STUDIES OF THERMAL DECOMPOSITION

THESIS

submitted for the degree of

Doctor of Philosophy

by

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I should also like to thank Dr. J. Falconer for carrying out a number of gas chromatographic analyses.

I am indebted to the Department of Chemistry, who have allowed me to fulfil the Ph.D. requirements while I have been a member of the full-time teaching staff.

D. Price

RESEARCH BY FOURTH YEAR STUDENTS

During the course of the present work the author was privileged to contribute to two fourth year problems. The results of these studies are given in two papers published in the Journal of the Chemical Society. Preprints of these papers have been bound in at the front of the thesis. The personal contributions of the present author to these researches are outlined below.

(a) The Thermal Decomposition of cycloPentyl Bromide

The kinetic apparatus which had previously been constructed was prepared for use. A few preliminary runs were carried out to establish the general feasibility of studying the decomposition in a static system. The problem was then taken over by the fourth year student, R. Shaw, who carried out the majority of the runs. Occasional consultations on problems arising from the day to day work were held. At the conclusion of Shaw's work one outstanding problem remained. At the end of a number of his runs he had titrated the products of the decomposition with alkali. The quantity of hydrogen bromide found in this way was erratic and high. The present author therefore carried out a number of runs following which the hydrogen bromide was separated from the remaining products by low temperature distillation. Its amount was then determined by pressure measurements and by dissolving the gas in water and titrating the solution for hydrogen and bromide ions. The results of the three determinations were in excellent agreement.

(b) The Pyrolysis of tert-Butyl Formate

The kinetic apparatus previously employed in the study of cyclopentyl bromide was prepared for use. A series of preliminary runs was carried

out to determine the conditions required for the decomposition of the ester. The problem was then turned over to Gordon, who carried out all further experiments. Occasional consultations were held to sort out problems arising from the work.

TABLE OF NOMENCLATURE

A	Pre-exponential factor of the Arrhenius equation
A,B,C	Moments of inertia for a molecule
D	Bond dissociation energy
E	Arrhenius activation energy; Mean bond energy
E_o	Arrhenius activation energy determined at infinite pressure
h	Planck's constant
K	Transmission coefficient
k	Boltzmann's constant
$k_1, k_2,$ etc.	Specific rate constants
k_∞	Specific rate constant determined at infinite pressure
m	Mass of one molecule
n	Number of atoms in a molecule
n'	Number of effective oscillators in a molecule
R	Gas constant
R_1, R_2	Free radical groups
$R(X)$	Rate of formation of X
T	Absolute temperature
ΔH_f^o	Standard heat of formation at 25°C
ν	Vibrational frequency
θ	A parameter proportional to (pressure x $T^{-\frac{1}{2}n'}$)
σ	Symmetry number

INTRODUCTION

A. General Introductory Remarks

Little is known of the dissociation energies of the metal-carbon bonds in metallic alkyls and aryls. An analysis of the available results is left to a later section of the thesis. It is sufficient to note at this point that of all the experimental activation energies reported, only those of Gowenlock, Polanyi and Warhurst for dimethyl mercury (1) and of Carter, Chappell and Warhurst for diethyl mercury, phenyl mercury chloride and phenyl mercury bromide (2) can be accepted as a measure of the dissociation energy of the first metal-carbon bond in the compound under study.

Mean bond energies are known for a considerably larger number of metallic alkyls. These have been derived from heats of combustion in static bomb calorimeters, heats of hydrolysis, heats of halogenation, and in one recent investigation from the heat of combustion in a rotating bomb calorimeter. The static bomb method often gives incomplete combustion of the alkyl. The extent of combustion is usually estimated and the observed heat of combustion adjusted accordingly. Seven of the heats of formation of metallic alkyls calculated from experiments using static bomb calorimeters have also been determined by heat of hydrolysis or heat of halogenation experiments. The agreement between the methods is satisfactory in six of these cases. In the seventh, di-isopropyl mercury, the heat of formation calculated from the heat of combustion is certainly much too high. Unfortunately, in a number of cases, although the heat of formation of the alkyl has been accurately determined, the value for the heat of atomization of the metal is very uncertain. Large limits of error must therefore be assigned to mean bond values that would otherwise be known with considerable accuracy.

The immediate aim of the present research was to establish reliable values for the dissociation energies of the metal-carbon bonds in dimethyl cadmium and dimethyl zinc, and to confirm the results of Gowenlock, Polanyi and Warhurst for dimethyl mercury. Research on the methyl derivatives of the metals of other groups was then to be initiated. Methyl derivatives were selected so that the reactions of the radicals released on decomposition might be as simple as possible. Furthermore, there exists a considerable body of reliable information on the reactions of methyl radicals. The choice of dimethyl cadmium and dimethyl zinc as the initial compounds to be studied was governed by three factors. Thermochemical values of $D(CH_3M-CH_3)$ plus $D(M-CH_3)$ were available for both compounds, the mechanism of dissociation could be expected closely to parallel that for dimethyl mercury, and the results from these compounds, coupled with the confirmation of the value for dimethyl mercury, would complete the study of suitable group II metals. The trimethyl derivatives of arsenic, antimony, and bismuth, the suitable group V metals, were chosen next because mean bond energies were available for all three. Satisfactory results were obtained for trimethyl bismuth but the kinetics of the decomposition of trimethyl antimony proved so complex that it was felt little would be gained by a study of trimethyl arsenic. Dimethyl tin dichloride was chosen as the final compound for study in the hope that the results might be useful in assessing the work of Waring and Horton on tetramethyl tin (3).

B. Experimental Methods

The methods that can be used to determine the metal-carbon bond dissociation energies in metallic alkyls are rather limited. The radicals produced in the initial split are too reactive to allow any thermal equilibrium

method to be used. The molecules are too complex for the successful application of a spectroscopic method. Electron impact experiments will give only an upper limit of the dissociation energy. The derivation of dissociation energies from photochemical results would require a detailed knowledge of the mechanism by which the molecule absorbs energy. If the absorption is adiabatic, measurement of the photochemical threshold would place an upper limit on the dissociation energy. Activation energies for the thermal decomposition of metallic alkyls have been determined using both static and flow systems. If the process observed experimentally is a unimolecular decomposition producing two radicals whose energy of activation for recombination is small, the experimental activation energy will be a good approximation to the bond dissociation energy. The complexity of the reactions in static systems is such that unambiguous interpretation of the results is almost impossible. The interpretation of data from experiments in flow systems has been much more satisfactory. In these investigations (1, 2) nitrogen, carbon dioxide and carbon dioxide with added toluene were used as carrier gases. Gowenlock, Polanyi and Warhurst consider their most reliable results to be those obtained in the presence of toluene. In the present work a system has been adopted using toluene as the sole carrier gas. This carrier gas can be completely condensed without removing the hydrocarbon products required for analysis. The apparatus needed is therefore much simpler than the circulating system of Gowenlock, Polanyi and Warhurst and the estimation of the gaseous products is always direct rather than by difference.

C. Bond Dissociation Energies by the Kinetic Method

The bond dissociation energy, $D(R_1 - R_2)$, may be defined as the heat of the reaction

$$R_1R_2 = R_1 + R_2$$

at absolute zero and in the ideal gas state. The recombination of R_1 and R_2 may have a finite activation energy (Figure 1, a) or zero activation energy (Figure 1, b). Studies of band spectra indicate that the latter is probably the case when R_1 and R_2 are atoms. The activation energy of the following reactions would also appear to be very small

$$CH_3 + CH_3 = C_2H_6 \qquad (4, 5)$$
$$C_2H_5 + C_2H_5 = C_4H_{10} \qquad (6)$$
$$C_3H_7 + C_3H_7 = C_6H_{14} \qquad (7)$$
$$CF_3 + CF_3 = C_2F_6 \qquad (8)$$
$$C_6H_5CH_2 + Br = C_6H_5CH_2Br \qquad (9)$$

The first four reactions have been studied directly. The activation energy of the fifth reaction has been estimated by an indirect method. Acceptance of the fifth reaction as an example of a reaction with a small activation energy must be rather tentative. The value estimated is 2 kcal $mole^{-1}$ but a possible error of $\pm$ 6.6 kcal $mole^{-1}$ must be associated with this result. Although the evidence is not conclusive it is commonly assumed that if either R_1 or R_2 is a simple radical the energy of activation for the recombination is small.

