5. Carbon oxides ratio CO_2/CO remained in the range of 8-5, decreasing with reactor temperature. The ratio of rate to carbon oxides relative to rate of conversion to all products, r_c/r_t, increased from 0.5 to 0.8 as reactor temperature was raised from 500 to 600°C. No MA was formed but the 87, 180 and 450 sec. compounds were formed at 500°C. The 180 sec. compound peaked at 550°C. At 600°C, traces of the 60 sec. compound, and a profusion of other compounds were evident. Those other compounds had standard chromatograph retention times of 70, 150, 390 and 610 seconds.

Fragments of fused silica catalyzed PA oxidation during series 56. The CO_2/CO ratio decreased from 12 to 6 with increased reactor temperature. The ratio r_c/r_t was 0.5 at 600°C and 0.2 sec. contact time. This ratio showed that half the converted PA appeared as carbon oxides. At low chromatograph sensitivity, no MA was detected. The 60, 87 and 180 sec. compounds were evident at 600°C reactor temperature.

On stainless steel, in series 57, oxidation of PA yielded a CO_2/CO ratio of 10-6, decreasing with reactor temperature. Ratio of carbon oxides to total products, shown by r_c/r_t increased from 0.55 to 0.85. No MA was evident. Minor products, in order of appearance with increased reactor temperature, were 180 sec., 87 sec. and 60 sec. compounds. The 180 sec. compound concentration peaked at 550°C and this was accompanied with genesis of the 87 sec. compound. During series 57, on-line hot-product IR analyses were made of the reactor effluent. Compounds found were CO_2, CO, H_2O, and a trace of unreacted PA, but no MA. Very small unassigned IR adsorptions occurred at 727, 962, 1937 and 2790 cm^{-1}. (Instrument reference was CO_2 peaks at 665, 718 and centered at 2320 cm^{-1}). The 727 cm^{-1} adsorption was not due to CO_2.

Series 58 oxidized PA on Alundum. The CO_2/CO ratio decreased from 6 to 4 with increased reactor temperature. No MA was detected. The 87 and 180 sec. compounds were formed at reactor temperatures above 500°C. Again reduction in the 180 sec. compound at high temperature was related to an increase in the 87 sec. compound. A small amount of the 60 sec. compound(s) was evident.

8. Discussion of Results

A. Products of PA Oxidation

The recognized products of PA oxidation are MA, carbon oxides and water. Experimental work was done to test the hypothesis that the PA oxidation scheme substantially follows two parallel paths: (1) from PA to COX, and (2) from PA, via MA, to COX. Attention was paid to minor products of PA oxidation that have not been reported, because their existence would help to define the reaction scheme from PA to complete combustion products.

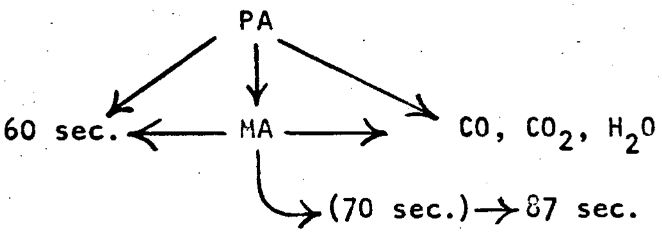
Series 36 oxidized PA on V_2O_5, and measured the IR spectrum of the hot product stream. Major products were identified using spectra tabulated in the appendix. Those major products were CO, CO_2, H_2O, MA and traces of unreacted PA. The ratio of carbon oxides, CO_2/CO was ca. 3 to 1. A small adsorption peak at 962 cm^{-1} could, with reservations, be associated with acrolein. That IR adsorption is existent in the acrolein spectrum (Sadtler Standard Spectrum no. 6645).[187] Another adsorption peak at 1940 cm^{-1} remains unidentified. Although acrylic acid does have an adsorption at that wave number (Sadtler Standard Spectrum no. 11017), other adsorption peaks of acrylic acid were not observed.

Series 38 and 66 oxidized PA on V_2O_5 to MA, carbon oxides and small amounts of other products characterized by their standard chromatograph retention times of 60 and 87 seconds. Concentrations of these compounds increased with reactor temperature; this indicated that they were stable, terminal products rather than intermediates. No benzoic acid was detected. During these two series carbon oxides constituted 80-100% of the oxidation products.

When PA was oxidized on the von Heyden Kontakt-S catalyst, the ratio of carbon oxides, CO_2/CO, increased with reactor temperature from 3 to 10. This increase showed that CO was readily oxidized to CO_2 on that catalyst. MA produced was oxidized to its 87 sec. daughter product.

From series 49, the major products of MA oxidation on V_2O_5 were carbon oxides and water. The minor compounds were the 60 sec. terminal product(s), plus a 70 sec. intermediate compound and its 87 sec. terminal product.

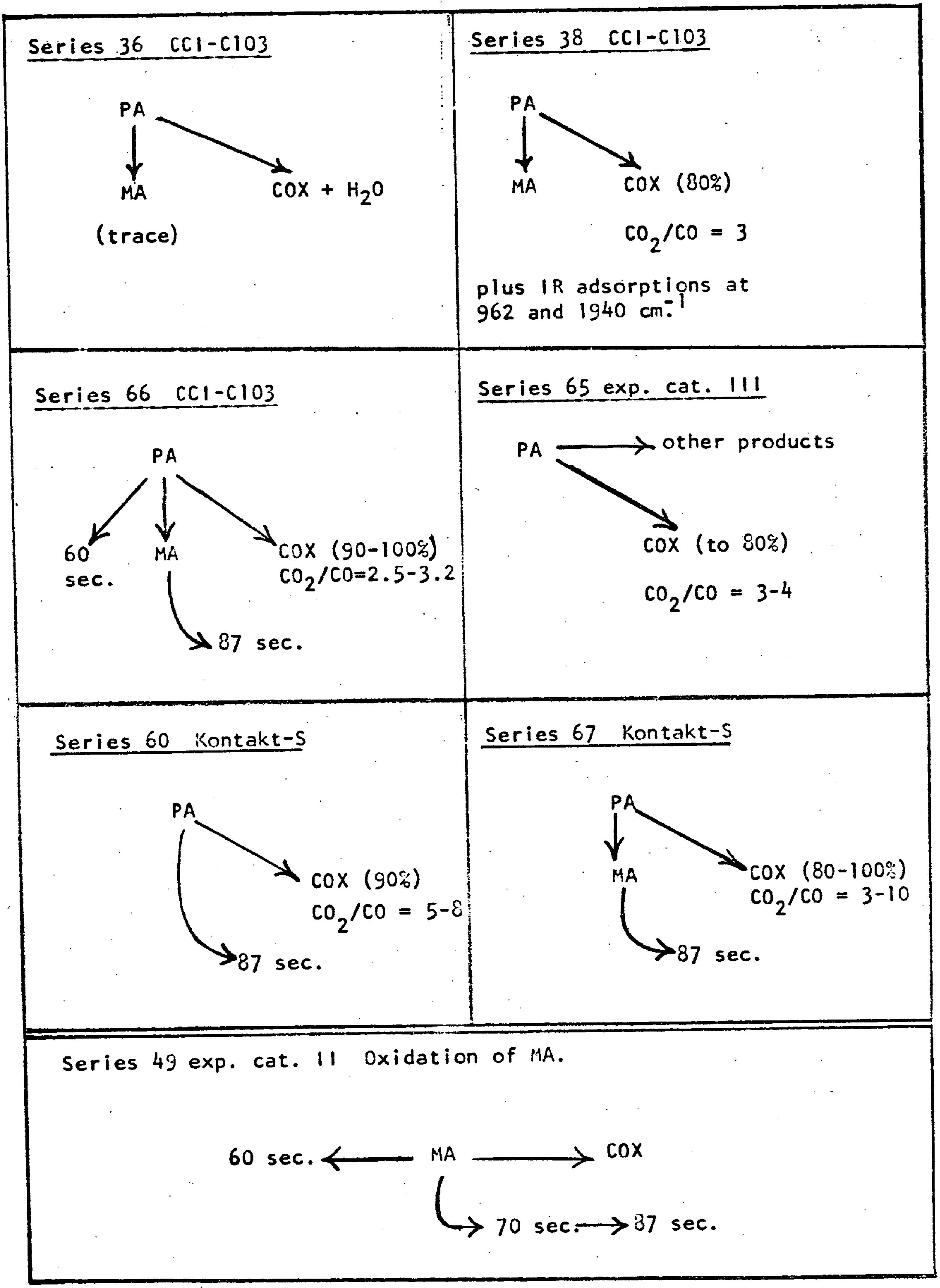
Data from experiments using vanadia catalysts are summarized in figure 21. From that information, a partial reaction scheme of PA oxidation may be constructed:



This scheme permits catalyst activity and selectivity to influence the amount of MA recovered as an oxidation product of PA. Secondary combustion of CO to CO_2 may similarly affect the observed CO_2/CO product ratio.

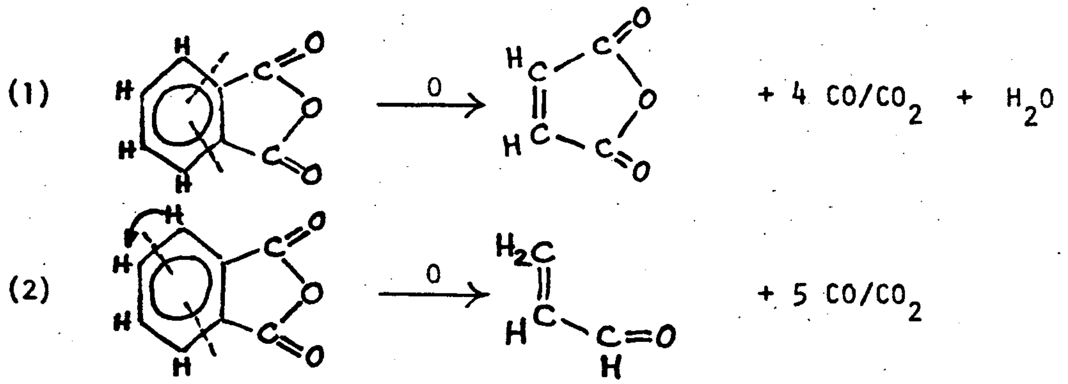
Figure 21

Oxidation Products on V_2O_5



Contrary to the findings of Pollak,[87] and to early findings of Craver,[163] no benzoic acid was observed as a product of PA oxidation on V_2O_5.

Acrolein is a possible product from PA; due to hydrogen deficiency, it is not a logical product of MA. Therefore, acrolein may be one of several unseparated compounds which can pass through that particular chromatograph column, without retention at 60 seconds. A direct route from PA to carbon oxides, by-passing MA, may exist. No carbon oxides were observed before some MA was present in the system. Therefore, MA and carbon oxides are likely to be concurrent products. Aromatic ring rupture and fragmentation of the ring could occur from an attack on the tertiary carbons according to reaction (1) below:



Reaction (2) is one possible way that acrolein could result from PA oxidation. Acetylene and its C_2 oxidation products are other low molecular weight compounds that might be expected from either PA or MA.

There are no published investigations of the products of PA oxidation on structural surfaces, other than statements that PA was oxidized to combustion products. During the experimental investigation, PA was oxidized on aluminum, steel, fused silica and porous Alundum.

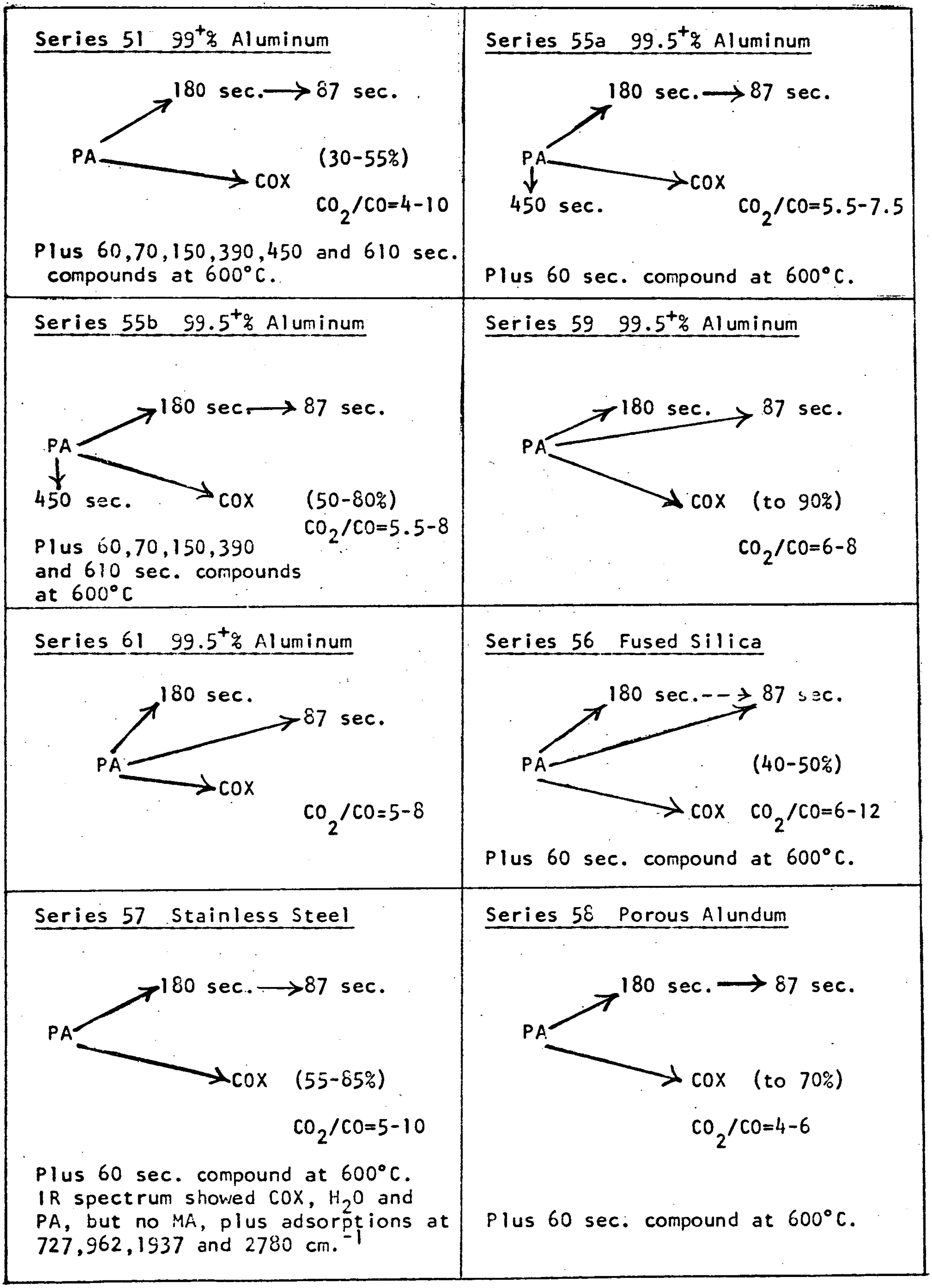
PA was oxidized on aluminum surfaces during series 51, 55ab, 59 and 61. Products were expected to be the same as those produced on vanadia, but modified in amount by the different activity and selectivity of the catalytic surfaces.