If there is no potential energy barrier for the recombination of two radicals (Figure 1, b) the transition state theory predicts that the unimolecular rate constant is

$$k_1 = K \frac{kT}{h} \frac{\phi^*(T)}{\phi(T)} e^{-D/RT} \qquad (1)$$

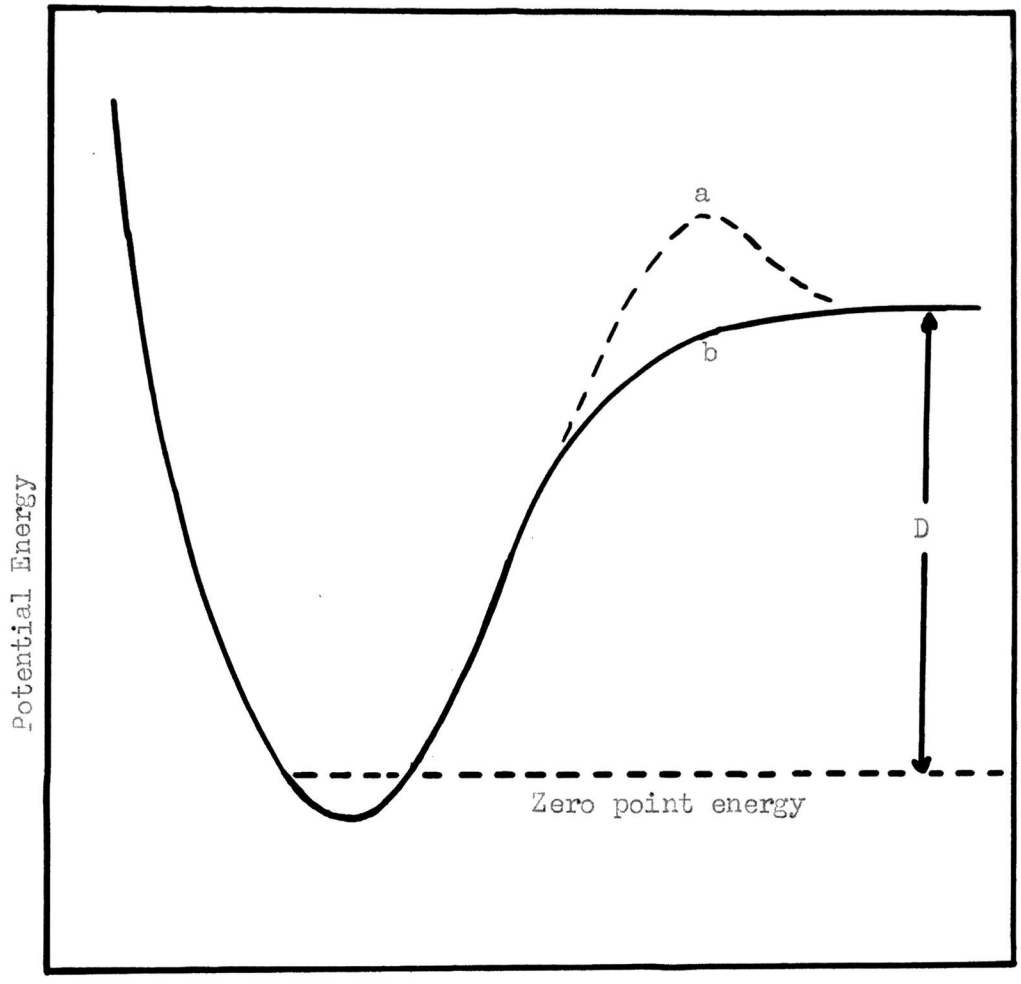

FIGURE 1 Potential energy curve for unimolecular decomposition into two radicals: (a) Energy of activation for recombination finite; (b) Energy of activation for recombination zero.

The total partition functions, $\phi(T)$ for the normal molecule and $\phi^*(T)$ for the activated complex, may each be separated into translational ($\lambda(T)$), rotational ($r(T)/\sigma$), and vibrational contributions. The translational partition function

$$\lambda(T) = (2\pi mkT)^{3/2}/h^3$$

will be the same for the normal molecule and the activated complex. The rotational partition function will be of the form

$$r(T)/\sigma = 8\pi^2 AkT/\sigma h^2$$

for a linear molecule and of the form

$$r(T)/\sigma = 8\pi^2 (2\pi kT)^{3/2} (ABC)^{\frac{1}{2}}/\sigma h^3$$

for a nonlinear molecule. If each mode of internal vibration behaves as a linear harmonic oscillator equation (1) applied to a nonlinear molecule may be written

$$k_1 = K \frac{kT}{h} \frac{\sigma^*}{\sigma} \left(\frac{A^* B^* C^*}{A B C}\right)^{\frac{1}{2}} \frac{\prod^{3n-6} (1-e^{-h\nu/kT})}{\prod^{3n-7} (1-e^{-h\nu/kT})} e^{-D/RT} \quad (2)$$

If $h\nu << kT$ the terms $(1-e^{-h\nu/kT})$ approach $h\nu/kT$ and equation (2) becomes

$$k_1 = K \frac{\sigma^*}{\sigma} \left(\frac{A^* B^* C^*}{A B C}\right)^{\frac{1}{2}} \frac{\prod^{3n-6} \nu}{\prod^{3n-7} \nu^*} e^{-D/RT} \quad (3)$$

Taking the logarithms of both sides of equation (3) and differentiating with respect to temperature gives

$$\frac{d \ln k_1}{dT} = \frac{D}{RT^2}$$

The Arrhenius activation energy is therefore equal to the bond dissociation

energy. At the other extreme, $h\nu >> kT$, the term $(1 - e^{-h\nu/kT})$ approach unity and equation (2) becomes

$$k_1 = K \frac{\sigma^*}{\sigma} \left(\frac{A^* B^* C^*}{A B C}\right)^{\frac{1}{2}} \frac{kT}{h} e^{-D/RT} \qquad (4)$$

Differentiating the logarithmic form of equation (4) with respect to temperature and rearranging gives

$$RT^2 \frac{d \ln k_1}{dT} = D + RT$$

Hence the limits $D \ll E \ll D + RT$ may be placed on the experimental activation energy. It would therefore appear that if the experimental activation energy for a unimolecular decomposition can be accurately determined it should be a reasonable approximation to the dissociation energy of the bond broken.

D. Pressure Dependence of the Experimental Activation Energy

It has been postulated by Slater (10) that if the unimolecular rate constant is measured in a pressure dependent region the experimental activation energy, E, is related to the experimental activation energy at infinite pressure, Eo, by the equation

$$E = E_o - \tfrac{1}{2} n'RT\, g(\theta)$$

where n' is the number of effective oscillators in the molecule and $g(\theta)$ represents the fractional drop of E from the high value (E_o) towards the low value ($E_o - \frac{1}{2} n'RT$). In the previous section it was shown that the experimental activation energy for a unimolecular dissociation lies within the limits $D \ll E \ll D + RT$. The assumption that $E = E_o$ is inherent in the derivation of this result. Therefore if the experimental activation energy has been determined in a pressure dependent region the magnitude of E_o-E must be determined in order to estimate the bond dissociation energy.

It is first necessary to choose a value for n', the number of effective oscillators in the molecule. In a molecule with several heavy nuclei the contribution of C-H bonds will usually be small. Thus in azomethane ($CH_3N = NCH_3$) the number of vibrational degrees of freedom would be six. Slater (11) has pointed out, however, that the three C-H bonds near the point of rupture may contribute appreciably. If full weight is given to these C-H bonds the molecule would have 15 effective degrees of vibrational freedom. The actual value of n' for azomethane will probably be somewhere between these limits. The calculation of k/k_∞, and hence of $g(\theta)$, requires a complete vibrational analysis of the molecule in question. This is generally not available. An approximate value of k/k_∞ may be obtained by comparing the slope of the curve log k versus log p obtained experimentally with the slope of the log k/k_∞ versus log p curve for some similar molecule. Values of k/k_∞ as a function of the pressure dependent parameter, θ, have been tabulated by Slater (10) for various values of n' from one to thirteen. The necessary data for the conversion of θ to the corresponding pressure are also given. The model used by Slater differs to some extent from the compounds used in the present research. However, if allowance is made for the difference in the frequency factors the values of k/k_∞ obtained by comparison with the model should be sufficiently accurate for the present purpose.

For the dimethyl metallic alkyls n' may reasonably be assigned a value of 9. The value of k/k_∞ estimated for these compounds at 16 mm pressure is 0.3. This corresponds to a value for $g(\theta)$ of $\sim .35$(11). Hence at 800°A

$$E \approx E_0 - 2,5 \text{ kcal mole}^{-1}.$$

The number of effective oscillators in trimethyl antimony may reasonably be

assigned a value of 12. The value of k/k_∞ is again 0.3. Hence at 800°A

$$E \approx E_o - 3.3 \text{ kcal mole}^{-1}.$$

The observed pressure dependence of the rate contents of trimethyl bismuth and dimethyl tin dichloride was so small that at 16 mm pressure $E \approx E_o$. For the compounds studied it is not unreasonable to assume that $h\nu/kT \approx 1$ at 800°A ($\nu = 10^{13} - 10^{14}$). Hence

$$E_o \approx D + 1.5T = D + 1.2 \text{ kcal mole}^{-1}.$$

Therefore the error involved in assuming D = E will be 1 - 2 kcal mole^{-1}. The values of $E_o - E$ calculated above are of a very approximate nature. A correction to the observed experimental activation energy based on these values cannot be justified. It is therefore assumed in the ensuing sections that if an experimental activation energy can be associated with the unimolecular dissociation of a bond it is a good approximation to the dissociation energy of this bond.

E. Toluene Carrier Technique

The experimental activation energy may be determined by measuring the unimolecular rate constant at various temperatures. Careful experimentation may lead to a high degree of precision but unless competing surface and side reactions are absent the rate constant determined will not be that of the unimolecular decomposition. Simple flow systems have often been used in an attempt to reduce side reactions by working at very low concentrations. Total pressures of 2 - 15 mm are used, much of which may be a noncondensable carrier gas such as hydrogen or nitrogen. Szwarc (12) made a study of toluene by a modification of this method in which toluene acted as both reactant and carrier gas. He found that if only a very small percentage of the toluene decomposed the reaction could be represented by the simple mechanism

$$C_6H_5CH_3 = C_6H_5CH_2 + H$$

$$H + C_6H_5CH_3 = C_6H_5CH_2 + H_2$$

$$H + C_6H_5CH_3 = C_6H_6 + CH_3$$

$$CH_3 + C_6H_5CH_3 = C_6H_5CH_2 + CH_4$$

$$2\ C_6H_5CH_2 = (C_6H_5CH_2)_2$$

The useful application of this method is limited to compounds that satisfy two conditions. First, that they form radicals that are considerably stabilized by resonance and hence lose atoms or small radical groups fairly readily. Second, that the radicals produced do not readily decompose.

In order to study radical elimination reactions which do not satisfy the requirements of the simple flow technique Szwarc developed the toluene carrier technique (13). The technique is based on the stability of the benzyl radical and the ease of the hydrogen abstraction reaction between many radicals and toluene,

$$C_6H_5CH_3 + R = C_6H_5CH_2 + RH$$

The benzyl radicals produced do not react in the hot zone under the experimental conditions used and eventually dimerize outside the main reaction zone. The experimental conditions necessary for the study of a compound by this method should meet certain general requirements. If, with a contact time of one second, temperatures in excess of ~775°C are required the accuracy of the results is likely to be limited by the accuracy of the correction for the decomposition of toluene. For example, if in a 30 minute run at 775°C 0.11 mole of toluene is used 0.8×10^{-4} mole of methane will be produced (assuming $\log$ (A sec^{-1}) = 13.3, E = 77.5 kcal $mole^{-1}$, $C H_4 : H_2 = 1 : 1.5$). If 10×10^{-4} mole of a reactant which gives two methyl radicals per molecule is

50% decomposed under these conditions the yield of product will be equivalent to 10 x 10^{-4} mole of methane. It is not unreasonable to assign a possible error of a factor of two to the calculated rate of the toluene decomposition. Therefore under the conditions stated a correction for the decomposition of toluene based on the A and E values of Szwarc may easily result in a 20% error in the rate constant. If a distinctive product is formed, such as HBr in the thermal decomposition of phenyl bromide the maximum temperature used may be extended to ~875°C. Above this temperature too many permanent gases are formed for most simple diffusion pump systems to handle. No simple estimate can be made of the lowest temperature at which the toluene carrier technique may usefully be employed. Even at temperatures sufficiently low that the methyl radicals produced by the decomposition of metallic alkyls largely dimerize the toluene still performs its essential function of reducing the attack on the parent substance.

The technique enables reactant pressure and percentage decomposition to be varied widely. In previous work (14) reactant pressures of 0.05 - 2.0 mm have been employed. Percentage decompositions of 0.1 - 88% have been used although the lower figure is usually somewhat larger, 1-3%. In calculating the rate constants from flow system data the assumption is made that no mixing occurs in the reaction zone. The use of contact times larger than a few seconds is therefore unadvisable. The use of very short contact times has also been questioned. Blades, Blades and Steacie (15) found that below a contact time of 0.3 second the rate constant for the decomposition of toluene fell markedly. At contact times of 0.07 second the activation energy for the decomposition was found to be 90 kcal $mole^{-1}$, 13 kcal $mole^{-1}$ higher than the value reported by Szwarc.

EXPERIMENTAL TECHNIQUE

A. Apparatus and Procedure

The toluene carrier flow system is shown in figure 2. Reservoir R_1 contained the bulk of the alkyl which after degassing was stored at -196°C. The supply of alkyl for immediate use was kept similarly frozen down in R_2. Reservoir R_4 contained sulphur free toluene purified by partial pyrolysis and thoroughly degassed. The reaction vessel was made of fused quartz with graded quartz to pyrex seals a few centimeters beyond either end of the furnace. The reaction zone (RZ) was 18 cm long and 155 cm^3 in volume. Packing with fine quartz tubing increased the surface to volume ratio by a factor of five and decreased the volume to 127 cm^3. The packing completely filled the cross-section of the reaction zone over a length of 12 cm. It should therefore have been adequate to detect any significant heterogeneous reaction (16).

The temperature of the furnace was controlled by a Sunvic Resistance Thermometer Controller Type RT2. The heating element was tapped at seven points so that the temperature profile could be adjusted by shunt resistors. Temperatures were measured in the axial thermocouple well of the reaction vessel. Thermocouples constructed from a commercial thermocouple wire were used in conjunction with a Doran d.c. potentiometer. A change in temperature of one centigrade degree caused a deflection of approximately 2 cm on the galvanometer scale. Temperatures could therefore be read to within 0.1°C. With an inconel liner extending over the length of the reaction zone the temperature profile within the zone was kept within ± 2°C with a steep fall off at either end.

The flow rate through the reaction vessel was regulated by the sealed in capillary at the outlet of the reaction vessel (Fig. 2, B). All tubing on the inlet side of the reaction vessel was heated to 40°C. The injection system

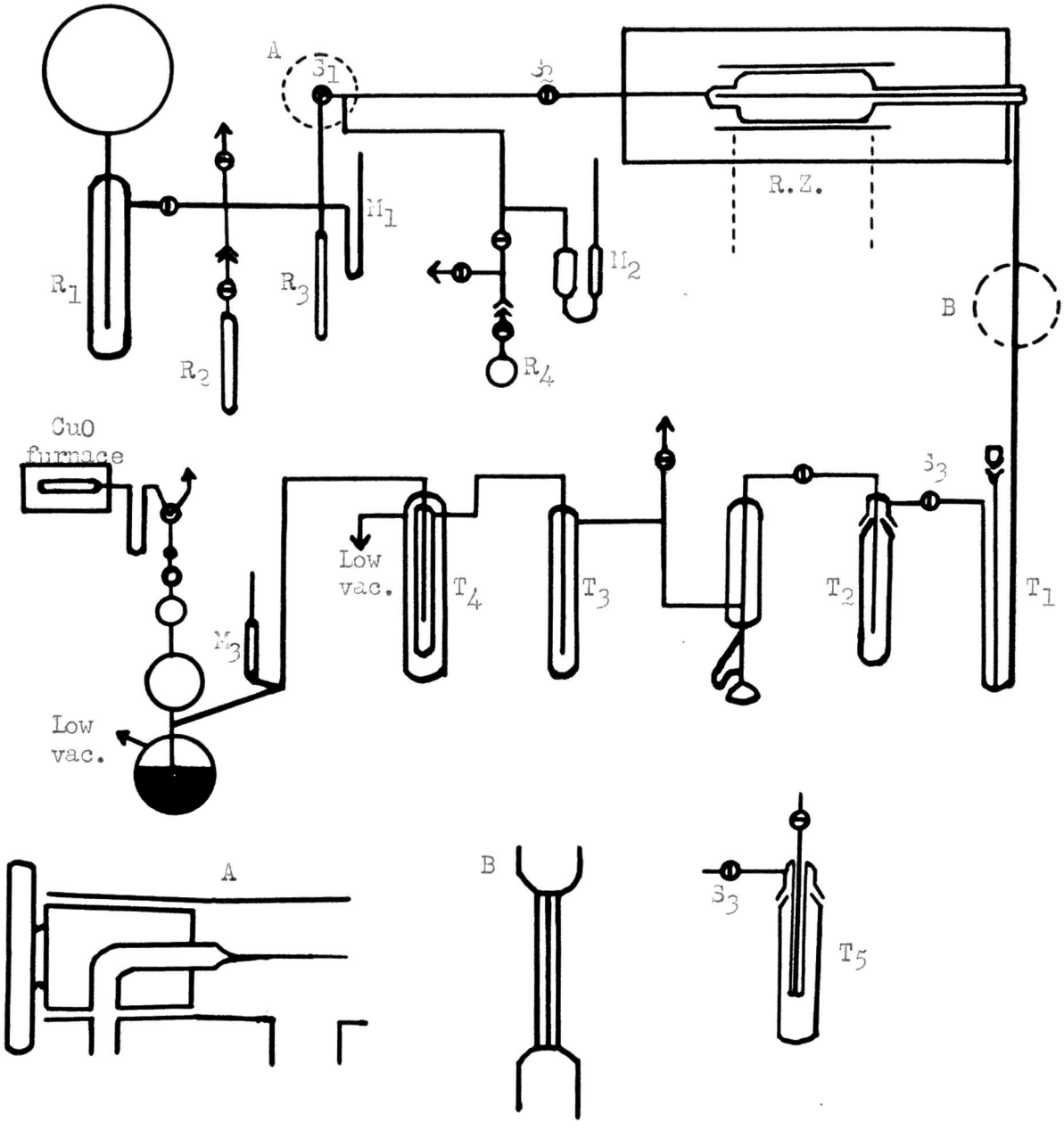

FIGURE 2 Toluene Carrier Flow System

was heated as required. The tubing from the outlet of the furnace to T_1 was kept at 80°C.

With the exception of dimethyl tin dichloride the procedure employed in a run was essentially the same for all compounds studied. A small sample of the alkyl was distilled from R_2 into R_3. Water baths were placed around R_3 and R_4 to bring the alkyl and toluene to precalculated temperatures. The flow of toluene was commenced and the pressure, as measured by the differential manometer (M_2), recorded. After a five minute flow of toluene tap S_1 was opened. The flow of alkyl continued for thirty minutes and was followed by another five minute flow of toluene alone. The alkyl remaining in R_3 was redistilled into R_2. The amounts of alkyl and toluene used were determined from the loss in weight of R_2 and R_4 respectively.

Trap T_1 (0°C) removed some dibenzyl and any other involatile substance. Toluene, any unreacted alkyl, and the remaining dibenzyl were condensed in T_2 (-72°C). A quartz diffusion pump capable of working against a backing pressure of several centimeters of mercury then transferred the remaining gaseous products to the analysis system. Here the ethane and ethylene were frozen out in T_3 (-196°C) and T_4 (-205°C) while the methane and hydrogen were continually transferred to the gas burette by means of the Toepler pump. A small McLeod gauge (M_3) was used to indicate complete transfer of a gas to the burette. Hydrogen was estimated by oxidation in the copper oxide furnace (300°C). After the burette was cleared of methane and hydrogen T_4 was brought to room temperature and T_3 to -165°C. The ethane and ethylene were similarly transferred to the gas burette and measured. Ethylene was then estimated by gas phase chromatography.