Figure 22 was constructed from an analysis of minor products growth and decline, using tabular data in the appendix. In each case, the question was asked, "What simplest reaction sequence could yield that product distribution?" During those PA oxidations, no MA and no benzoic acid were detected at any time. Principal products were carbon oxides and water. A new 180 sec. minor product was formed at and above 500°C reactor temperature. This new product and PA both appeared to form the 87 sec. compound. There was no clear evidence to support a contention that the 180 sec. compound was the sole parent of the 87 sec. compound. Since the 87 sec. compound had been shown to originate from MA, the lack of MA appearance can be explained by very rapid MA oxidation.

During the series 57 oxidation of PA on stainless steel, IR spectra of the hot product stream showed CO_2, CO, H_2O and a trace of unreacted PA, plus adsorptions at 727, 962, 1937 and 2780 $cm.^{-1}$ The 727 cm^{-1} adsorption matches the major adsorption of acetylene (Sadtler Standard Spectrum no. 3961). The 962 and 2780 cm^{-1} adsorptions match those of acrolein. The 180 sec. compound could conceivably be o-benzoquinone, on the bases of its probable formation from PA, column retention time, and

Figure 22

PA Oxidation Products on Structural Surfaces



Series 51 99$^+$% Aluminum

Plus 60,70,150,390,450 and 610 sec. compounds at 600°C.

Series 55a 99.5$^+$% Aluminum

Plus 60 sec. compound at 600°C.

Series 55b 99.5$^+$% Aluminum

Plus 60,70,150,390 and 610 sec. compounds at 600°C

Series 59 99.5$^+$% Aluminum

Series 61 99.5$^+$% Aluminum

Series 56 Fused Silica

Plus 60 sec. compound at 600°C.

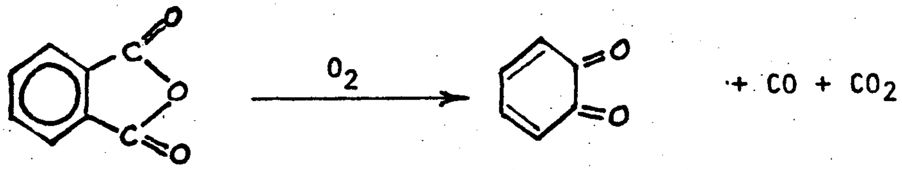
Series 57 Stainless Steel

Plus 60 sec. compound at 600°C. IR spectrum showed COX, H_2O and PA, but no MA, plus adsorptions at 727,962,1937 and 2780 cm.$^{-1}$

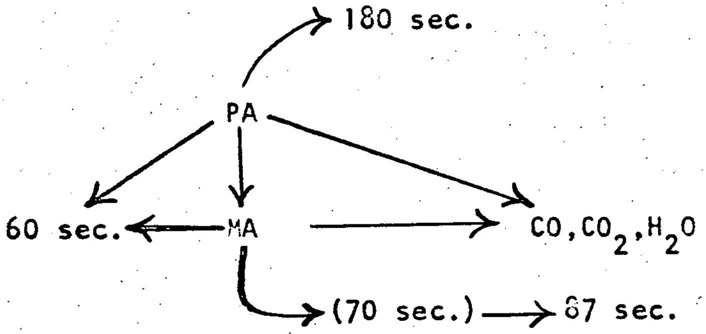
Series 58 Porous Alundum

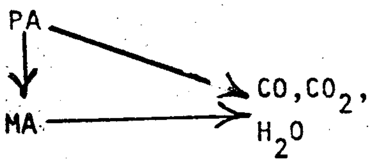
Plus 60 sec. compound at 600°C.

good thermal stability. Neither the compound nor its IR spectrum were available for comparison. o-Benzoquinone could be produced by oxidative decarboxylation of PA:



Data of figure 22 lead to the addition of the 180 sec. compound to the previous reaction sequence for PA oxidation; and adoption of a simplified sequence for inclusion in the overall o-xylene reaction sequence.





MA was present as a reaction product on some V_2O_5 catalysts, but MA was combusted on Kontakt-S and on structural materials. The 180 sec. compound was formed on structural materials.

Previous figure 2 summarized the literature data on reaction sequences involved in PA production from naththalene. Marek and Hahn[125] showed PA as source of benzoic acid and MA. Deficiency of two hydrogen atoms precludes benzoic acid formation from PA in an oxidative environment. No benzoic acid was found from any oxidation of PA conducted herein.

PA oxidation schemes used by other investigators were:

(1) $PA \rightarrow MA \rightarrow COX$ Ioffe and Sherman,[164] Volfson et al[140]

(2) $PA \rightarrow MA$ Ushakova et al[138]

(3) $PA \rightarrow MA + COX$ D'Alessandro and Farkas,[137]

Peterson[146] recalculated Ioffe and Sherman's data, and used scheme (2) in his derived reaction schemes.

Previous figures 3 and 4 summarized the literature data on reaction schemes involved in PA production from o-xylene. PA oxidation sequences used were:

(1) $PA \rightarrow MA \rightarrow COX$ Levine,[72] Vrbaski and Matthews,[80,87] Bernardini and Ramacci[85]

(4) $PA \rightarrow COX$ Costa-Novella and Escardino-Benlloch,[117] Froment,[88] Herten and Froment,[92] Vanhove and Blanchard[94]

(5)
$$\begin{tikzcd} PA \arrow[d] \arrow[dr] & \\ MA \arrow[r] & COX \end{tikzcd}$$
Carra and Beltrame,[118] Lyubarskii et al.[106]

Hughes and Adams[83] measured PA disappearance rate. They offered no reaction scheme, but their MA and COX reaction products fit above categorie (3).

Schemes used by the various investigators may be considered to be abbreviations of scheme (5), with which the simplified reaction sequence of this investigation agrees. The hypothesis that the PA oxidation scheme substantially follows two parallel paths to COX has been confirmed. The existence of the 180 sec. compound (possibly o-quinone) provides an alternate source of carbon oxides, independent of MA formation by ring rupture.

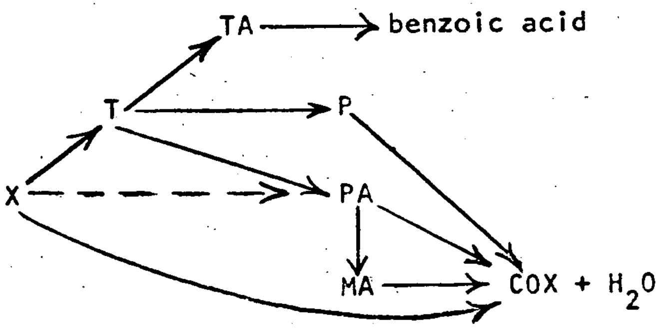
B. Products of o-Xylene Oxidation on V_2O_5

Unreacted o-xylene, o-tolualdehyde, o-toluic acid, phthalide, PA, MA, carbon oxides, water and benzoic acid are recognized products of industrial o-xylene oxidation.

Product distribution diagrams obtained during oxidations of o-xylene on V_2O_5 catalysts were each analyzed to determine the simplest reaction scheme that was consistent with the observed product sequences. The object was to summarize these, and to synthesize one reaction scheme that was consistent with all of the experimental observations.

Figure 23 is a summary of the simplest reaction schemes consistent with experimental findings. In figure 23, the abbreviations are the same as used in figures 3 and 4 that showed literature schemes: o-xylene (X), o-tolualdehyde (T), o-toluic acid (TA), phthalide (P), PA, MA and carbon oxides (COX).

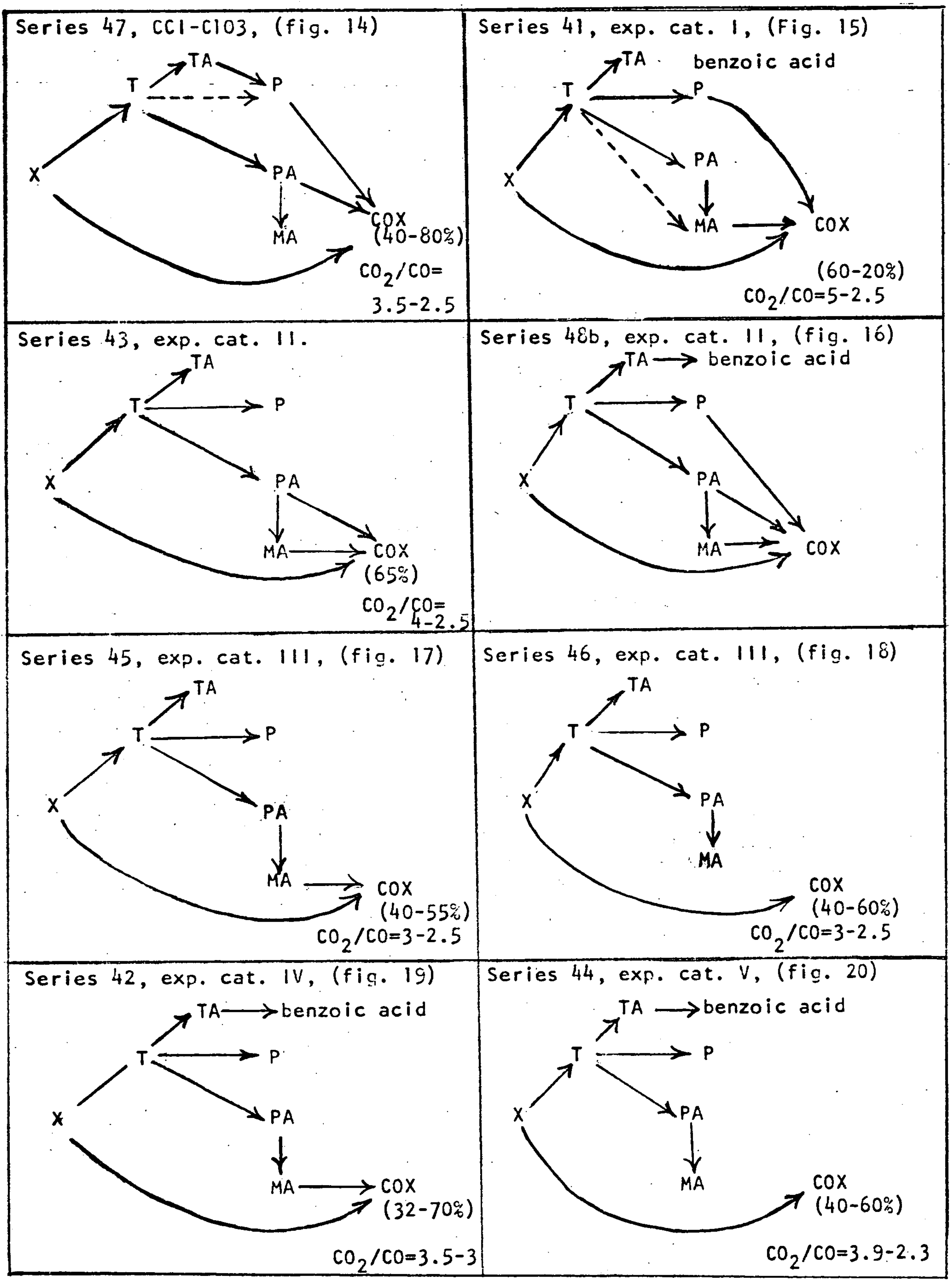
The simplest composite scheme derived from figure 23 would be:



This composite scheme disagrees with the scheme offered by Levine[72] who, in disagreement with all later investigators, showed o-toluic acid as the key step between xylene and phthalide. He also showed phthalic acid as a key intermediate to PA and benzoic acid. All others have considered that dehydration of phthalic acid is very rapid, and none have isolated phthalic acid.

Figure 23

Major o-Xylene Oxidation Products on V_2O_5



Series 47, CCl-C103, (fig. 14)

Series 41, exp. cat. I, (Fig. 15)

Series 43, exp. cat. II.

Series 48b, exp. cat. II, (fig. 16)

Series 45, exp. cat. III, (fig. 17)

Series 46, exp. cat. III, (fig. 18)

Series 42, exp. cat. IV, (fig. 19)

Series 44, exp. cat. V, (fig. 20)

The composite scheme is in agreement with Vanhove and Blanchard,[94] who also found that o-tolualdehyde can directly yield carbon oxides. The composite is in basic agreement with Carra and Beltrame,[118] who simplified theirs by omision of the key o-tolualdehyde intermediate. The composite similarly reduces to the more simplified schemes of Ellis,[98] Froment[88] and Caldwell.[96]

The composite scheme disagrees with Vrbaski and Matthews[80] who predicated their scheme on o-methylbenzyl alcohol (OMBA) as the key intermediate. No other investigators have isolated OMBA, so that the original Vrbaski and Matthews scheme is not considered applicable. A later Vrbaski and Matthews scheme[87] was based upon o-tolualdehyde as the key intermediate, and showed tolualdehyde to MA, phthalide, toluic acid, PA and COX. The direct route to MA could not be an important one since 80 mole % PA and 3 mole % MA were formed. That small amount of MA could easily have resulted from the PA present.