In seventeen runs with trimethyl antimony, the antimony and involatile antimony compounds produced were also determined. For these

experiments a chlorine reservoir similar to the main alkyl reservoir (R_1) was connected between S_2 and the furnace. All tubing in this region was heated to 100°C. At the end of a run, all the antimony and involatile antimony compounds deposited in the reaction vessel were converted into a mixture of antimony trichloride and pentachloride by the action of chlorine. To facilitate removal of the mixed chlorides T_1 was replaced by T_5. The tubing from the outlet of the furnace to the lower end of the inlet tube of T_5 was heated to 100°C. The chlorides were distilled out into T_5, dissolved in hydrochloric acid and reduced to the trivalent state by boiling with sodium sulphite. The antimony was then titrated with standard potassium bromate using methyl red as an indicator (17).

In three runs the undecomposed trimethyl bismuth was determined. The alkyl was destroyed by passing a very slow stream of oxygen through the toluene solution removed from the CO_2-spirits trap. The toluene was distilled off, the bismuth oxide dissolved in sulphuric acid, and the bismuth determined by a colourimetric estimation employing potassium iodide (18).

For dimethyl tin dichloride the injection system used for the other alkyls was replaced by a U-tube. Before a run, a quantity of the alkyl was distilled from a weighed storage tube into the U-tube. The toluene stream was saturated with alkyl vapour as it flowed through the U which was maintained at a convenient temperature (25°C to 40°C). At the end of the run the remaining alkyl was distilled back into the storage tube and the amount used determined by weighing. Except for a few centimeters at the bottom of the U-tube, all tubing from this section of the apparatus to the entrance of the furnace was heated to 80°C. The tubing from the outlet of the furnace to T_5 was also maintained at this temperature.

The first order rate constants were calculated from the equation

$$k = \frac{2.303}{t_c} \log \frac{1}{1-x}$$

where x represents the fraction of the alkyl decomposed and the contact time, t_c, is given by the expression

$$t_c = \frac{V \times P \times 273}{R \times T \times 760 \times 22416} \text{ sec.}$$

In this expression:

V = volume of the reaction zone (cm^3)

P = pressure in the reaction vessel (mm)

T = temperature of the reaction zone in ^oA

R = total rate of flow through the reaction vessel in moles per second.

B. Preparation of Materials

a. Toluene Sulphur free toluene was purified by passing it twice through a quartz tube at 870°C and 25 mm pressure. Purification by this method has been shown to be necessary in order to obtain reproducible rate constants in the pyrolysis of toluene itself (12, 15). The product was twice fractionated and stored over sodium wire. Before use it was thoroughly degassed by bulb to bulb distillation under vacuum.

b. Dimethyl mercury Dimethyl mercury was prepared from mercuric chloride and methyl magnesium iodide (19). When all the mercuric chloride had been added to the Grignard reagent the reaction vessel was equipped with a condenser set for distillation. The water bath around the reservoir was brought slowly to a boil and was maintained at this temperature for one hour. The mixture was stirred continually during the distillation and heating. The water bath was cooled, the solvent returned to the reaction vessel and

the whole mixed thoroughly. The excess Grignard reagent was then hydrolysed by pouring the solution onto cracked ice. The ether layer was separated and dried over calcium chloride. The bulk of the ether was removed by a rapid fractionation. The crude product was dried over calcium chloride and twice fractionated. The fraction boiling at 91.8°C (corrected) was stored under vacuum at room temperature. Analysis by gas chromatography showed a maximum of 0.1% impurity.

c. Dimethyl cadmium Dimethyl cadmium was prepared by the action of anhydrous cadmium chloride on methyl magnesium iodide (20). The preparation of the Grignard reagent was carried out in an atmosphere of dry nitrogen. The ether solution of the reagent was siphoned into the production unit. This unit consisted of a three neck flask equipped as follows. One side neck was fitted with two condensers in series. The top of the second condenser was connected to a mercury bubbler valve. The center neck was fitted with a mercury seal stirrer. The other side neck was fitted with a Y-adaptor. One arm of the adaptor was connected through a condenser to the nitrogen supply. A conical flask containing the anhydrous cadmium chloride was attached to the other arm of the adaptor by an 8 inch length of inch diameter rubber tubing. The production unit was swept with nitrogen during the transfer of the Grignard reagent. The flow of nitrogen was continued for several minutes after the transfer was complete. Stirring with a nichrome stirrer was started and the anhydrous cadmium chloride was added in small portions at about five minute intervals. When an addition was not being made the weight of the flask bent the rubber tubing, thus sealing off the cadmium chloride in the flask from the rest of the unit. The addition of 165 grams ofcadmium chloride required four hours. The solution was cooled to room temperature and was siphoned into the fractionating unit. The bulk of the ether was removed by careful fractionation

at atmospheric pressure in an atmosphere of dry nitrogen. A previous attempt to remove the ether rapidly resulted in a large loss of product. The crude product was twice fractionated and the fraction boiling at 70.4°C at 240 mm was stored under vacuum at -183°C.

d. Dimethyl zinc Dimethyl zinc was prepared by the reaction of methyl iodide with a freshly prepared zinc-copper couple (21, 22). The couple was placed in a quickfit flask equipped with a dropping funnel and a reflux condenser. The top of the condenser was connected to a mercury bubbler valve and the system was flushed by passing dry nitrogen through the dropping funnel. The nitrogen supply was disconnected and the methyl iodide mixed with a few drops of methyl acetate was placed in the dropping funnel. The mixture was run onto the couple and the whole left at room temperature in an atmosphere of nitrogen for 16 hours. The flask was then heated on a water bath for 8 hours. The mixture was frozen with liquid nitrogen and the reflux condenser replaced by a simple distilling unit. The system was evacuated and then filled to atmospheric pressure with dry nitrogen. This technique of freezing, making the necessary changes, evacuating, and filling to atmospheric pressure with nitrogen, was employed throughout the preparation. The crude dimethyl zinc was collected by distillation, transferred to a fractionating unit and carefully fractionated. The fractionating head used was a one piece model constructed with a magnetically controlled tapered glass rod valve. The fraction boiling at 42-46°C was collected. A weighed sample of this fraction was decomposed with water and the residual methyl iodide determined by gas chromatography. The sample contained only 60% dimethyl zinc. The crude product was therefore returned to the production flask and refluxed for a further 24 hours with a fresh portion of zinc-copper couple. The crude product was further purified by passing the vapour 5 times over a portion of zinc-copper

couple heated electrically to 150°C. The crude alkyl was again fractionated, the fraction boiling at 46.4 - 46.5°C at 758 mm being collected. Three weighed samples were decomposed by air plus water or air alone. Analysis by gas chromatography indicated that the residual methyl iodide constituted considerably less than 1% of the sample.

e. Trimethyl bismuth Trimethyl bismuth was prepared by the action of anhydrous bismuth trichloride on methyl magnesium iodide (23). The method used was similar to that employed in the preparation of dimethyl cadmium. The excess Grignard reagent was destroyed by the addition of aqueous ammonium chloride. The flask containing the ether solution was kept in an ice bath during the hydrolysis. The ether layer was separated and dried over sodium sulphate. The bulk of the ether was removed by fractional distillation. The crude product was again dried over sodium sulphate. It was twice fractionated and the fraction distilling at 55 - 56°C at approximately 120 mm was stored under vacuum at -196°C. This fraction had a vapour pressure of 21.6 mm at 16°C.

f. Trimethyl antimony Trimethyl antimony was prepared by heating antimony powder with dimethyl mercury using mercuric chloride as a catalyst (24). The reaction was carried out in a sealed tube at 150°C. The crude product was fractionally distilled in an atmosphere of dry nitrogen. The fraction boiling at 78.5°C was stored under vacuum at -196°C. This fraction had a vapour pressure of 72 mm at 17°C and 30.5 mm at 0°C.

g. Dimethyl tin dichloride Dimethyl tin dichloride was prepared by bubbling methyl chloride through molten tin containing 10% of fine copper powder as a catalyst (25). The metal mixture was heated to 350°C and any oxides reduced by passing hydrogen for one hour. The temperature was then raised to 375°C and the flow of methyl chloride initiated. As the product

formed it distilled from the metal mixture and was collected as needle-like white crystals in an air condenser. The first product appeared in 12 minutes. After 30 minutes at 375°C the temperature was reduced to 315°C. Ten grams of product, m.p. 106°C, was obtained in 13 hours.

EXPERIMENTS AND RESULTS

A. Dimethyl Mercury

The complete experimental results are given in table 1. Their satisfactory interpretation depends upon the selection of the correct mechanism for the system. A possible mechanism for the decomposition of dimethyl mercury in the presence of toluene is as follows (1):

$$Hg(CH_3)_2 = HgCH_3 + CH_3 \quad (1)$$

$$HgCH_3 = Hg + CH_3 \quad (2)$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \quad (3)$$

$$2\ CH_3 = C_2H_6 \quad (4)$$

$$2\ C_6H_5CH_2 = (C_6H_5CH_2)_2 \quad (5)$$

Reaction 2 is assumed to be very much faster than reaction 1.

According to the mechanism the number of moles of ethane plus half the number of moles of methane formed during a run should be equal to the number of moles of the alkyl which have decomposed. The rate constants shown in table 1 have been calculated on this basis.