The composite scheme disagrees with those of Pichler and Obenaus[84] and Bernardini and Ramacci.[85] Those investigators showed PA only via phthalide. Their findings were not in accord with other investigators, nor with this work. In defense of their work, their particular catalysts may have had little selectivity towards the tolualdehyde to PA route. Pichler and Obenaus used tin vanadate, while Bernardini and Ramacci used a V_2O_5 on corundum catalyst prepared in their laboratory.

Several groups of workers have reported a direct route from o-xylene, by-passing tolualdehyde, to PA. Simard et al[73] oxidized o-xylene, Lyubarskii et al[106] oxidized o-tolualdehyde, PA and MA, Andreikov et al[111] oxidized o-xylene and o-tolualdehyde, while

Herten and Froment[92] oxidized o-xylene. If the oxidation mechanism involves o-xylene adsorption and oxidation by mobile oxygen on the catalytic surface, then o-tolualdehyde would be more easily desorbed than higher oxidation products. o-Tolualdehyde in the vapor phase would be detectable in the products stream, and be subject to readsorption and further oxidation. Higher sidechain oxidation products such as phthalaldehyde (o-formylbenzaldehyde), phthalaldehydic acid (o-formylbenzoic acid) and phthalic acid might not be desorbed until the anhydride ring structure of PA is formed. Few investigators have reported phthalaldehyde or phthalaldehydic acid in their product streams. Product distribution diagrams of this work show PA and tolualdehyde co-existent in the vapor phase during two of the cases examined, and show PA following tolualdehyde in the remainder. In no case was any PA detected prior to tolualdehyde presence in the vapor phase. Because of the heterogeneous mechanism involved, results of this work can be considered to confirm the prior findings that PA can result from one o-xylene residence on the catalyst surface.

The main objective of the o-xylene products distribution studies was to determine whether MA resulted from early xylene ring rupture, or whether MA was primarily produced from PA. It is granted that o-xylene could be adsorbed on the catalyst surface and be subject to sequential oxidations all the way to easily desorbed products, such as carbon oxides and water. Since PA appears in the product stream it was desorbed prior to further oxidation to MA. The pertinent concern is about the extent of ring rupture that occurs while o-xylene et seq. reside on the catalyst surface. Many investigators have shown direct routes from o-xylene to MA and to carbon oxides in their reaction schemes. The product distribution diagrams support early carbon oxides formation, but MA presence in the vapor phase was not observed in any case until PA was present. The reactor temperature for initial MA formation was 75°C above initial PA formation, in most cases. Since MA, which could originate from aromatic ring rupture, does not appear until after PA is present, one must conclude that there is some minimum temperature before ring rupture does occur. It has been experimentally shown that PA is produced before MA, therefore PA can be produced free of MA at low reactor temperatures. It is concluded that observed MA is formed from PA at intermediate reactor temperatures. No conclusion can be drawn at high temperatures.

During these o-xylene oxidations, three minor products were consistently produced; these were the 60 sec., 105 sec. and 201 sec. compounds. The 70, 87 and 180 sec. compounds from MA and PA were observed in several cases. A 150 sec. compound could have been present during many of the series at reactor temperatures around 600°C. A compound with 150 sec. retention time had been observed during PA oxidation on aluminum at 600°C.

There were several possible sources of the low molecular weight compounds that exhibited 60 sec. transit time through the chromatograph column without retention. Often these compounds were formed from o-xylene, concurrent with carbon oxides and tolualdehyde at low reactor temperature. The 60 sec. compounds had also resulted from PA and MA oxidations. Both acetylene and acrolein found from PA and MA oxidations could result from rupture of any aromatic ring.

The 105 sec. compound was existent in each of the o-xylene oxidations. Concentrations of this compound followed o-tolualdehyde, suggesting that o-tolualdehyde could be its parent. The 105 sec. compound was not existent before tolualdehyde, and, by its increase with reactor temperature, demonstrated its resistance to further oxidation. Because its chromatograph retention time is shorter than o-xylene and MA, the 105 sec. compound would be expected to be non-aromatic, though reasonably polar. It is unlikely that the 105 sec. compound could be methyl- or dimethyl-maleic anhydride because those compounds should have longer retention times than 122 sec. MA. Thus, the 105 sec. compound remains unidentified.

The 201 sec. compound was also existent in each of the o-xylene oxidations. Concentrations of the 201 sec. compound followed o-tolualdehyde concentrations, and were not existent before o-tolualdehyde. The 201 sec. retention time is midway between that of 145 sec. o-xylene and 256 sec. o-tolualdehyde. Since longer chromatograph retention times are based upon increased polarity and reduced volatility, the 201 sec. retention time is more likely associated with a less polar quinone structure, than with an aromatic structure that is more highly oxidized than o-tolualdehyde. The 201 second compound increased with reactor temperature and demonstrated stability towards further oxidation on all except the highly oxidative experimental catalyst II. The 201 sec. compound may be tentatively associated with a benzoquinone structure, possible p-benzoquinone.

Minor products of o-xylene oxidation, given in the literature are summarized on the next page:

Quinones:	p benzoquinone,[91,93] unstable quinones,[110] quinone,[70,76,115,116] methyl- and dimethyl-1,4-benzoquinones,[95] quinones.[73]
Aromatics:	phthalaldehydic acid (o-formylbenzoic acid),[84] o-hydroxymethyl-benzoic acid,[72,107] o-phthalaldehyde (diphthalaldehyde)(o-formylbenzaldehyde),[34,91,95,95] benzyl alcohol,[79] acid phthalate of o-methylbenzyl alcohol,[79]
Non-Aromatics:	citraconic anhydride (methyl-MA),[79,84,107] citraconic acid,[78] dimethyl-MA,[84,95,107] acetic acid,[84] succinic acid,[107] acrolein,[72] methylacrolein.[72]
Condensed Products:	Several investigators have reported analyses of condensed products recovered from industrial PA distillation residues (tars).[34,90,107,150]

The existence of p-benzoquinone as a minor product from the literature lends credence to the tentative assignment of a benzoquinone structure to the 201 sec. compound.

C. Kinetics of PA Oxidation

The kinetics of PA oxidation were studied to test the hypothesis that a single adsorption type heterogeneous rate equation was applicable over the range of temperatures and PA concentrations encountered in PA production.

Experimental series 20-29 oxidized PA on an aluminum-diluted V_2O_5 catalyst in a tubular aluminum reactor under isothermal conditions at 380-500°C. Ten PA inlet partial pressures and four reactor temperatures generated a matrix of kinetic data for PA conversion to carbon dioxide and conversion to all products. These data could be represented by an exponential form of rate equation that was pseudo zero-order in oxygen and varied in order from 0.5 to 0.7 with respect to PA. Order with respect to PA increased with reactor temperature, as was shown in previous figure 11. Rate data from series 20-29 were fitted to a Langmuir-Hinshelwood rate equation of the form:

$$r = \frac{k_1 P}{1+k_2 P}, \text{ where P is partial pressure in the reactor.}$$

Manipulation of this equation yields $r = \dfrac{k_1}{k_2}\left[1 - \dfrac{1}{1+k_2P}\right]$.

This shows that, when k_2P is large and most catalyst sites are occupied, the rate approaches $\dfrac{k_1}{k_2}$ as a limit, giving a zero order rate equation. When k_2P is small and few catalyst sites are occupied, the original equation approaches a first order rate equation. When a non specific catalyst is involved, the denominator term of the Langmuir Hinshelwood rate equation may be expanded to contain additional terms for each species that occupies catalyst sites, for example:

$$r = \frac{k_1 P}{1+k_2 P + k_3 P_1 + \ldots}$$

In the PA oxidation studied, slowly desorbable products such as a quinone or MA may occupy catalyst sites and may be further oxidized thereon. In the case of PA in the presence of much o-xylene, the catalyst sites may be so occupied by o-xylene and interim products that desorbed PA has few available sites for readsorption and further oxidation. During this study of the effect of PA concentration on reaction rate, the MA partial pressure existent in the vapor phase was a small fraction of the PA partial pressure. Desorption of MA from catalyst surface was assumed on the basis of vapor pressure to be much greater than PA. Therefore, $k_2 P_{PA}$ was assumed >> $k_3 P_{MA}$. Lyubarskii used a similar simplification.[106] The use of simplified rate equations containing as few parameters as can be justified by the data and a reasonable mechanistic model have been advocated by White and Churchill,[188] Weller,[189] Edelson and Allara,[190] Froment[191] and Boudart.[192]

Data from the PA concentration study may be compared with few literature data. Ioffe and Sherman[164] gave six data points for the rates of PA oxidation to carbon oxides and MA. These six rates were at five temperatures (350-480°C) two flowrates and two PA partial pressures (0.009 and 0.012 atm.) in their tubular reactor. Limited amount of data and narrow range of the concentration variable precluded determination of the applicable form of rate equation. Their data were reduced on a simple first order basis. Costa-Novella and Escardino-Benlloch[117] presented a derived first order rate equation for PA oxidation at

310-370°C. They oxidized o-xylene in a fluid bed reactor and interpreted their data on a plug-flow basis. Derived rates for all steps were determined by fit of their product distribution diagrams to homogeneous first order rate equations. Hughes and Adams[83] oxidized PA to MA and carbon oxides at three temperatures (497-575°C), one contact time (0.1 sec.) and a span of reactor PA partial pressures (0.002-0.012 atm.). Their fourteen data points were fitted to a simple Langmuir-Hinshelwood rate equation. Lyubarskii et al[106] oxidized PA to MA and carbon oxides at four temperatures (440-500°C) and four PA partial pressures in the range 0.0006-0.0024 atm. Their sixteen data were fitted to a single Langmuir-Hinshelwood rate equation.

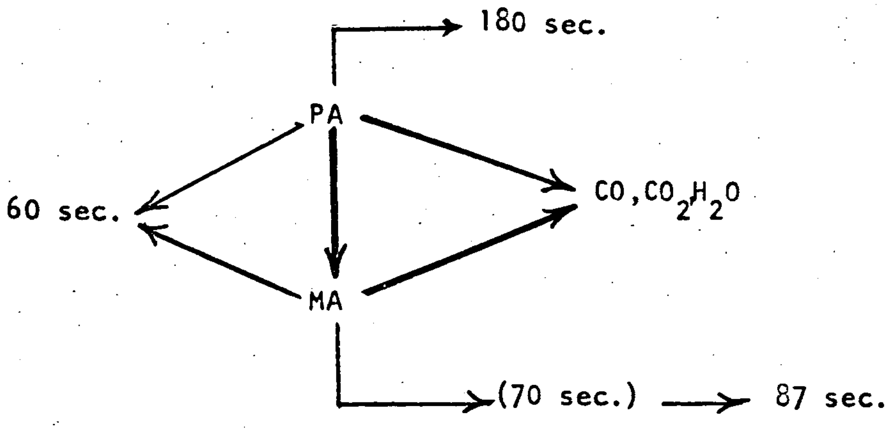
The latter two groups used the same heterogeneous Langmuir-Hinshelwood rate equation as was used in this study. Hughes and Adams covered a high PA partial pressure range; Lyubarskii et al covered the low PA partial pressure range. There was no concentration overlap, but their results were significantly different. The difference was shown, in previous figure 6, by a major discontinuity in slopes of the least squares of deviations lines used to determine parameters. In this study one line fitted data over their combined PA partial pressure range.

Temperature dependence of the kinetics of PA oxidation was found to be uniform among V_2O_5 catalysts at temperatures to 400°C. An apparent Arrhenius activation energy of 28.6 Kcal/mole was shown by data for 3 catalysts at the same PA partial pressure. Above 400°C, behavior of the three catalysts shown in figure 13 was as different as had been shown by the literature data of figure 5. It is apparent from this study of PA oxidation that generalizations are inappropriate with respect to catalyst activity and specificity.

9. Conclusions and Recommendation

A. Conclusions

1. The products of PA oxidation are CO_2, CO, H_2O, MA and four other minor compounds. These minor compounds are designated by their 60, 70, 87 and 180 sec. standard chromatographic retention times. Acetylene and acrolein were shown by their IR spectra to be existant among the minor compounds. The 180 sec. compound is assumed to be o-benzoquinone.
2. The products of MA oxidation are CO_2 CO and H_2O plus three minor compounds designated by their 60, 70, and 87 sec. standard retention times.
3. The reaction sequence from PA to products is:

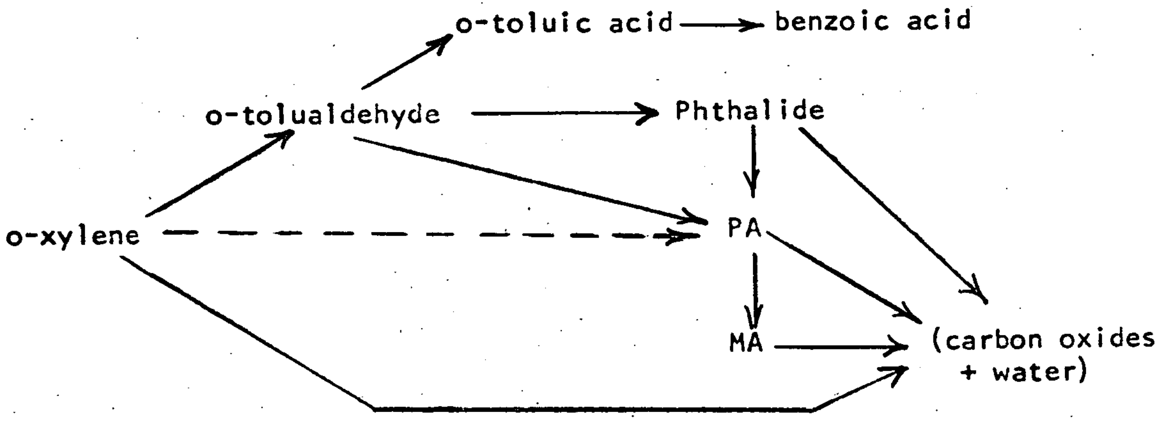


Ignoring minor products, this sequence may be simplified to the center PA, MA and carbon oxides triangular scheme.

4. The products of o-xylene oxidation on six V_2O_5 catalysts consisted of o-tolualdehyde, o-toluic acid, phthalide, PA, MA, carbon oxides and water, plus traces of benzoic acid at high temperature. In addition to the four minor products

observed from PA oxidations, two other minor products with standard retention times of 105 and 201 sec. were observed. The 105 sec. compound is unidentified, but is most likely non-aromatic and polar. The 201 sec. compound may be tentatively associated with a benzoquinone structure.

5. From product distribution diagrams, the following reaction sequence for o-xylene oxidation was derived:



6. No evidence was found to support a direct route from o-xylene to MA at low reactor temperatures. MA is believed to be derived from PA oxidation.

7. Kinetics of PA oxidation on V_2O_5 followed a Langmuir-Hinshelwood type heterogeneous rate equation that was pseudo zero order in oxygen partial pressure. Parameters varied widely among catalyst types.

B. Recommendation for Further Work

One major unsolved problem revealed during the literature search was interaction among reactive species during catalytic oxidations. Occupancy of catalyst sites can result in an apparent inhibition on non-specific catalysts. It is probable that Langmuir-Hinshelwood heterogeneous rate equations must contain added denominator terms for the summation of all oxidizable or difficulty desorbed species that can occupy catalyst sites. Indications that oxidations are inhibited by other species have been mentioned by Bernardini and Ramacci,[85] Lyubarskii,[106] Andreikov,[110] Korneichuk,[139] Ushakova,[138,165] Roiter,[144] Ioffe and Sherman,[163,154] and Volf'son.[167]

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Appendix Experimental Data

Series 1 Reactor: L, Catalyst: 0.44 cm diam SA-201 Alundum Spheres
W = 50.06 gm (16.0cc), L = 38 cm, V_r = 32 cc, $\Delta P \leq$ 1 psig,
feed: PA, 3.6 cm^2 stainless steel/gm.

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
400	1.00	.0014	-	0.2	-	12.5	-
425	"	"	.30	0.4	-	24.9	20.9
450	"	"	.71	0.6	-	37.4	49.5
500	"	"	>.995	1.1	-	68.5	69.8

Series 2 Reactor: L, Catalyst: 0.5 cm diam soft glass spheres
W = 68.4 gm (22.5cc), L = 38 cm, V_r = 25.5cc, $\Delta P \leq$ 1 psig,
feed: PA, glass area 275 cm^2, SS area 184 cm^2.

T, °C	q	P_i*		$\Delta\%CO_2$	%CO	$r'_c \cdot 10^6$ per $10cm^2$	$r_t \cdot 10^6$ per $10cm^2$
500	12.2	~.005	-	0.15	-	126.	-
"	4.06	"	-	0.40	-	110.	-
"	1.03	"	-	1.25	-	88.	-
425	12.2	"	-	0.05	-	43.	-
"	7.10	"	-	0.20	-	96.	-
"	2.18	"	-	0.30	-	44.	-

r'_c is based on both glass and SS areas.

*feed stream was pilot plant reactor product containing 1.2-1.3% CO_2 (indicating about 50% conversion) through 2.5 cm. diam. tubular reactor at 450°C (non-isothermal) on 1% vol. o-xylene feed.

Series 3 Reactor: L, Catalyst: stainless steel cylinders
W = 151.2 gm (18.9cc), L = 38 cm, V_r = 29.1cc, $\Delta P \leq$ 1 psig,
feed:PA, 427 cm^2 total SS area.

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r'_c \cdot 10^6$ per $10cm^2$	
500	5.10	.00028	-	$\leq$0.2	-	$\leq$74.	
500	"	.0014	-	0.7	-	261.	
460	"	"	-	0.25	-	93.	
390	"	"	-	0.0	-	0.	
425	1.00	"	-	0.7	-	51.	

Series 4 Reactor: A, Catalyst: empty, L = 123 cm, V_r = 2.44cc
ΔP = 1.5 psig, feed: PA , 61 cm^2 SS.

T, °C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per $10cm^2$	$r_t \cdot 10^6$
390	0.800	.00145	.029	-	-	-	14.
425	"	"	.162	-	-	-	77.
460	"	"	.792	0.50	-	204.	375.
500	"	"	>.99	0.60	-	245.	>469.
500	"	.00253	>.99	1.20	-	491.	>819.
390	1.60	.00145	<.01	-	-	-	< 9.
425	"	"	.028	-	-	-	27.
460	"	"	.369	-	-	-	350.
500	"	"	>.99	0.50	-	409.	>939.

Series 5 Reactor: A, Catalyst: empty, L = 123 cm, V_r = 2.44cc
ΔP = 1.5 psig, feed: PA , 61 cm^2 SS.

T, °C	q	P_i	X_t	%CO_2	%CO		$r_t \cdot 10^6$ per $10cm^2$
390	0.800	.00724	<.01	-	-		< 24.
425	"	"	<.03	-	-		< 72.
460	"	"	.164	-	-		388.
500	"	"	.336	-	-		796.
390	"	.00158	<.01	-	-		< 5.
425	"	"	.058	-	-		30.
460	"	"	.624	-	-		323.
500	"	"	>.99	-	-		512.

Series 6 Reactor: M, Catalyst: Stainless steel cylinders (A = $82cm^2$)
+$237cm^2$ reactor, V_r = 52 cc, ΔP = 1 psig, feed: PA, 319 cm^2 SS.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per $10cm^2$	
330	1.54	.00153	-	0.0	-	0.	
380	"	"	-	0.01	-	1.5	
400	"	"	-	0.02	-	3.	
420	"	"	-	0.03	-	4.5	
430	"	"	-	0.04	-	6.	
440	"	"	-	0.07	-	11.	
450	"	"	-	0.11	-	17.	
460	"	"	-	0.16	-	24.	
470	"	"	-	0.22	-	33.	
480	"	"	-	0.28	-	42.	
490	"	"	-	0.35	-	53.	

Series 7 Reactor: M, Catalyst: CCI-C103, W = 7.3gm (2.84cc), V_r = 52cc ΔP = 1 psig, feed: PA, 32 cm^2 SS/gm.

T, °C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	1.49	.0016	.00	0.0	-	0.	0.
330	"	"	.00	0.0	-	0.	0.
365	"	"	<.005	0.0	-	0.	< 4.
380	"	"	<.01	0.00	-	0.	< 8.
400	"	"	.15	0.05	-	32.	122.
420	"	"	.23	0.10	-	64.	187.
460	"	"	-	0.20	-	127.	-
475	"	"	.52	0.33	-	210.	424.
480	"	"	-	0.40	-	255.	-
485	"	"	.56	0.42	-	267.	473.

Series 8 Reactor: B, Catalyst: empty, L = 123 cm, V_r = 9.76cc ΔP = 0.5-1.0 psig, feed: PA, 123 cm^2 SS.

T, °C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
390	1.74	.0014	<.01	0.0	-	0.	< 5.
425	"	"	.200	0.15	-	66.	99.
460	"	"	.573	0.50	-	220.	283.
480	"	"	>.99	0.60	-	265.	>489.
500	"	"	1.00	0.55	-	243.	494.

Series 9 Reactor: C, Catalyst: empty, L = 120 cm, V_r = 8.46cc ΔP $\leq$ 0.5 psig, feed: PA, 112 cm^2 borosilicate glass.

T, °C	q	P_i	X_t	%CO_2	%CO		$r_t \cdot 10^6$ per 10cm^2
390	2.04	.0015	.00	-	-		0.
425	"	"	.00	-	-		0.
460	"	"	.00	-	-		0.
480	"	"	.00	-	-		0.
500	"	"	<.01	-	-		< 7.
500	0.320	.0014	<.03	-	-		< 3.
500	"	.00635	<.03	-	-		<14.

Series 10 Reactor: D, Catalyst: empty, L = 117 cm, V_r = 20.8cc ΔP see below, feed: PA, 175 cm^2 Al.

T, °C	q	P_i	X_t	ΔP	%CO_2	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
500	5.00	.0014	<.01	4.0	0	0.	<10.
500	0.790	"	.06	nil	0	0.	9.

Series 11 Reactor: E, Catalyst: Mild steel, W = 14.67 gm (1.90cc), $S = 82$ cm^2, L = 24 cm, $V_r = 2.8$cc, $\Delta P \leq 1$ psig, feed: PA Steel then reactor void configuration, no preheat void. 23 cm^2 glass/10 cm^2 mild steel.

T, °C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	0.535	.0014	.00	0.0	-	0.	0.
440	"	"	.281	0.3	-	64.	61.
460	"	"	>.99	0.5	-	>226.	102.
480	"	"	1.00	0.5	-	228.	102.
500	"	"	1.00	0.5	-	228.	102.

Series 12 Reactor: E, Catalyst: thoroughly oxidized mild steel, W = 14.67 gm (1.90cc), S = 82 cm^2, L = 24 cm, $V_r = 2.8$cc $\Delta P \leq 1$ psig, feed: PA. Reversed configuration from Series 11, long preheat void then the oxidized mild steel no exit void. 23 cm^2 glass/10 cm^2 ox. mild steel.

T, °C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	0.535	.0014	.00	0.0	-	0.	0.
400	"	"	.030	0.0	-	0.	7.
420	"	"	.172	0.2	-	41.	39.
440	"	"	(.78?)	0.35	-	71.	(178.?)
460	"	"	>.99	0.45	-	92.	>226.
480	"	"	1.00	(0.4?)	-	(81.?)	228.
500	"	"	1.00	0.5	-	102.	228.
300	"	.0070	.00	0.0	-	0.	0.
440	"	"	.04	0.4	-	81.	46.
460	"	"	.11	0.9	-	183.	125.
480	"	"	>.99	3.2	-	651.	>1128.
500	"	"	1.00	3.2	-	651.	1139.

Series 13 Reactor: E, Catalyst: 20 Cr-80 Ni short pieces of wire, W = 13.67 gm, (1.65cc), S = 100cm^2, L = 24 cm, $V_r = 3.05$cc $P \leq 1$ psig, feed: PA same configuration as Series 12. 23 cm^2 glass/10 cm^2.

T, °C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	0.535	.0070	.00	0.0	-	0.	0.
500	"	"	.10	-	-	-	93.
500	"	.0014	.40	0.25	-	42.	75.
after 16 hrs. operation at 500°C							
500	0.535	.0014	.45	0.30	-	50.	84.
480	"	"	.16	0.15	-	25.	30.
460	"	"	.10	0.04	-	7.	19.

Series 14 Reactor: E, Catalyst: CCI-C103 (1.0-1.4mm diam) W = 3.09gm (1.1cc) followed by 8.9cm length, ($46cm^2$) of 1.26mm soft glass beads to hold bed in place. L of CCI-C103 bed 17cm V_r = 2.3cc, $\Delta P \leq 1$ psig, feed: PA

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	0.535	.0014	.00	0.0	-	0.	0.
500	"	"	.668	0.30	-	162.	404.
after 16 hrs. operation at 500°C							
380	0.535	.0014	.076	-	-	-	46.
400	"	"	.144	0.0	-	0.	87.
420	"	"	.283	-	-	-	171.
440	"	"	.402	-	-	-	243.
460	"	"	.491	0.13	-	70.	297.
480	"	"	.588	0.15	-	81.	356.
500	"	"	.681	0.25	-	135.	412.*
380	"	.0070	.005	(0.10?)	-	(54.)?	15.
400	"	"	.078	0.25	-	135.	235.
420	"	"	.127	0.45	-	243.	383.
440	"	"	.216	0.70	-	378.	653.
460	"	"	.318	0.90	-	486.	961.
480	"	"	.438	1.15	-	621.	1324.
500	"	"	.523	1.50	-	810.	1581.

*note: ΔT=38°C measured in bed

Series 15 Reactor: E, Catalyst: 1.26mm soft glass beads, W = 8.21gm (2.70cc) S = $130cm^2$, L = 26cm, V_r = 2.3cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per $10cm^2$	$r_t \cdot 10^6$ per $10cm^2$
300	0.535	.0014	.00	0.0	-	0.	0.
460	"	"	.162	0.0	-	0.	23.
480	"	"	.239	0.05	-	6.	34.
500	"	"	.396	0.12	-	15.	57.
420	"	"	.031	-	-	-	4.
440	"	"	.051	0	-	0.	7.
460	"	"	.089	0	-	0.	13.
480	"	"	.200	0.08	-	10.	29.
500	"	"	.307	0.13	-	17.	44.
460	0.535	.0070	.06	0.05	-	6.	43.
500	"	"	.14	0.35	-	45.	101.

Series 16 Reactor: E, Catalyst: Duraluminium drilling chips, W = 3.41gm (1.3cc) S = 116cm^2, L = 25.4cm, V_r = 3.7cc, $\Delta P \leq 0.5$ psig, feed: PA

T,°C	q	P_i	X_t	$\%CO_2$	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
after 16 hrs. operation at 500°C to condition the metal surface							
460	0.535	.0014	.080	-	-	-	13.
480	"	"	.110	0.0	-	0.	18.
500	"	"	.102	0.0	-	0.	16.

Series 17 Reactor: E, Catalyst: 1.2-1.4mm fragments of SA-203 Alundum, W = 4.93gm (1.5cc), L = 25 cm, V_r = 3.35cc, $\Delta P \leq 1$ psig, feed: PA

T,°C	q	P_i	X_t	$\%CO_2$	%CO	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	0.535	.0014	.00	0.0	-	0.	0.
500	"	"	.022	0.0	-	0.	8.
after 22 hours operation at 500°C							
380	0.535	.0014	.00	0.0	-	0.	0.
420	"	"	.00	0.0	-	0.	0.
460	"	"	.005	0.0	-	0.	2.
500	"	"	.017	0.0	-	0.	6.