The proposed mechanism for the decomposition will only be valid of the reaction

$$CH_3 + C_6H_5CH_2 = C_6H_5CH_2CH_3 \quad (6)$$

can be neglected as a possible means by which methyl radicals might be removed from the system. The rate of this reaction has not been measured so there is no direct evidence on this point. However, extensive work by Gowenlock, Polanyi and Warhurst has shown that the percentage decomposition based on the number of moles of ethane plus half the number of moles of methane is generally in good agreement with that calculated from the weight of mercury produced. The loss of methyl radicals by reaction 6 must therefore be small. These

TABLE 1 - THE PYROLYSIS OF DIMETHYL MERCURY

run no.	temp. (°C)	contact time (sec)	toluene (mm)	$Hg Me_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)	k_1 (sec^{-1})
1 a	560	1.35	17.0	4.55	5.46	0.38	0.830
2 a	560	1.37	16.1	12.00	12.50	1.57	0.810
3 a	543	1.39	16.1	14.90	11.50	1.49	0.477
4 a	542	1.44	16.0	12.90	10.06	1.15	0.460
5 a	585	1.33	16.5	13.40	15.50	2.06	0.990
6 a	531	1.41	16.3	15.30	8.82	1.09	0.317
7 a	505	1.45	16.2	15.20	3.90	0.39	0.115
8 a	483	1.52	16.2	14.20	1.60	0.12	0.044
9 a	465	1.51	16.1	16.20	0.71	0.04	0.016
10 a	466	1.52	16.1	14.60	0.69	0.05	0.018
11 c	608	.405	16.0	3.42	4.49	0.19	3.12
12 b, c	585	.425	16.2	6.71	7.50	0.48	2.33
13 c	573	.459	16.1	7.80	6.59	0.58	1.49
14 c	562	.435	16.1	10.30	6.80	0.56	1.11
15 c	562	.426	16.5	10.40	7.12	0.58	1.03
16 c	562	.425	16.1	21.10	12.40	1.61	1.07
17	543	1.72	10.3	15.60	10.30	2.30	0.376
18	543	2.28	4.4	12.10	6.36	2.70	0.290
19 c	543	1.13	25.5	14.10	12.00	1.16	0.625

a H_2 1 $\pm$ 0.5%; C_2H_4; ca. 0.5% of C_1 and C_2 fractions;

b H_2 nil; c length of run 20 min.

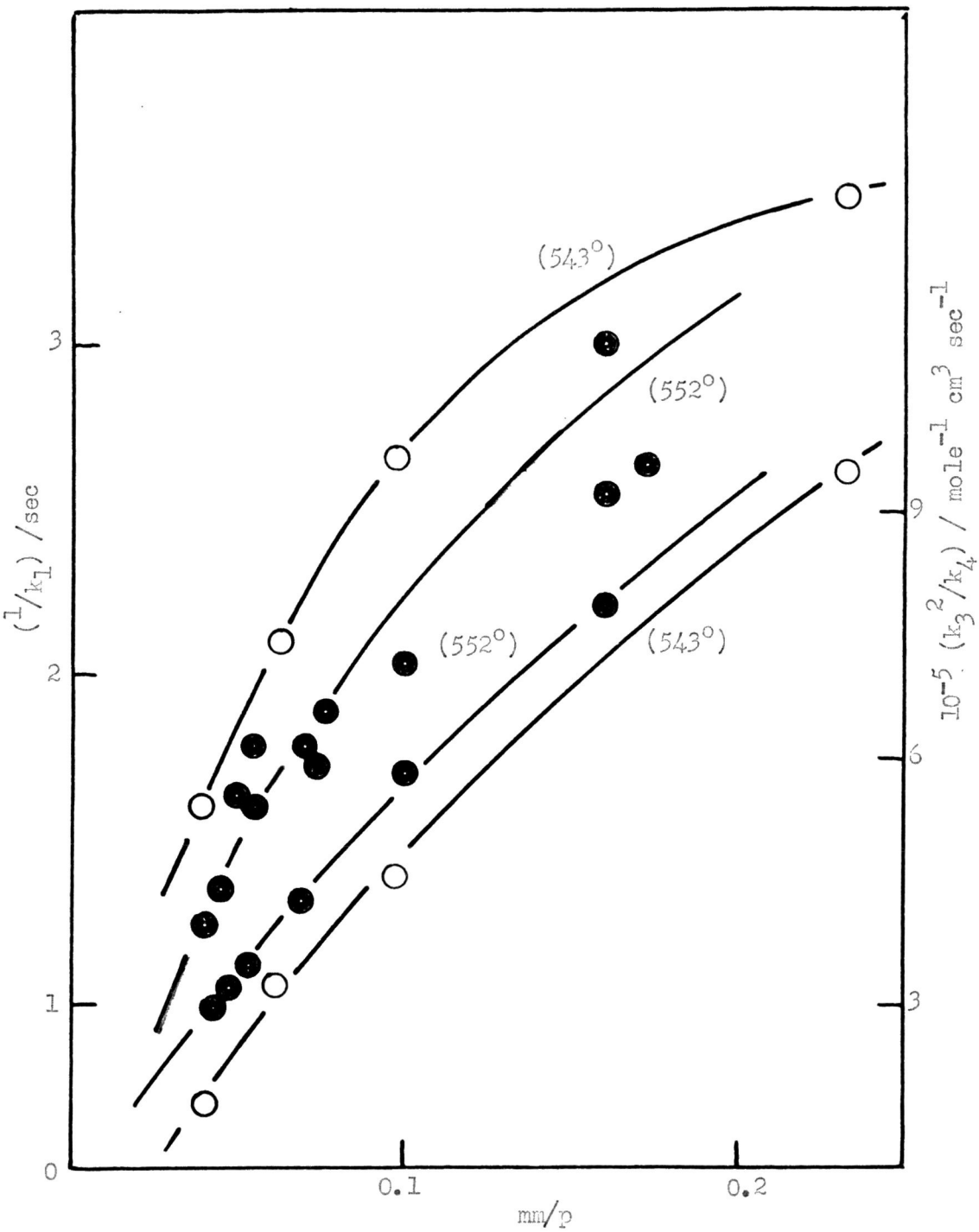

FIGURE 3 The variation of the rate constants with pressure. The right-hand scale refers to the two lower curves. The full points were obtained in the study of dimethyl cadmium, the open points in the study of dimethyl mercury.

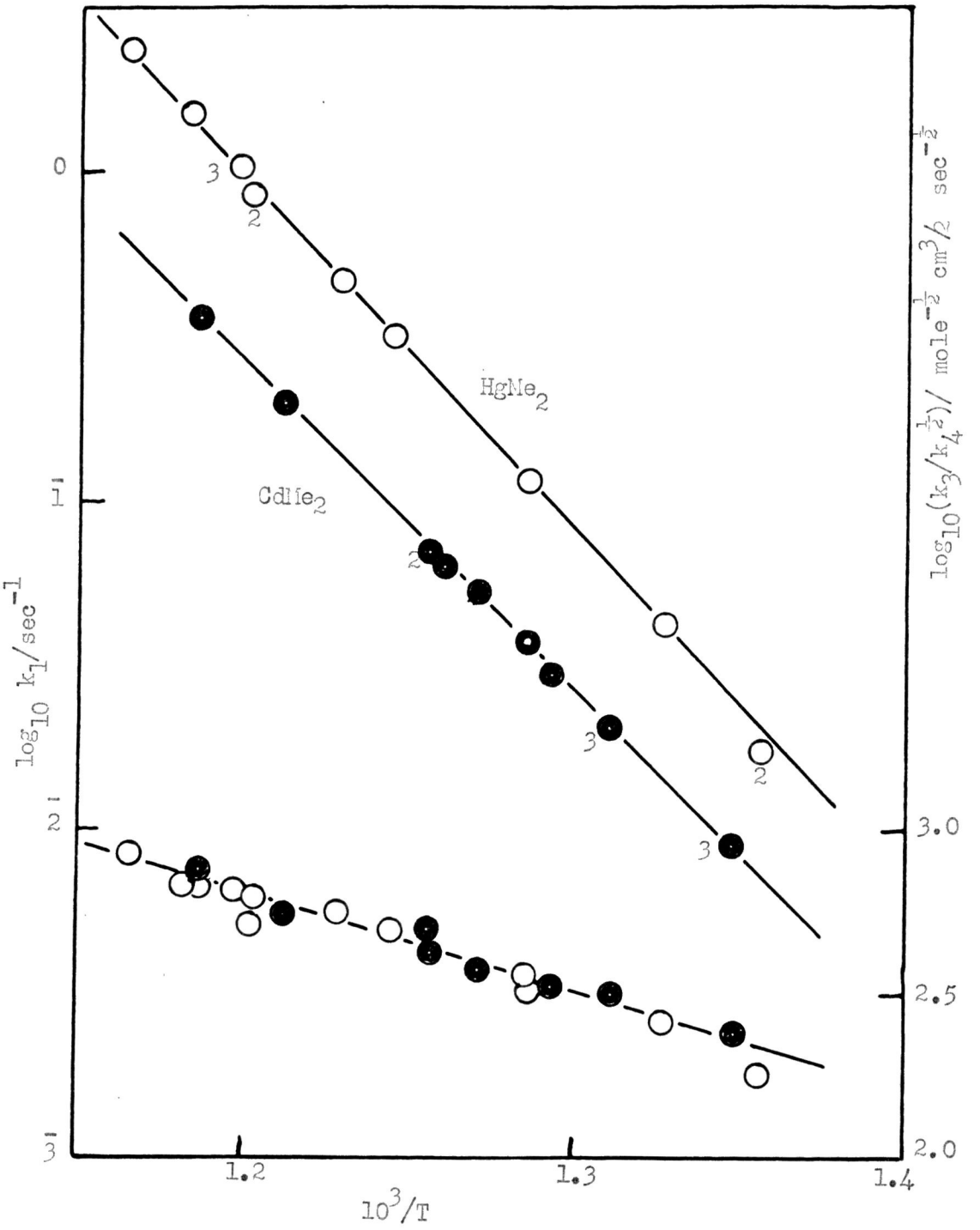

FIGURE 4 Arrhenius plots for the decomposition of dimethyl mercury and dimethyl cadmium, and the reaction of methyl radicals with toluene. The figures beside the point indicate the number of runs averaged to obtain the plotted value. The values for the decomposition of dimethyl cadmium have been displaced downwards by 0.5 log units.

workers have also shown that the decomposition is first order and largely homogeneous. Therefore the present work does not include a systematic study of the effects of concentration, contact time, or surface to volume ratio.