Series 18 Reactor: E, Catalyst: Stainless steel pieces cut from reactor (L), W = 13.54gm (1.7cc) S = 63cm^2, L = 17cm
V_r = 1.9cc,ΔP $\leq$ 0.5 psig, feed: PA

T,°C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	0.535	.0014	.00	0.0	-	0.	0.
500	"	"	.665	0.30	-	80.	198.
380	"	"	<.005	0.00	-	0.	<1.
500	"	"	.578	0.25	-	66.	172.
after 16 hrs. operation at 500°C							
500	0.535	.0014	.472	0.23	-	61.	140.
380	"	"	.00	0.00	-	0.	0.
420	"	"	<.01	0.00	-	0.	<3.
440	"	"	<.03	0.00	-	0.	<9.
460	"	"	.063	0.04	-	11.	19.
480	"	"	.206	0.15	-	40.	61.
500	"	"	.462	0.25	-	66.	137.
380	"	.0070	<.01	0.00	-	0.	<15.
460	"	"	<.05	0.07	-	18.	<74.
480	"	"	.12	0.18	-	48.	178.
500	"	"	.22	0.33	-	87.	326.

Series 19 used-reactor D, Catalyst: EC grade Aluminium wire clippings tumbled to near spherical 2mm diam., W = 32.1gm (11.9cc)
S = 393cm^2, L = 117 cm, V_r = 8.9cc, ΔP = 5-7psig, feed: PA
Reactor S = 175cm^2 Al, total 568 cm^2.

T,°C	q	P_i	X_t	%CO_2	%CO	$r'_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
500	0.495	.0014	.294	-	-	-	8.9
after 16 hrs. operation at 500°C to condition surfaces for subsequent series							
300	0.605	.00133	<.01	-	-	-	<0.4
460	"	"	.11	-	-	-	3.9
480	"	"	.17	-	-	-	6.0
500	"	"	.27	0.07	-	2.3	9.5

Series 20 used-reactor D, Catalyst: CCI-C103 (1.2mm diam) W = 2.85gm (1.0cc) about 1100 spheres admixed with EC aluminium from Series 19 displacing only a very small portion of it. 31.2gm Al remained. L = 117cm, V_r = 8.3cc, ΔP at inlet noted at each temp. 195 cm² Al/gm.

T, °C	q^* l/min	P_i atm.	ΔP psig	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.542	.00149	4.5	.00	0.00	0.	0.
380	.556	"	5.5	.062	0.00	0.	45.
420	.556	"	5.5	.169	0.09	55.	123.
460	.567	"	6.3	.395	0.20	124.	292.
500	.577	.00150	7.0	.669	0.375	236.	507.

*q(ambient) increases with system ΔP at same rotameter indications.

Series 21, same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.546	.00204	4.8	.00	0.00	0.	0.
380	.559	.00206	5.7	.061	0.05	31.	61.
420	.561	.00204	5.9	.191	0.135	83.	191.
460	.567	.00206	6.3	.402	0.275	171.	411.
500	.577	"	7.0	.575	0.40	252.	598.

Series 22, same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.545	.00279	4.7	.00	0.00	0.	0.
380	.552	"	5.2	.083	0.07	42.	112.
420	.559	.00281	5.7	.195	0.17	104.	268.
460	.569	.00282	6.4	.393	0.37	230.	552.
500	.577	"	7.0	.623	0.62	391.	887.

Series 23 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.549	.00392	5.0	.00	0.00	0.	0.
380	.560	.00393	5.8	.089	0.12	74	171.
420	.567	.00395	6.3	.188	0.25	155.	368.
460	.577	.00396	7.0	.336	0.455	287.	676.
500	.583	.00393	7.4	.622	0.77	491.	1247.

Series 24 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.552	.00657	5.2	.00	0.00	0.	0.
380	.563	.00658	6.0	.041	0.085	52.	133.
420	.567	"	6.3	.107	0.26	161.	349.
460	.574	.00659	6.8	.261	0.53	333.	864.
500	.583	.00658	7.4	.530	1.01	644.	1779.

Series 25 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.540	.00107	4.4	.00	0.00	0.	0.
380	.555	"	5.4	.158	0.057	35.	82.
420	.562	"	5.9	.239	0.090	55.	126.
460	.566	"	6.2	.486	0.175	108.	258.
500	.570	"	6.5	.716	0.27	168.	382.

Series 26 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	%CO_2	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.534	.000431	4.4	.00	0.00	0.	0.
380	.544	.000427	5.2	.266	(0.04)	24.	54.
420	.551	.000429	5.7	.391	(0.06)	36.	81.
460	.560	.000440	6.3	.612	0.08	49.	132.
500	.563	.000436	6.6	.819	0.12	74.	176.

Series 27 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	$\%CO_2$	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.601	.00864	5.7	.00	0.00	0.	0.
380	.611	.00865	6.3	.030	0.09	60.	139.
420	.619	.00868	6.8	.104	0.32	217.	489.
460	.631	.00867	7.5	.232	0.61	421.	1111.
500	.639	"	8.0	.474	1.27	888.	2298.

Series 28 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	$\%CO_2$	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.535	.00217	4.6	.00	0.00*	0.	0.
380	.544	.00216	5.3	.078	(0.08)	48.	80.
420	.552	.00219	5.8	.245	(0.22)	133.	259.
460	.559	"	6.3	.414	(0.40)	245.	444.
500	.567	.00218	6.9	.652	(0.63)	391.	705.

*(CO_2 analysis problem)

Series 29 same as Series 20, except for changed PA inlet concentration.

T, °C	q	P_i	ΔP	X_t	$\%CO_2$	$r'_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.539	.00170	4.3	.00	0.00	0.	0.
380	.548	.00172	4.9	.085	0.05	30.	70.
420	.552	"	5.2	.215	0.14	85.	179.
460	.560	.00171	5.8	.436	0.25	153.	365.
500	.563	.00172	6.0	.629	0.39	240.	533.
500	.574	"	6.8	.617	0.34	213.	533.

Series 30 Reactor: F, Catalyst: experimental cat. II, W = 14.20gm (5.82cc), L = 34 cm, V_r = 10.5cc, $\Delta P \leq 1$ psig, feed: PA 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.478	.0056	-	0.00	0.00	0.	-
350	"	"	-	0.02	0.00	2.	-
400	"	"	-	0.04	0.00	4.	-
450	"	"	-	0.06	0.01	7.	-
500	"	"	-	0.10	0.02	13.	-

Series 31 extension of Series 30 into higher temperature reactor conditions. Same reactor and bed. Chromatograph not used.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
550	.478	.0056	-	0.24	0.04	29.	-
575	"	"	-	0.32	0.08	42.	-
590	"	"	-	0.42	0.12	57.	-

Series 32 Reactor: F, Catalyst: experimental cat. III, W = 14.2gm (4.86cc), L = 34 cm, V_r = 11.5cc, $\Delta P \leq 1$ psig, feed: PA, 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	r_t 10^6 per gm
300	.478	.0056	-	0.00	0.00	0.	-
350	"	"	-	0.02	0.00	2.	-
400	"	"	-	0.045	0.015	6.	-
450	"	"	-	0.07	0.03	10.	-
500	"	"	-	0.12	0.04	17.	-
550	"	"	-	0.18	0.05	24.	-
600	"	"	-	0.24	0.06	31.	-

Series 33 Reactor: F, Catalyst: experimental Cat. I, W = 14.22gm (6.03cc) L = 34 cm, V_r = 10.3cc, $\Delta P \leq 1$ psig, feed: PA 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.478	.0056	-	0.00	0.00	0.	-
350	"	"	-	0.02	0.00	2.	-
400	"	"	-	0.05	0.00	5.	-
450	"	"	-	0.08	0.01	9.	-
500	"	"	-	0.11	0.01	13.	-
550	"	"	-	0.17	0.03	21.	-
600	"	"	-	0.25	0.06	33.	-

Series 34 Reactor: F, Catalyst: experimental cat. V, W = 14.2gm (5.24cc), L = 34 cm, V_r = 11.1cc, $\Delta P \leq 1$ psig, feed: PA 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.478	.0056	-	0.00	0.00	0.	-
350	"	"	-	0.02	0.00	2.	-
400	"	"	-	0.05	0.01	6.	-
450	"	"	-	0.09	0.01	10.	-
500	"	"	-	0.13	0.02	16.	-
550	"	"	-	0.17	0.03	21.	-
600	"	"	-	0.25	0.06	33.	-

Series 35 Reactor: F, Catalyst: experimental cat IV, W = 14.2gm (5.13cc), L = 34 cm, V_r = 10.9cc, $\Delta P \leq 1$ psig, feed: PA 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.478	.0056	-	0.00	0.00	0.	-
350	"	"	-	0.02	0.00	2.	-
400	"	"	-	0.07	0.01	8.	-
450	"	"	-	0.09	0.02	12.	-
500	"	"	-	0.13	0.02	16.	-
550	"	"	-	0.15	0.03	19.	-
600	"	"	-	0.19	0.04	24.	-

Series 36 Reactor: F, Catalyst: CCI-C103, W = 14.23gm (5.98cc) $L = 34$ cm, $V_r = 10.4$cc, $\Delta P \leq 1$ psig, feed: PA, 13.1cm^2 Al/gm cat.

This series was conducted with high resolution Infrascan H-900 IR equipment on-line with 20cm heated cell and piping at reactor exit. CO and CO_2 IR Luft-type equipment following that.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.478	.0056	-	0.00	0.00	0.	-
350	"	"	-	0.035	0.01	5.	-
400	"	"	-	0.11	0.03	15.	-
450	"	"	-	0.23	0.06	30.	-
500	"	"	-	0.36	0.09	47.	-
600	"	"	-	0.81	0.24	110.	-

Series 37 after above analyses, operated continuously, same feed condition, to determine catalyst stability, measuring only CO_2 and CO.

hrs. operation	T, °C	%CO_2	%CO	$r_c \cdot 10^6$ per gm
24	400	0.11	0.03	15.
48	"	0.11	0.035	15.
72	"	0.10	0.030	15.
96	"	0.10	0.030	15.
144	"	0.10	0.030	15.
"	500*	0.33	0.115	47.
"	600*	0.76	0.275	109.
168	400	0.11	0.030	15.

*at steady state after 1 hour temporary reactor temp. change

Series 38 Reactor: F, Catalyst: CCI-C103, W = 14.10gm (5.93cc), $L = 34$ cm, $V_r = 10.1$cc, $\Delta P \leq 1$ psig, feed: PA, 13.3cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.478	.0055	<.001	0.005	0.00	< 0.5	< 0.5
350	"	"	.011	0.04	0.015	6.	5.
400	"	"	.065	0.175	0.06	25.	30.
450	"	"	.130	0.38	0.115	52.	60.
500	"	"	.196	0.51	0.17	72.	91.
550	"	"	.283	0.70	0.25	100.	132.
600	"	"	.435	1.10	0.37	155.	202.

Series 39 Reactor: F, Catalyst: CCI-C103, unchanged reactor and catalyst bed used in Series 36. W = 14.23gm (5.98cc), L = 34 cm, V_r = 10.4cc, $\Delta P \leq 1$ psig, Feed: <u>o-xylene</u>, 13.1cm^2 Al/gm cat.

T,°C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	-	0.01	0.00	1.	-
350	"	"	-	0.09	0.02	12.	-
400	"	"	-	0.56	0.13	75.	-
450	"	"	→1.0	2.68	1.04	403.	→ 833.
500	"	"	→1.0	2.79	1.10	422.	→ 833.

Series 40 continuation of Series 39 after 16 hrs. operation at 500°C

T,°C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.01	0.00	1.	0.
350	"	"	.016	0.09	0.02	12.	13.
400	"	"	.111	0.65	0.16	88.	92.
450	"	"	.997	2.26	0.94	347.	830.
500	"	"	1.00	2.66	1.10	408.	833.
550	"	"	1.00	2.96	1.20	451.	833.
600	"	"	1.00	3.66	1.40	549.	833.

Series 41 Reactor: F, Catalyst: experimental Cat. I, W = 14.18gm (6.0cc), L = 29 cm, V_r = 7.9cc, $\Delta P \leq 1$ psig, feed: o-xylene 13.2cm^2 Al/gm cat.

T,°C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.02	0.01	3.	0.
350	"	"	.014	0.09	0.02	12.	12.
400	"	"	.041	0.16	0.03	21.	34.
425	"	"	.069	0.24	0.05	32.	58.
450	"	"	.096	(0.34)	0.07	(45.)	80.
475	"	"	.151	0.30	0.06	39.	126.
500	"	"	.219	0.30	0.05	38.	183.
525	"	"	.315	0.40	0.08	52.	263.
550	"	"	.411	0.55	0.14	75.	344.
575	"	"	.273	0.30	0.11	45.	228.
600	"	"	.219	0.33	0.14	51.	183.

Series 42 Reactor: F, Catalyst: experimental cat IV, W = 14.2gm (5.1cc), L = 24 cm, V_r = 6.4cc, $\Delta P \leq 1$ psig, feed: o-xylene, 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO$_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.015	0.005	2.	0.
400	"	"	.076	0.35	0.09	48.	63.
450	"	"	.163	0.76	0.24	109.	136.
500	"	"	.576	1.49	0.45	211.	481.
525	"	"	.859	1.58	0.46	222.	717.
550	"	"	.961	1.84	0.57	262.	802.
575	"	"	.963	1.95	0.67	285.	804.

Series 43 Reactor: F, Catalyst: experimental cat II, W = 14.04gm (5.8cc), L = 32 cm, V_r = 9.4cc, $\Delta P \leq 1$ psig, feed: o-xylene, 13.3cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO$_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.01	0.00	1.	0.
400	"	"	.059	0.24	0.06	33.	50.
450	"	"	.119	0.45	0.11	62.	100.
475	"	"	(.158)	0.65	0.17	90.	(133.)
500	"	"	.158	0.72	0.18	99.	133.
525	"	"	.178	0.73	0.18	100.	150.
550	"	"	.277	0.99	0.28	140.	234.
575	"	"	.287	1.08	0.38	160.	242.
600	"	"	.257	1.26	0.48	191.	217.
further deactivated during 16 hrs. operation at 600°C							
600	.495	.0096	.202	0.67	0.29	106.	170.