The rate constant for the decomposition depends markedly on the total pressure in the reaction system. This is shown in figure 3. The reaction is being investigated under conditions such that the rate of energy transfer is not sufficient to maintain the high pressure rate constant. This is to be expected for molecules containing only three heavy atoms. Accordingly, the majority of the runs have been carried out near 16 mm total pressure and corrected to this selected pressure by making use of the empirically determined relation between the rate constants and the pressure.

The Arrhenius plot of the rate constants is given in figure 4. The straight line corresponds to

$$\log_{10} k_1/\text{sec}^{-1} = 13.1 - (50100 \pm 1000/2.303\ RT)$$

for mercury dimethyl at 16 mm pressure.

B. Dimethyl Cadmium

The complete experimental results are given in table 2. The mechanism for the decomposition of dimethyl cadmium in the presence of toluene may be expected to closely parallel that given for dimethyl mercury. That is:

$$Cd(CH_3)_2 = CdCH_3 + CH_3 \quad (1)$$

$$CdCH_3 = Cd + CH_3 \quad (2)$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \quad (3)$$

$$2\,CH_3 = C_2H_6 \quad (4)$$

$$2\,C_6H_5CH_2 = (C_6H_5CH_2)_2 \quad (5)$$

where reaction 2 is again assumed to be much faster than reaction 1.

Hence the number of moles of dimethyl cadmium decomposed will be equal to one half the number of moles of methane plus the number of moles of ethane. Using this measure of the progress of the reaction it was found that the decomposition of dimethyl cadmium obeys first order kinetics at a constant total pressure in the system. The results given in table 3 show that changing the alkyl concentration by a factor of 35 does not affect the observed rate constant. The effect of contact time on the first order rate constant is shown in table 4. No significance is attached to the slight variation at 552°C.

Two runs (39 and 40) were carried out with the reaction vessel packed as previously described. When due allowance is made for temperature and total pressure the rate constants calculated for these runs are in excellent agreement with those determined in the unpacked vessel. Therefore within the limits of the present experimental technique the thermal decomposition of dimethyl cadmium in the presence of toluene appears to be a homogeneous gas phase reaction.

The effect of the total pressure in the system on the observed rate constant has been studied. Using contact times of one to two seconds the total pressure has been varied in several steps from 5.2 mm to 24.4 mm. The results of these experiments are shown in fig. 3. The pressure dependance of the rate constant is very similar to that observed for dimethyl mercury. This similarity is to be expected for two molecules so similar in structure. Because of the marked dependance of the observed rate constant on total pressure the majority of runs have been carried out near 18 mm and corrected to this selected pressure. The rate constants given in table 2 are the uncorrected values for the toluene pressure indicated. All values in table 3 and table 4 have been corrected to 18 mm. Similarly all values for dimethyl cadmium plotted in fig. 4 are based

TABLE 2 - THE PYROLYSIS OF DIMETHYL CADMIUM

run no.	temp. (°C)	contact time (sec)	toluene (mm)	$CdMe_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)	k_1 (sec^{-1})
1	552	0.93	15.6	1.52	0.88	0.11	0.48
4	552	1.10	15.6	18.70	12.60	1.55	0.47
7	552	1.30	19.2	9.20	8.90	0.57	0.60
8	552	1.02	18.7	48.80	28.50	6.70	0.55
9	552	1.23	5.2	27.40	10.80	5.64	0.39
10	552	1.03	24.4	9.66	10.50	0.41	0.79
12	552	0.59	21.8	25.60	15.90	1.15	0.74
13	552	0.74	13.2	17.20	8.60	1.28	0.53
15	552	0.63	15.4	26.60	14.40	1.74	0.64
16	552	0.68	13.8	21.60	11.10	1.55	0.58
17 d	552	0.83	14.4	14.90	8.40	1.34	0.56
18	552	1.72	18.0	19.30	18.60	2.22	0.53
19	552	1.73	18.6	19.30	17.80	2.31	0.56
20	552	0.62	18.6	16.30	8.85	0.87	0.63
21	552	1.37	20.0	3.78	3.94	0.16	0.61
22	552	2.13	6.3	18.10	10.90	3.48	0.32
23	552	1.71	10.0	19.90	15.40	3.70	0.49
24	552	2.08	5.8	22.20	12.30	6.06	0.38
26	571	1.38	17.0	17.30	19.00	2.70	0.90
27	524	1.43	18.3	14.40	6.83	0.68	0.233
28	490	1.47	17.5	23.00	3.64	0.32	0.065
30 c	469	1.72	18.6	24.90	2.20	0.17	0.028
32	469	5.55	19.9	14.90	3.62	0.47	0.030
33 a	501	5.57	18.5	14.30	8.34	1.65	0.094

TABLE 2 continued

run no.	temp. (°C)	contact time (sec)	toluene (mm)	$CdMe_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)	k_1 (sec^{-1})
34	524	3.47	16.5	19.60	14.80	3.30	0.206
35	522	4.03	17.6	10.70	9.60	0.93	0.190
36	490	5.05	19.3	21.20	8.48	2.16	0.070
37	469	6.60	19.3	20.00	5.30	0.87	0.029
38 c	571	0.64	17.0	22.22	17.80	2.23	1.09
39 b	517	3.42	18.9	19.10	12.80	2.17	0.174
40 b	508	3.00	19.0	24.20	10.70	1.97	0.124

a complete analysis CH_4 82.6%; C_2H_6 15.9%; H_2 0.8%; C_2H_4 0.7%;

b packed vessel; c H_2 1.25 ± 0.25% of C_1 fraction; d length of run 20 min.

TABLE 3 - THE EFFECT OF DIMETHYL CADMIUM CONCENTRATION ON THE VELOCITY CONSTANT (k_1)

temperature = 552°C pressure = 18 mm.

run no.	t_c (sec)	$CdMe_2$ (10^{-9} mole cm^{-3})	k_1 (sec^{-1})
1	0.93	0.51	0.53
21	1.37	1.86	0.56
7	1.30	4.29	0.57
4	1.10	7.38	0.52
8	1.02	17.83	0.53

TABLE 4 - THE EFFECT OF CONTACT TIME ON THE VELOCITY CONSTANT (k_1) FOR DIMETHYL CADMIUM

temperature = 552°C pressure = 18 mm

run no.	t_c (sec)	k_1 (sec^{-1})	run no.	t_c (sec)	k_1 (sec^{-1})
12	0.59	0.63	7	1.30	0.57
20	0.62	0.62	18	1.72	0.53
4	1.10	0.52	19	1.73	0.55

temperature = 490°C temperature = 469°C

run no.	t_c (sec)	k_1 (sec^{-1})	run no.	t_c (sec)	k_1 (sec^{-1})
28	1.47	0.066	30	1.72	0.027
36	5.05	0.067	32	5.55	0.028
			37	6.60	0.028

on the rate constants adjusted to 18 mm total pressure.

In the course of the investigation of dimethyl cadmium further evidence has been obtained which indicates that the reaction

$$CH_3 + C_6H_5CH_2 = C_6H_5CH_2CH_3 \qquad (6)$$

can be neglected as a possible means by which methyl radicals are removed from the system. The evidence consits of two facts, neither of which is compatible with reaction 6 being important in this system. First, the rate constants calculated for reaction 1 are independant of the rate of release of methyl radicals into the system; this has been checked by varying the concentration of alkyl by a factor of 35 (table 3). Second, in a run carried out at 595°C with a contact time of 5.6 seconds methane and ethane were produced in quantities corresponding to 98.7% decomposition of the alkyl. Furthermore, the A factor of reaction 6 may be calculated from the results of Szwarc for the thermal decomposition of ethyl benzene (26) and reasonable estimates of the entropies of the methyl and benzyl radicals and of ethyl benzene.

Trotman-Dickenson has estimated the entropy of the methyl radical at 25°C to be 45.5 eu (27). The entropy of the benzyl radical is assumed to be identical to that of toluene, due allowance (1.4 eu) being made for the unpaired electron in the radical. The entropies of toluene (76.42 eu) and ethyl benzene (86.15 eu) at 25°C were taken from Selected Values of Physical and Thermodynamic Properties (28). The entropy change of the reaction

$$C_6H_5CH_2 - CH_3 = CH_3 + C_6H_5CH_2 \qquad (-6)$$

at 25°C is therefore

$$\Delta S = 45.5 + 77.8 - 86.2$$
$$= 37.1 \text{ eu.}$$

The entropy values used are for one mole of the substance at 760 mm and 25°C.

The entropy change in concentration units (ΔS_c) of moles cm^{-3} is then

$$\Delta S_c = 37.1 - 20.1 = 17 \text{ eu}$$

The experimental A factor of the decomposition of ethyl benzene is given by Szwarc as $10^{13.0}$. The frequency factor for the combination of methyl radicals with benzyl radicals (A_6) may therefore be calculated from the expression

$$\log \left(A_{-6}/A_6\right) = \frac{\Delta S_c}{2.303\ R}$$

The use of this expression implies that reactions in flow systems are studied at constant pressure rather than at constant volume. If A_{-6}/A_6 is independent of temperature

$$\log A_6 = 13.0 - 3.73 = 9.27$$

This result is accurate to an order of magnitude for all temperatures used. If the calculation is made using entropies at 1000°A the value obtained is

$$\log A_6 = 8.85$$

Therefore the maximum value of k_6 is approximately 10^9 $mole^{-1}cm^3sec^{-1}$. Hence under the experimental conditions used reaction 6 cannot compete successfully with reactions 3 or 4.

The Arrhenius plot of the rate constants is given in figure 4. The straight line corresponds to

$$\log_{10} k_1/sec^{-1} = 11.9 - (45800 \pm 1000/2.303\ RT)$$

for cadmium dimethyl at 18 mm pressure.

C. Dimethyl Zinc

The complete experimental results are given in table 5. Their satisfactory interpretation depends upon the selection of the correct mechanism for the system.

It was expected that the mechanism for the decomposition of dimethyl

zinc would be very similar to that for the decomposition of dimethyl mercury and dimethyl cadmium:

$$Zn(CH_3)_2 = ZnCH_3 + CH_3 \quad (1)$$

$$ZnCH_3 = Zn + CH_3 \quad (2)$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \quad (3)$$

$$2\ CH_3 = C_2H_6 \quad (4)$$

$$2\ C_6H_5CH_2 = (C_6H_5CH_2)_2 \quad (5)$$

The XCH_3 radical formed by the other two alkyls decomposed so rapidly that it could be assumed that two methyl radicals were formed from each molecule that underwent reaction 1. However, it was soon found that this assumption was not tenable for dimethyl zinc. It appeared that even as high as 670°C reaction 2 did not occur to any great extent under the experimental conditions used. Only above 730°C was reaction 2 an important source of methyl radicals. The decompositions of dimethyl zinc and methyl zinc were therefore treated as successive reactions. At the highest temperatures all the dimethyl zinc was converted to methyl zinc in a very small fraction of the contact time. The rate of decomposition of methyl zinc could then be readily determined; the only interference came from the decomposition of the toluene carrier. At low temperatures the decomposition of methyl zinc was negligible and the decomposition of dimethyl zinc could be simply treated as a unimolecular reaction yielding one methyl radical. At intermediate temperatures the appropriate treatment for successive reactions of comparable rate had to be applied. The detailed methods of calculating were as follows.

(a) <u>The High Temperature Range</u> (k_2)

The total amount of methane produced in a run was found by analysis of the methane-hydrogen fraction. In order to obtain the net amount from the decomposition of the alkyl a correction had to be applied for the methane

TABLE 5 - THE PYROLYSIS OF DIMETHYL ZINC

run no.	temp. (°C)	toluene (mm)	t (sec)	CH_4	C_2H_6	H_2	$ZnMe_2$	k_1 (sec^{-1})
				10^{-4} mole				
1	597	22.4	6.74	14.40	0.73	-	18.2	0.246
2	597	12.5	9.00	11.70	1.25	-	17.1	0.179
3	597	7.2	10.85	9.46	2.41	-	17.3	0.139
4	597	28.5	4.91	13.50	0.40	-	17.4	0.280
5	597	16.0	4.73	11.00	0.57	-	17.9	0.218
6	597	9.8	5.66	9.34	0.94	-	16.8	0.187
7	597	26.5	3.53	10.70	0.27	-	17.1	0.273
8	597	6.6	6.30	8.58	1.50	-	18.0	0.154
9	597	16.5	1.13	3.72	0.04	-	18.3	0.208
11	597	5.8	1.50	4.04	0.13	-	18.2	0.170
12	597	4.6	1.44	2.76	0.19	-	19.1	0.146
13	597	10.0	1.17	3.60	0.13	-	18.4	0.190
14	597	16.5	0.98	12.36	0.61	-	72.0	0.212
15	597	16.5	0.97	6.32	0.16	-	35.5	0.214
17	648	16.6	0.94	12.00	0.20	0.10	19.0	0.988
18	672	16.8	0.89	16.60	0.28	0.15	20.0	1.94
19	672	16.3	0.90	16.20	0.31	0.15	19.6	1.92
20	672	5.8	1.11	13.85	0.65	0.10	19.5	1.29
21	672	5.3	1.15	13.60	0.70	0.10	19.2	1.26
22	672	16.4	0.91	15.80	0.25	0.15	18.1	2.10
23	701	16.6	0.86	18.20	0.30	0.30	18.5	4.12
24	701	16.5	0.86	17.10	0.31	0.30	17.7	3.75
25	701	16.0	0.87	18.10	0.37	0.30	18.5	4.12
29	624	16.0	0.93	4.90	0.05	-	13.9	0.47
30 a	672	16.3	0.75	14.00	0.26	0.10	18.4	1.90
31 a	624	16.2	0.84	7.30	0.28	-	21.1	0.517

Table 5 (continued)

run no.	temp. (°C)	toluene (mm)	t (sec)	CH_4	C_2H_6	H_2	$ZnMe_2$	k_1 (sec^{-1})
				10^{-4} mole				
32 a	672	16.1	0.78	14.50	0.32	0.10	18.9	1.89
33 a	701	16.1	0.74	17.40	0.39	0.20	18.8	3.40
40	658	16.3	1.06	12.55	0.29	0.15	17.0	1.27
41	658	16.3	0.99	12.10	0.21	0.15	17.0	1.27
42	573	16.0	1.10	1.18	0.01	-	12.9	0.090
43	700	16.6	0.90	17.30	0.23	0.30	17.1	3.60
								k_2 (sec^{-1})
26	730	16.6	1.01	19.9	0.44	0.60	18.2	0.147
27	730	16.3	1.04	19.9	0.47	0.60	18.7	0.122
34a	755	16.8	0.72	21.6	0.56	3.00	19.7	0.200
35 a	793	16.8	1.28	25.8	1.40	4.10	19.4	0.420
36 a	793	16.4	0.73	23.3	0.90	6.90	19.1	0.450
37 a	825	16.0	0.71	25.3	1.02	11.90	18.7	0.670
38	827	16.0	0.90	24.7	0.97	11.90	17.8	0.590
39	762	16.3	0.88	19.5	0.49	2.70	16.7	0.250
44	758	16.1	0.89	19.1	0.60	2.20	17.2	0.210
45 c	783	15.8	0.89	27.8	1.52	4.70	20.6	0.320
47	783	6.3	0.60	20.4	0.80	2.60	17.7	0.146
48 b	783	9.5	1.27	22.5	1.03	3.20	17.2	0.196
49	783	15.8	0.95	25.8	0.77	5.70	16.9	0.303
50	783	16.2	0.97	7.96	0.31	3.04	5.7	0.350
51 c	825	16.2	0.91	16.85	0.71	8.95	11.2	0.660

a runs in packed reaction vessels
b complete analysis (10^{-4} mole) CH_4: 22.5; C_2H_6: 0.31; H_2: 3.20; C_2H_4: 0.72;
c run 20 min;
t is the contact time.

The quantities given in the table are total (uncorrected) amounts of products.

produced by the decomposition of the toluene carrier. An experiment on the pyrolysis of pure toluene at 783°C yielded a value of k in good agreement with that calculated from Szwarc's expression for the rate constant (12)

$$\log_{10} k/\text{sec}^{-1} = 13.3-(77500/2.303\ RT).$$

In arriving at this expression Szwarc assumed the ratio of hydrogen to methane in the products of the decomposition was exactly 1.5:1. The ratio found in the present experiment confirmed this value. Hence the correction for the methane produced by the decomposition of toluene was based on a hydrogen methane ratio of 1.5:1 and the Arrhenius parameters of Szwarc. The percentage decomposition of methyl zinc was then equal to

$$\frac{(\text{corrected moles of methane} + 2 \times \text{moles of ethane})100}{\text{moles of dimethyl zinc used}} - 100.$$

First order rate constants were calculated from these percentage decompositions. This calculation implies that the dimethyl zinc is converted to methyl zinc immediately it enters the reaction zone.

(b) The Low Temperature Range (k_1)

The value of the rate constants, k_1, was calculated from the usual formula for successive unimolecular reactions:

$$CH_4 + 2C_2H_6 = Zn(CH_3)_2 \text{ used } \left\{ 2-\frac{k_1}{k_1-k_2} \exp(-k_1t) + \exp(-k_2t) \right\}$$

The equation was solved using successive approximations of k_1. The first value of k_1 used was that calculated from the extrapolated Arrhenius curve for results obtained at low temperatures and short contact times. Usually only one or two approximations were required to obtain substantial agreement between $(CH_4 + 2C_2H_6)_{calc.}$ and $(CH_4 + 2C_2H_6)_{obs.}$. The value of k_2 was calculated from the Arrhenius parameters for the decomposition of methyl zinc determined from experiments in the high temperature range. The values of k_2 thus obtained may be considerably in error. However,

the values of k_1 obtained were not very sensitive to the value selected for k_2 as the percentage decomposition of methyl zinc was of the order of 1% at 597°C, 3% at 648°C, and 6% at 710°C.

The method of calculation depends upon the assumption that the methyl zinc radicals which do not decompose do not react in any other way while within the reaction zone. Presumably they eventually form stable saturated molecules in some cooler portion of the apparatus.

The rate constants k_1 and k_2 were found to be markedly dependent upon the total pressure in the reaction system, as is shown in figure 5. This was not due to any heterogeneous reaction. Packing the vessel with silica tubing so as to increase the surface to volume ratio by a factor of five had no appreciable effect on the rates, as is shown in figure 6. The values of the rate constants given in table 5 are the experimental values for the pressures indicated. The values given in tables 6, 7 and 8 have been corrected to a selected pressure.

Tables 6 and 7 show that at a fixed temperature and total pressure the rate constants for reaction 1 and reaction 2 are independent of large changes in the substrate concentration.