Series 44 Reactor: F, Catalyst: experimental cat V, W = 14.2gm (5.2cc), L = 24 cm, V_r = 6.3cc, $\Delta P \leq 1$ psig, feed: O-xylene, 13.2cm^2 Al/gm cat.

T, °C	q	P_i	X_t	%CO$_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.01	0.00	1.	0.
400	"	"	.051	0.39	0.10	53.	43.
450	"	"	.232	0.81	0.26	116.	194.
500	"	"	.697	1.81	0.54	256.	582.
550	"	"	.758	1.76	0.49	245.	633.
600	"	"	.828	2.06	0.90	322.	691.

Series 45 Reactor: F, Catalyst: experimental cat III, $W = 14.15$gm (4.8cc), $L = 22$ cm, $V_r = 5.8$cc, $\Delta P \leq 1$ psig, feed: o-xylene, 13.2cm^2 Al/gm cat.

T,°C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.01	0.00	1.	0.
400	"	"	.115	0.38	0.12	55.	96.
425	"	"	.190	0.61	0.20	88.	159.
450	"	"	.816	1.98	0.67	289.	684.
475	"	"	.960	2.21	0.76	324.	804.
500	"	"	.980	2.42	0.87	359.	821.
operated for 16 hours at 500°C							
500	.495	.0096	.987	2.34	0.89	352.	827.
525	"	"	.989	2.61	1.05	399.	829.
550	"	"	.991	2.66	1.07	407.	830.
575	"	"	1.00	2.53	1.03	388.	838.
600	"	"	1.00	2.86	1.12	434.	838.

Series 46 same reactor, catalyst and conditions of Series 45. This Series is to confirm reproducibility of the catalyst evaluation method, and equipment stability.

T,°C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.01	0.00	1.	0.
350	"	"	.034	0.12	0.03	16.	28.
375	"	"	.078	0.28	0.09	40.	65.
400	"	"	.180	0.61	0.20	88.	151.
425	"	"	.378	1.11	0.38	163.	317.
450	"	"	.775	1.89	0.71	284.	649.
475	"	"	.961	2.31	0.91	351.	805.
500	"	"	.983	2.37	0.99	367.	824.
operated for 16 hours at 500°C							
500	.495	.0096	.988	2.52	1.01	385.	828.
525	"	"	1.00	2.85	1.08	429.	838.
550	"	"	1.00	3.30	1.18	489.	838.
575	"	"	1.00	3.36	1.23	501.	838.
600	"	"	1.00	3.86	1.33	566.	838.

Series 47 Reactor: F, Catalyst: CCI-C103 V_2O_5-SiC, W = 7.58gm (3.2cc), L = 22 cm, V_r = 7.4cc, $\Delta P \leq 1$ psig, feed: o-xylene, 24.7cm^2 Al/gm cat.

$T, ^{\circ}C$	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	0.005	0.00	1.	0.
350	"	"	.010	0.035	0.01	9.	16.
400	"	"	.048	0.26	0.07	67.	75.
425	"	"	.964	2.06	0.77	576.	1508.
450	"	"	.986	2.18	0.87	621.	1542.
475	"	"	.989	2.80	1.10	794.	1547.
500	"	"	.992	3.36	1.25	933.	1551.
550	"	"	1.00	4.44	1.55	1220.	1564.

Series 48 Reactor: F, Catalyst: experimental cat. II, W = 10.87gm (4.5cc), L = 26 cm, V_r = 7.8cc, $\Delta P \leq 1$ psig, feed: o-xylene, 17.2cm^2 Al/gm cat.

$T, ^{\circ}C$	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0096	.00	-	-	-	0.
400	"	"	.010	-	-	-	11.
450	"	"	.064	-	-	-	70.
475	"	"	.172	-	-	-	187.
500	"	"	.301	-	-	-	328.
525	"	"	.592	-	-	-	645.
550	"	"	.774	-	-	-	844.
600	"	"	.890	-	-	-	970.

Series 49 Same reactor and catalyst bed as Series 48. Feed: changed to MA

$T, ^{\circ}C$	q	P_i		$\%CO_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	.495	.0067	<.005	-	-	-	< 4.
400	"	"	.34	-	-	-	259.
500	"	"	>.99	-	-	-	>753.

Series 50 new reactor G, Catalyst: none, S = 187cm^2 Al, L = 76cm, V_r = 36.3cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_c \cdot 10^6$ per 10cm^2
300	.231	.0045	<.005	0.01	0.00	0.4	< 1.
400	"	"	.03	0.04	0.01	2.	4.
500	"	"	.33	0.93	0.17	42.	46.
600	"	"	>.99	2.81	0.32	121.	>138.
500	.480	.0044	-	0.86	0.10	77.	-
600	"	"	>.99	2.50	0.39	232.	279.

Series 51 much used reactor G, Catalyst: none, S = 187cm^{2}Al, L = 76cm, V_r = 36.3cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	1.33	.0041	.00	0.00	0.00	0.	0.
400	"	"	.01	0.01	0.00	2.	7.
500	"	"	-	0.36	0.04	89.	-
600	"	"	(.98)?	1.46	0.34	399.	(712.)?

Series 52 brushed out used reactor G, Catalyst: none, S = 187cm^2 Al, L = 76 cm, V_r = 36.3cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
600	0.286	.0048	>.99	2.30	0.66	141.	181.
600	1.33	.0045	-	1.31	0.40	379.	-

Series 53 used reactor G, Catalyst: none, S = 187cm^2 Al, L = 76cm V_r = 36.3cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	$\%CO_2$	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
600	1.33	.0046	.58	0.90	0.28	262.	473.

these are mean values from many determinations.

Series 54 new reactor H, Catalyst: none, $S = 91 cm^2$ Al, $L = 37 cm$, $V_r = 17.7 cc$, $\Delta P = \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per $10 cm^2$	$r_t \cdot 10^6$ per $10 cm^2$
600	1.33	.0043	-	0.16	0.04	91.	-
operated 16 hours at 600°C							
600	1.33	.0044	-	0.06	0.02	36.	-
"	.634	.0049	-	0.15	0.04	41.	-
"	.286	.0046	-	0.33	0.10	42.	-

Series 55 reactor H after above Series 54, Catalyst: EC grade aluminium C-rings, $W = 22.05 gm$ (8.16cc) $S = 176 cm^2$ plus $91 cm^2$ reactor surface, $L = 37 cm$, $V_r = 9.5 cc$, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per $10 cm^2$	$r_t \cdot 10^6$ per $10 cm^2$
300	1.33	.0046	-	0.00	0.00	0.	-
400	"	.0046	-	0.00	0.00	0.	-
450	"	.0048	-	0.015	0.00	2.	-
500	"	.0047	-	0.075	0.01	13.	-
550	"	.0046	-	0.22	0.04	40.	-
600	"	.0047	-	0.67	0.12	123.	-
300	.287	.0050	<.01	0.01	0.00	0.3	< 1.
500	"	.0051	-	0.32	0.04	12.	-
operated 16 hours at 500°C							
500	.287	.0048	.18	0.31	0.04	12.	23.
550	"	"	.54	0.94	0.17	37.	70.
600	"	"	.99	2.65	0.44	104.	128.

Series 56 reactor H, Catalyst: fused silica fragments, $E = 15.41 gm$ (6.4cc), $S = 196 cm^2$, $L = 37 cm$, $V_r = 11.3 cc$, $\Delta P \leq 1$ psig, feed: PA, $4.6 cm^2$ Al/$10 cm^2$ fused silica.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per $10 cm^2$	$r_t \cdot 10^6$ per $10 cm^2$
300	1.33	.0047	.00	0.00	0.00	0.	0.
350	"	"	< .005	0.00	0.00	0.	< 4.
400	"	"	-	0.02	0.00	4.	-
450	"	"	-	0.11	0.01	25.	-
500	"	"	(.28)*	0.36	0.03	82.	(223.)
550	"	"	-	0.62	0.08	148.	-
600	"	"		1.05	0.18	260	533.

*

Series 57 Reactor H, Catalyst: stainless steel short cylinders, $W = 63.94$ gm (8.0cc), $S = 108\text{cm}^2$, $L = 37$cm, $V_r = 9.7$cc, $\Delta P \leq 0.5$ psig, feed: PA, 8.3cm^2 Al/10cm^2

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	1.33	.0047	<.005	0.00	0.00	0.	< 7.
410	"	"	-	0.02	0.00	8.	-
450	"	"	-	0.10	0.01	42.	-
500	"	"	.28	0.51	0.06	219.	404.
550	"	"	.99	2.29	0.32	1002.	1430.
600*	"	"	→ 1.00	2.72	0.46	1221.	→ 1444.

*plus on-line IR hot product stream examination

Series 58 Reactor H, Catalyst: 132 4.4mm diam. SA-201 Alundum spheres, $W = 18.24$ gm (5.8cc), $L = 37$cm, $V_r = 11.9$cc, $\Delta P \leq 0.5$ psig, feed: PA, 5.0cm^2 Al/gm alundum

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	1.33	.0047	<.005	0.00	0.00	0.	< 4.
400	"	.0049	-	0.015	0.01	6.	-
450	"	"	-	0.065	0.01	17.	-
505	"	"	-	0.29	0.05	77.	-
550	"	"	-	0.69	0.14	188.	-
595	"	"	.69	1.25	0.32	357.	615.
615	"	"	>.99	2.32	0.52	645.	> 882.

Series 59 used reactor H, Catalyst: none, $S = 91\ \text{cm}^2$ Al, $L = 34$cm $V_r = 17.7$cc, $\Delta P \leq 0.5$ psig, feed: PA. This experiment also diverted a portion of condensed product stream through the quantitative combustor to determine an upper limit for amount of low molecular wt. carbon compounds not analyzed chromatographically.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	1.33	.0046	-	0.00	0.00	0.	-
500	"	.0047	-	0.11	0.01	55.	-
operated 16 hours at 500°C							
500	1.33	.0047	-	0.07	0.01	36.	-
550	"	.0048	-	0.25	0.03	128.	-
600	"	.0047	.20	0.57	0.10	305.	343.
300	"	.0047	<.005	0.00	0.00	0.	< 8.

Series 60 Reactor H, Catalyst: new SO_2-activated Kontakt-S, $W = 11.02$gm (3.1cc), $L = 21.5$cm, $V_r = 7.2$cc, $\Delta P \leq 0.5$ psig, feed: PA, 8.2cm^2 Al/gm. No sulfur compounds added to feed.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	1.33	.0045	-	0.00	0.00	0.	-
400	"	"	-	0.08	0.03	41.	-
450	"	"	-	0.34	0.10	166.	-
500	"	"	-	0.95	0.17	422.	-
550	"	"	-	1.47	0.16	614.	-
600	"	"	.64	1.85	0.21	775.	867.

Series 61 Reactor H after Series 60, Catalyst: none, $L = 37$cm, $S = 91$cm^2 Al, $V_r = 17.7$cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	1.33	.0045	-	0.00	0.00	0.	-
400	"	"	-	0.005	0.00	2.	-
500	"	"	-	0.08	0.01	41.	-
550	"	"	-	0.26	0.04	137.	-
600	"	"	-	0.81	0.16	442.	-

Series 62 New reactor I, Catalyst: none, $L = 37$cm, $S = 91$cm^2 Al, $V_r = 17.7$cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	1.33	.0045	-	0.00	0.00	0.	-
600	"	"	-	0.06	0.01	32.	-

Series 63 New reactor J, Catalyst: none, $L = 37$ cm, $S = 91$cm^2 Al $V_r = 17.7$cc, $\Delta P \leq 0.5$ psig, feed: PA

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
300	1.33	.0049	.00	0.00	0.00	0.	0.
615	"	"	.01	0.03	0.00	14.	18.

Series 64 New reactor K, Catalyst: none, L = 37cm, S = 91cm^2 Al, V_r = 17.7cc, $\Delta P \leq$ 0.5 psig, feed: PA

T, °C	q	P_i	x_t	%CO$_2$	%CO	$r_c \cdot 10^6$ per 10cm^2	$r_t \cdot 10^6$ per 10cm^2
295	1.33	.0049	.00	0.00	0.00	0.	0.
590	"	.0049	.01	0.04	0.00	18.	18.

Series 65 Reactor K immediately after Series 64. Catalyst: experimental Cat.III, W = 11.12gm (3.8cc), L = 21.5cm, V_r = 6.5cc, $\Delta P \leq$ 0.5 psig, feed: PA with inlet concentrations determined by quantitative combustor. 8.2cm^2 Al/gm cat.

T, °C	q	P_i	x_t	%CO$_2$	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
300	1.33	.0049	.00	0.00	0.00	0.	0.
400	"	.0048	.034	0.02	0.005	9.	49.
450	"	"	.039	0.03	0.010	15.	56.
500	"	.0047	.042	0.05	0.015	24.	59.
550	"	"	.067	0.09	0.025	43.	94.
600	"	"	.072	0.17	0.04	79.	101.
300	"	.0048	.00	0.00	0.00	0.	0.

Series 66 Reactor J immediately after Series 63. Catalyst: CCl-Cl03 W = 8.20gm (3.2cc), L = 21.5cm, V_r = 7.0cc, $\Delta P \leq$ 0.5 psig, feed: PA, determined by quantitative combustor, 11.1cm^2 Al/gm cat.

<table>
<tr><th>T, °C</th><th>q</th><th>P_i</th><th>x_t</th><th>%CO$_2$</th><th>%CO</th><th>$r_c \cdot 10^6$ per gm</th><th>$r_t \cdot 10^6$ per gm</th></tr>
<tr><td>300</td><td>1.33</td><td>.0050</td><td>.00</td><td>0.00</td><td>0.00</td><td>0.</td><td>0.</td></tr>
<tr><td>400</td><td>"</td><td>"</td><td>.027</td><td>0.08</td><td>0.03</td><td>56.</td><td>55.</td></tr>
<tr><td>(450)?</td><td>"</td><td>.0049</td><td>.070</td><td>0.17</td><td>0.07</td><td>121.</td><td>139.</td></tr>
<tr><td>500</td><td>"</td><td>.0046</td><td>.070</td><td>0.19</td><td>0.07</td><td>131.</td><td>130.</td></tr>
<tr><td>550</td><td>"</td><td>"</td><td>.109</td><td>0.29</td><td>0.10</td><td>197.</td><td>203.</td></tr>
<tr><td>605</td><td>"</td><td>.0045</td><td>.150</td><td>0.42</td><td>0.13</td><td>278.</td><td>273.</td></tr>
<tr><td colspan="8">above at linear velocities 1.4-2.2 meters/sec;
below at 0.6-0.9 meters/ sec.</td></tr>
<tr><td>602</td><td>.586</td><td>.0049</td><td>.315</td><td>0.86</td><td>0.27</td><td>252.</td><td>275.</td></tr>
<tr><td>285</td><td>.586</td><td>"</td><td>.00</td><td>0.00</td><td>0.00</td><td>0.</td><td>0.</td></tr>
</table>

Series 67 Reactor I immediately after Series 62. Catalyst: new SO_2-activated Kontakt-S, W = 10.26gm (2.9cc), L = 21.5cm, V_r = 7.4cc, $\Delta P \leq 0.5$ psig, feed: PA, determined by quantitative combustor, 8.8cm^2 Al/gm cat. No sulfur compounds added to feed.

T, °C	q	P_i	X_t	%CO_2	%CO	$r_c \cdot 10^6$ per gm	$r_t \cdot 10^6$ per gm
290	1.33	.0048	.00	0.00	0.00	0.	0.
400	"	"	.025	0.07	0.03	40.	39.
450	"	.0047	.115	0.27	0.07	137.	175.
500	"	"	.250	0.82	0.16	396.	380.
550	"	.0048	.415	1.25	0.16	570.	644.
600	"	"	.485	1.58*	0.16	703.*	753.*

*maximum, followed by loss of activity (SO_3) with time.

major products of o-xylene oxidation

Series, Catalyst	T, °C	xylene area	MA area	tolualdehyde area	toluic acid area	PA area	phthalide area	minor products areas
40 CCI-C103	300	63.	0	0	0	0	0	0
	350	62.	0	0.3	0.2	0	0	0
	400	56.	0	2.2	0	0	0	0
	450	0.2	1.5	0.1	0	30.	0	0
	500	0	1.9	0	0	27.	0	0
	550	(0.4)	1.6	0	0	23.	0	0
	600	(0.3)	0.9	0	0	19.	0	0
41 experimental catalyst I	300	73.	0	0.5	0	0	0	0
	350	72.	0	1.6	0	0.2	0	0
	400	70.	0	2.8	0	1.0	0	0
	425	68.	0	3.8	0	1.2	0	0
	450	66.	0	5.4	0	1.5	0.3	.04
	475	62.	0	8.2	0.2	1.8	0.6	.09
	500	57.	0	9.5	0.3	0.7	0.2	.15
	525	50.	0	11.2	0.5	0.9	0.3	.35
	550	43.	0	14.2	1.1	1.6	0.5	.44
	575	53.	0	9.5	0.9	0.3	0	.50
	600	57.	0	10.4	1.1	0.4	0	.62
43 experimental catalyst II	300	101.	0	0.4	0	0	0	0
	400	95.	0	5.4	0.1	2.5	0.2	0
	450	89.	0	9.8	0.2	3.6	0.9	.19
	475	85.	0.1	12.	0.3	5.5	1.0	.24
	500	85.	0.1	15.	0.5	5.5	1.5	.37
	525	83.	0	21.	0.9	2.6	1.3	.64
	550	73.	0	25.	2.0	3.6	1.9	.85
	575	72.	0	28.	3.0	4.4	2.5	1.2
	600	75.	0	25.	2.8	3.0	1.8	1.5
	operated for 16 hours at 600°C							
	600	79.	0	24.	2.5	2.3	0.7	1.6

Major Products of o-xylene Oxidation.

major products of o-xylene oxidation

Series, Catalyst	T, °C	xylene area	MA area	totualdehyde area	toluic acid area	PA area	phthalide area	minor products areas
45 experimental catalyst III	300	98.	0	0.3	0	0	0	0
	400	94.	0	3.8	0	2.6	0.1	0
	425	93.	0.2	6.4	0.1	4.6	0.5	.02
	450	18.	1.5	12.	0.4	44.	6.4	.19
	475	3.9	2.1	7.9	0.2	66.	5.7	.20
	500	2.0	1.8	5.5	0.1	62.	2.0	.16
	operated for 16 hours at 500°C							
	500	1.3	2.3	3.7	0.1	67.	4.4	.26
	525	1.1	1.9	2.3	0.1	73.	4.0	.42
	550	0.9	1.9	1.4	0.1	68.	4.3	.63
	575	1.0	1.4	3.2	0.2	59.	7.8	1.4
	600	0.9	0.6	7.6	1.4	45.	15.	2.0
42 experimental catalyst IV	300	92.	0	0.4	0	0.1	0	0
	400	85.	0	5.1	0	3.4	0.6	.04
	450	77.	0.3	11.	0.3	8.7	1.8	.08
	500	39.	0.7	19.	0.9	19.	4.9	.48
	525	13.	0.4	18.	1.0	22.	6.9	.54
	550	3.6	0.5	13.	1.0	30.	7.6	.64
	575	3.4	0.3	14.	1.9	22.	7.6	1.1
44 experimental catalyst V	300	99.	0	0.4	0	0	0	0
	400	94.	0.1	7.4	0	5.5	0.3	.45
	450	76.	0.4	13.	0.2	14.	2.7	.67
	500	30.	1.2	19.	0.6	30.	6.2	.80
	550	24.	0.1	30.	2.9	18.	8.4	1.4
	600	17.	0.3	28.	4.5	17.	7.5	2.0

Minor Products of o-xylene Oxidation.

minor products of o-xylene oxidation

Series, Catalyst	T, °C	area at standard retention times designated 60 sec.	105 sec.	122 sec. MA	180 sec.	201 sec.	other	sensitivity reference: feed area
45 experimental catalyst III	300-400	0	0	0	0	0		98.
	425	0	.03	0.2	0	0		
	450	.05	.08	1.5	0	.06		
	475	.03	.09	2.1	0	.09		
	500	.02	.05	1.8	0	.10		
	500	.05	.05	2.3	.05	.12		
	525	.08	.04	1.9	.08	.21		
	550	.15	.04	1.9	.16	.27		
	575	.32	.05	1.4	.38	.70		
	600	.67	.17	0.6	.48	.64	0	
42 experimental catalyst IV	300	0	0	0	0	0		92.
	400	.02	.02	0	0	0		
	450	.04	.04	0.3	0	0		
	500	.09	.08	0.7	0	.33		
	525	.09	.10	0.4	0	.34		
	550	.08	.14	0.5	.03	.39		
	575	.26	.17	0.3	.18	.52	.05 at 422	
44 experimental catalyst V	300	0	0	0	0	0		99.
	400	.45	0	0.1	0	0		
	450	.44	.05	0.4	0	.18		
	500	.36	.09	1.2	0	.35		
	550	.30	.17	0.3	0	.90		
	600	.60	.41	0.1	.28	.95	.20 at 422	

Notes: (1) Experimental catalyst II produced the 70 and 87 sec. MA products abundantly at 400°C and up.

(2) Possible existence of 150 sec. product obscured by 145 sec. xylene peak.

minor products of o-xylene oxidation

Series,	Catalyst	T, °C	area at standard retention times designated 60 sec.	105 sec.	122 sec. MA	180 sec.	201 sec.	other	sensitivity reference: feed area
47	CCI-C103	300-350	to .02	0	0	0	0		105.
		400	.07	.03	0	0	0		
		425	.05	.05	1.2	0	.16		
		450	.14	0	2.2	0	.29		
		475	.14	0	2.5	0	.25		
		500	.18	0	2.5	0	.14		
		550	.39	0	2.5	.38	.38	0	
41	experimental catalyst I	300-425	0	0	0	0	0	0	73.
		450	.02	0	0	0	.01		
		475	.01	0	0	0	.08		
		500	.02	0	0	0	.14		
		525	.05	.05	0	0	.25		
		550	.04	.05	0	0	.35		
		575	.10	.08	0	0	.25		
		600	.22	.15	0	0	.25	.05 at 422	
48a	experimental catalyst II	300-400	0	0	0	0	0	see note 1	93.
		450	0	.06	0	0	0		
		475	0	.11	0	.12	.10		
		500	0	.16	0	.32	.17		
		525	.02	.24	0	.43	.33		
		550	.05	.36	0	.55	.23		
		600	.25	.69	0	1.02	.19	.05 at 422	

Product areas observed during series 48 oxidation of o-xylene, et seq. at doubled xylene concentration and doubled contact time

T, °C	chromatograph area at indicated standard retention time													total area of major* products (ex-xyl)	total area of minor products
	60 sec.	70 sec.	87 sec.	105 sec.	122 sec.	145 sec.	180 sec.	201 sec.	256* sec.	422 sec.	490* sec.	650* sec.	770* sec.		
450	0.1	0.1	0.1	0.1	0.2	102.	0.8	0.5	22.	0	0.6	7.2	3.2	33.2	1.7
475	0.1	0.2	0.4	0.2	0.4	89.	1.2	0.5	25.	0	0.9	9.0	4.2	39.5	2.6
500	0.2	0.4	1.1	0.4	0.3	70.	1.8	0.7	28.	0	1.8	6.0	5.1	50.2	4.6
525	0.3	0.6	2.5	0.6	0.1	28.	2.3	0.7	29.	0.06	1.5	3.3	6.1	40.0	7.0
550	0.4	0.8	4.9	1.0	0	11.	2.5	0.5	22.	0.15	0.9	0.6	4.9	28.4	10.3
575	0.6	0.8	6.6	1.2	0	5.8	2.1	0.2	17.	0.18	0.4	0	2.3	19.7	11.7
600	0.8	0.8	6.9	1.6	0	4.3	2.1	0	15.	0.14	0.2	0	1.6	16.8	12.3
	?	?	?	?	MA	o-xylene	?	?	o-tolualdehyde	benzoic acid	o-toluic acid	PA	phthalide	Product identity	

Series,	Catalyst	T, °C	minor products of PA and MA oxidation area at standard retention times designated					sensitivity reference: feed area
			60 sec.	87 sec.	122 sec. MA	180 sec.	other	
51	empty Al tube	300-400	0	0	0	0	0	146.
		500	0	.02	0	.27	0	
		600	.03	.15	0	2.20	see note 1	
59	empty Al tube	300-500	0	0	0	0	0	66.
		550	0	.06	0	.04	0	
		600	0	.10	0	.21	0	
61	empty Al tube	300-500	0	0	0	0	0	30.
		550	0	.06	0	0	0	
		600	0	.15	0	.31	0	
55a	aluminium filled	300-450	0	0	0	0	0	182.
		500	0	0	0	.13	0	
		550	0	.02	0	.55	.02 at 450	
		600	.03	.09	0	1.48	.20 at 450	
55b	aluminium filled	300	0	0	0	0	0	182.
		500	.01	.04	0	.73	.30 at 450	
		500	0	.01	0	.45	0	
		550	0	.16	0	1.95	1.44 at 450	
		600	.02	.80	0	1.66	see note 2	

Series	Catalyst	T, °C	minor products of PA and MA oxidation area at standard retention times designated: 60 sec.	87 sec.	122 sec. MA	180 sec.	other	sensitivity reference: feed area
56	fused silica	300	0	0	0	0	0	13.
		600	.03	.11	0	.17	0	
57	stainless steel	300-410	0	0	0	0	0	9.
		500	0	0	0	.05	0	
		550	0	.18	0	.13	0	
		600	.06	.16	0	0	0	
58	alundum	300-450	-	0	0	0	0	13.
		505	-	.05	0	.04	0	
		550	-	.13	0	.09	0	
		595	.31	.21	0	.24	0	
		615	0	.48	0	.14	0	
65	experimental catalyst III	300-600	0	0	0	0	0	39.
38	CCI-C103	300-450	-	-	to .61	-	-	49.
		500	-	-	.86	-	-	
		550	-	-	1.08	-	-	
		600	-	-	.99	-	-	
66a	CCI-C103	300-500	0	0	to .56	0	0	61.
		550	0	.01	.79	0	0	
		605	.02	.05	.69	0	0	

Minor Products of PA and MA Oxidation

Series,	Catalyst	T, °C	minor products of PA and MA oxidation area at standard retention times designated					sensitivity reference: feed area
			60 sec.	87 sec.	122 sec. MA	180 sec.	other	
66b	CCI-C103	602	.09	.07	1.40	0	0	61.
67	activated Kontakt-S	290-550	0	0	.72 max.	0	0	156.
		600	0	.02	.51		0	
60	activated Kontakt-S	300-500	0	0	0	0	0	22.
		550	0	.03	0	0	0	
		600	0	.10	0	0	0	
49	experimental catalyst II (MA feed)	300	0	0	19.0	0	0	19.
		400	.16	0	12.5	0	.30 at 70	
		500	.30	.05	{0 ?	0	.05 at 70	
		600	1.25	.15	{est. 0 2	0	0	

Notes: (1) .04 at 70, .10 at 150, .77 at 390, .20 at 450, and .74 at 610 sec.

(2) .03 at 70, .05 at 150, .30 at 390, .34 at 610 sec.

(3) all except series 49 are PA feed

Metallic Materials

Used in (Series)	Metal	Density gm/cc	Nominal Composition	Sizes and Shapes used	Thermal k (note 1)
57 3 Reactor L 18 4,5 8	Stainless steel	7.96	Presumably type EN 58B (AISI type 321) (see note 2)	short cylinders 4.7mm diam x 4.0mm " " 4.7mm diam x 4.5mm 1.3cm i.d. tubing 1.5 x 1.5 x 2mm clippings of above 1.6mm i.d. tubing (Reactor A) 3.2mm i.d. tubing (Reactor B)	10-17
11,12	mild steel	7.87	AISI type 1020	clippings of sheet 0.8 x 1.7 x 3.0mm	33-36
13	20 Cr-80Ni	8.3	(see note 3)	wire: 0.75mm diam. x 3.mm long	8.
Reactor D Reactors, F,G,H	Aluminium	2.70	99^{+} % com'l type 2S	tubing: 6.3mm o.d., 4.7mm i.d. tubing: 9.5mm o.d., 7.8mm i.d.	118.
55 19-29 Reactors I,J,K	Aluminium	2.70	99.5^{+} %, EC grade	c rings 2.04mm diam x 9.8mm long irregular spheres 1.8mm diam tubing: 9.5mm o.d., 7.8mm i.d. (see note 4)	118-126
16	Dural	2.79	17S Aluminium alloy 4.5 Cu, 0.6Mn, 0.5 Mg	0.3 x 1.4 x 2.5mm clippings of drilling chips	100

Notes: (1) thermal k = BTU/(hr)(ft^2)(^{o}F/ft) at ambient, typically decreasing with temp.
(2) nominal composition: 17-19 Cr, 8-11 Ni, 0.9 Ti, 0.5-2.0 Mn
(3) "Torphet A" nichrome, source: Gilby-Brunton, Musselburgh
(4) source: Phase-Separations Ltd.

Non-metallic Materials

Used in (Series)	Material	Density gm/cc	Nominal Composition	Sizes and Shapes Used	Thermal k (note 1)
15 2	Soft glass	3.04	soda-glass	1.2mm diam. beads 5.0mm spheres	0.45
9 Reactor E	Borosilicate glass	2.32	"Pyrex" tubing	3.mm i.d. (Reactor C) 5mm i.d.	0.65
56	Fused silica	2.40	-	broken fragments 0.9 x 5. x 5.mm	ca 0.6
17	"Alundum"	3.28	SA-203 (see note 2)	1.2-1.4mm crushed pieces of porous spheres	low
1,58	"Alundum"	3.09	SA-201 (see note 2)	4.4mm porous spheres	low

Notes: (1) thermal k = BTU/(hr)(ft^2)($^\circ$F/ft)

(2) alpha alumina + mullite, catalyst carriers, source: Norton Grinding Wheel Co.

Physical Properties

Properties of PA

mol. wt. 148

b.p. 284.5°C (760mm)

f.p. 130.8°C

ΔH_s = 19.5 Kcal/gm mole @ 131°C

ΔH_f = 6.3 " " @ 131°C

ΔH_v = 13.2 " " @ 131°C see note (1)

$\Delta H_{comb.}$ = 779. Kcal/gm mole (to CO_2 and H_2O).

C_p solid = 0.2627 cal/gm °C at 27°C

density = 1.527 gm/cc at 4°C, solid

" 1.208 gm/cc at 135°C, liquid

" 1.181 gm/cc 160°C

" 1.142 gm/cc 200°C

" 1.105 gm/cc 240°C

very soluble in acetone

water solubility 20°C 0.6 gm/100 gm water see note (2)

" " 100°C 18 gm/100 gm " " " "

Vapor pressure:

ICT: $\log_{10}(P, \text{mm}) = 8.022 - \dfrac{2868.47}{T^{\circ}K}$

Chemical Rubber Handbook: 1mm at 96.5°C

" " " 10mm at 134°C

" " " 40mm at 172°C

" " " 100mm at 202.3°C

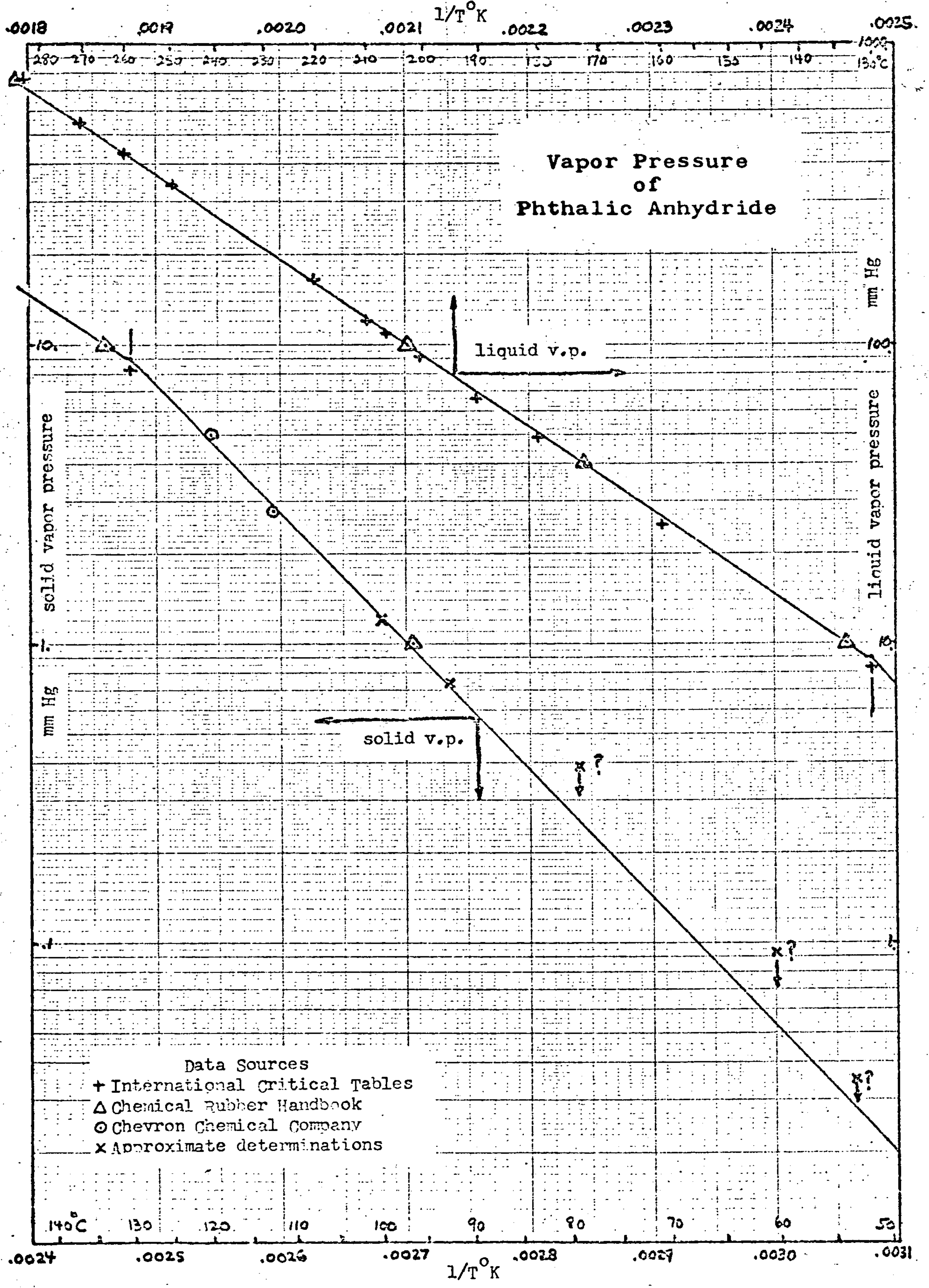
see note (2) 2.8mm at 110°C

" " " 5.0mm at 120°C

Notes:

(1) ICT vapor pressure data are fitted to ΔH_v = 13.2

(2) personal communication, Chevron Chemical Co.[186]


1/T°K
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Vapor Pressure
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Data Sources
+ International Critical Tables
△ Chemical Rubber Handbook
⊙ Chevron Chemical Company
× Approximate determinations
140°C
130
120
110
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1/T°K

Experimentally determined IR adsorptions for compound identification
the most persistent adsorptions at low concentration are underscored.

Benzene: 3060, 3020, 1950, 1940, 1805, 1790, 1475, 1033, 680, 668 cm^{-1}.

Benzaldehyde*: 3385, 3060, 2820, 2740, 2340, 1700, 1652, 1598, 1584, 1455, 1391, 1312, 1205, 1168, 1074, 1024, 828, 748, 688.

Benzoic acid: 3580, 3070, 1765, 1755, 1600, 1450, 1345, 1278, 1180, 1082, 1093, 1024, 712.

Carbon dioxide: 3725, 3695, 3620, 3595, 2320, 742, 718, 665.

Carbon monoxide: 2150, 2090.

Ethylene oxide: 3050, 3000, 2600, 1645, 1630, 1555, 1540, 1520, 1505, 1490, 1470, 1455, 1275, 1265, 1145, 873, 857, 820.

Maleic anhydride: 3630, 1800, 1785, 1280, 1270 1240, 1230, 1060, 1055, 890, 838, 698.

Methane: 3000 main peak in 2930-3160, 1300 main peak in 1250-1360.

Naphthalene: 3050, 1932, 1710, 1600, 1590, 1504, 1393, 1385, 1270, 1260, 1010, 955, 825, 780.

Phthalic anhydride: 3080, 1865, 1803, 1495, 1460, 1340, 1255. 1165, 1110, 1105, 910, 840, 790, 710.

Phthalide: 3010, 2950, 2850, 1805, 1755, 1620, 1460, 1450, 1360, 1285, 1210, 1035, 733.

o-Tolualdehyde*: 3060, 3010, 2960, 2920, 2810, 2720, 1710, 1597, 1570, 1485, 1452, 1390, 1267, 1190, 1125, 1045, 995, 860, 835, 750, 740.

o-Toluic acid: 3575, 3070, 2975, 2655, 1805, 1752, 1455, 1340, 1268, 1185, 1055, 900, 737.

Water: 1837, 1785, 1765, 1747, 1727, 1710, 1690, 1677, 1650, 1630, 1610, 1570, 1552, 1538, 1515. 1505, 1487, 1470, 1455. 1435, 1418, 1338, 775.

o-Xylene: 3060, 3020, 2930, 2870, 1935, 1890, 1600, 1498, 1488, 1470, 1455, 1388, 1053, 1023, 740.

These values were determined in vapor phase at low concentration in nitrogen using 20 cm cell at 150°C. Any systemmic error in the Hilger & Watt H-900 can be quantified by using the CO_2 adsorptions at 665, 718 and mid-1320 cm^{-1}. Reagent grade, but not specially purified, materials were used.

*confirmed with thin film, liquid phase to be free of associated acids.

Catalysts

CCI-C103 is a reference catalyst for o-xylene oxidations that has been previously used in this laboratory. It is 3-6 mesh, surface coated V_2O_5 on SiC, supplied ca. 1968 by Catalysts and Chemicals, Inc., Louisville, Kentucky. Its density is 2.57 gm/cc determined with liquid displacement volume. This lot was reported by Ellis[98] to contain no K_2O, as determined by flame photometry.

Kontakt-S was supplied in 1971 by Chemische Fabrik von Heyden GmbH., Regensberg. It consists of extruded, compact 6.5mm diameter short cylinders of a lightly sintered V_2O_5 and, presumably, K_2SO_4-$K_2S_2O_7$ mixture in clay-like substrate. Density is 3.60 gm/cc determined with liquid displacement volume.

This catalyst was fragmented to appropriate size and activated, prior to use in a separate reactor, by reaction during one-half hour operation with 1.% SO_2 in air feed at 380°C, per manufacturer's instructions.[40] This operation formed SO_3 in situ and established the active catalyst condition.

Experimental Catalysts

Porous Alundum spheres, 8.4mm diameter and with density of 1.79 gm/cc determined with liquid displacement volume, were heated to above 700°C in a temperature controlled laboratory furnace. These hot spheres were completely immersed in molten V_2O_5 or binary mixtures contained in porcelain crucibles at temperatures in excess of 700°C. Compositions of these binary mixtures are given in the following table:

Composition of Catalyst-Forming Mixtures

Binary mixture no.	Melting point, °C	V_2O_5 mixture composition mole fraction			Ratio: moles K_2O per mole V_2O_5	Final catalyst density (see note)
		V_2O_5	k_2SO_4	$K_2S_2O_7$		
I	ca. 550	0.83	0	0.17	0.2	2.36
II	ca. 550	0.83	0.17	0	0.2	2.44
III	670	1.0	0	0	0	2.92
IV	ca. 600	0.91	0	0.09	0.1	2.77
V	ca. 600	0.91	0.09	0	0.1	2.71

Note: gm/cc determined with liquid displacement volume.

The molten mixtures readily diffused throughout the Alundum support. No attempt was made to limit the amount adsorbed. The melt was poured off the spheres and they were transferred to empty Vitrosil dishes several times over a time span to allow excess melt to drain off. There was reaction between melts and substrate and net change of SO_3 content due to $K_2S_2O_7 \rightleftharpoons K_2SO_4 + SO_3$ equilibrium. Melting points and studies of some of the phase equilibria involved are given by Boreskov.[183]

After cooling, weight gain and density of each of the five different catalyst compositions were measured. No attempt is made to define catalyst compositions other than by initial compositions of the binary mixtures from which they were produced: Binary mixture I yielded experimental Catalyst I, etc.

High densities of the melt-impregnated support indicated 22.-35.% by weight, adsorption of the V_2O_5 binary mixtures. This high V_2O_5 content infers a severe degration of surface area caused by filling of support pores. Resulting catalyst spheres were metallic black in color and appearance, hard and vitreous, and were found to be visually homogeneous on fragmentation.

Materials used for experimental catalyst preparation were:

V_2O_5: BDH laboratory reagent grade, 98.5% minimum, was used without the usual purification step, via ammonium metavanadate, in this exploratory program.

K_2SO_4: BDH laboratory reagent grade, 99%.

$K_2S_2O_7$: BDH laboratory reagent grade, new sealed lot, presumably hydrated to less than 3% $KHSO_4$.

Alundum: Norton "macroport" catalyst carrier SA-5215 has specifications of Al_2O_3 83.% min. and SiO_2 14.% max. It is basically an alpha alumina and mullite ($Al_2O_3.5SiO_2$) structure with surface area specified to be below $1.m^2/gm$, pore diameter range 30.-200. microns, and porosity (void volume) of 44.-48.% of total volume.