A systematic study of the effect of contact time on k_2 has not been made. However, runs 35 and 36 indicate that an increase in the contact time by a factor of 1.75 causes no appreciable change in this rate constant. In the lower temperature region the effect of contact time on k_1 has been extensively investigated. Table 8 shows the results of a series of runs at 597°C. At 16 mm total pressure an increase in contact time from 0.98 sec to 6.74 sec, a factor of 6.9, does not affect the value of k_1. Similarly at 6.6 mm total pressure the rate constant is unaffected by an increase in contact time from 1.44 sec to 6.30 sec. Even the use of contact times as long as 10.85 seconds does not seriously affect the rate constant.

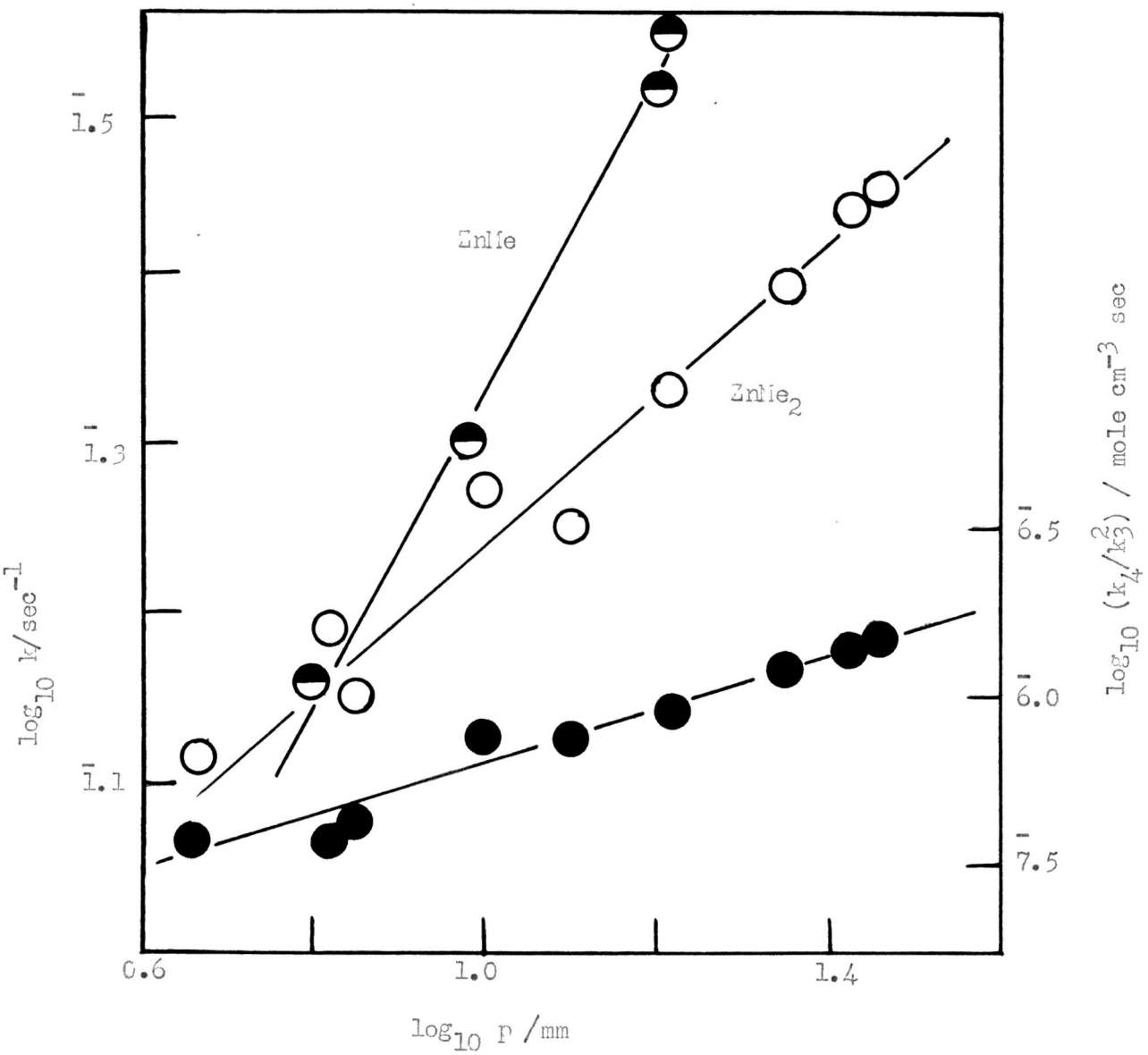

FIGURE 5 The variation of the rate constants with pressure. Open circles: the decomposition of dimethyl zinc (597°C); ◒ the decomposition of methyl zinc (783°C); full circles: k_4/k_3^2 (597°C).

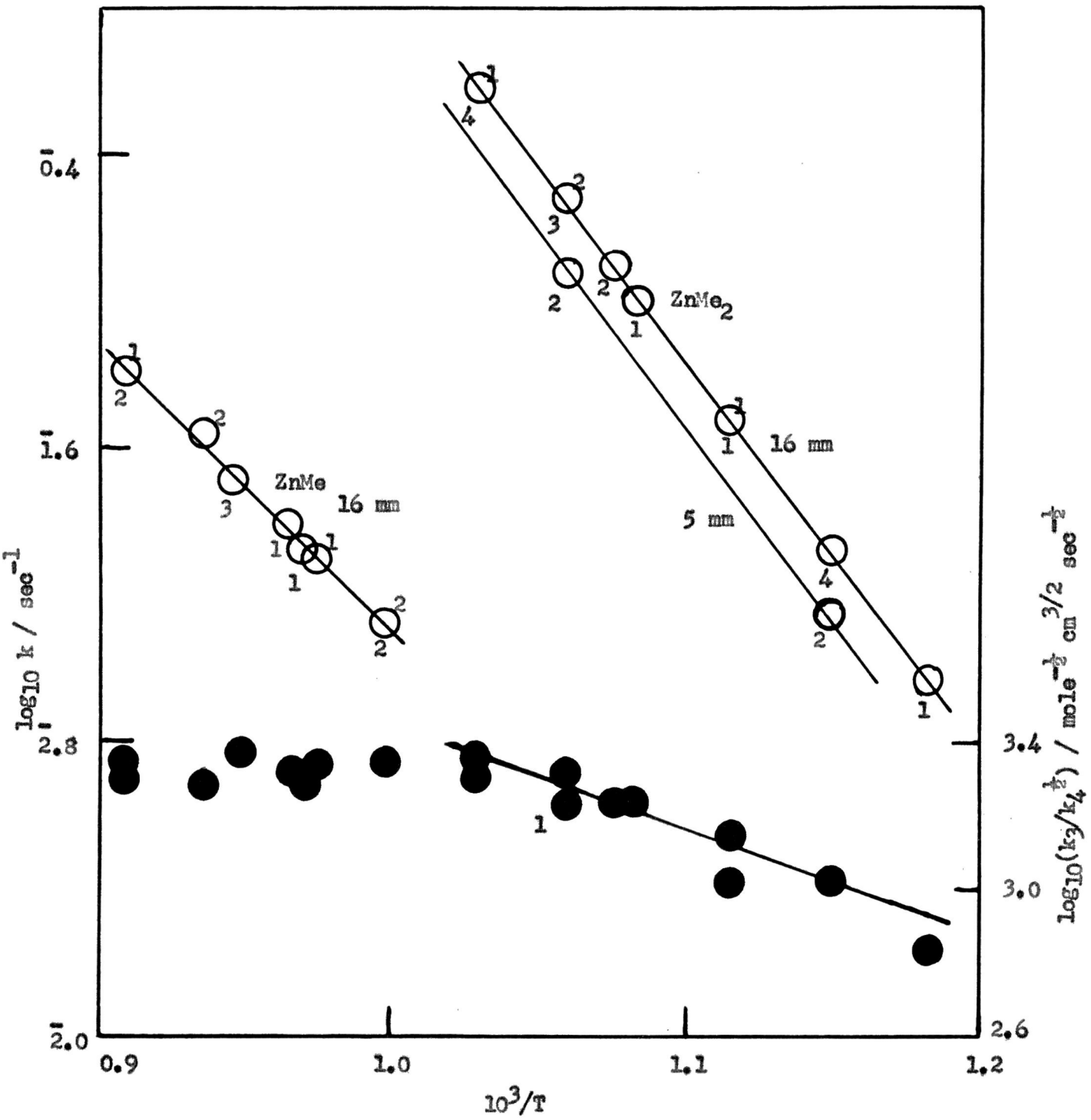

FIGURE 6 Arrhenius plots for the decomposition of dimethyl and methyl zinc and the reaction of methyl radicals with toluene. The figures besides the points indicate the number of runs averaged to obtain the value plotted; superscripts, runs in a packed vessel; subscripts, runs in an unpacked vessel; full circles: $k_3/k_4^{\frac{1}{2}}$.

As a check on the importance of reaction 6

$$C_6H_5CH_2 + CH_3 = C_6H_5C_2H_5 \qquad (6)$$

a run was carried out at 812°C with a contact time of 6 seconds. From the quantities of methane (corrected) and ethane formed it was deduced that 98% of the possible number of methyl radicals were released. The proportion that may be derived from the rate constants k_1 and k_2 under these conditions is 98.5%. This is direct evidence that reaction 6 is unimportant.

The rather large quantities of hydrogen found at the higher temperatures were not all the products of the unimolecular decomposition of toluene. It is possible that they were formed by the decomposition of benzyl radicals and of dibenzyl. A small quantity is probably formed by the decomposition of ethane into ethylene and hydrogen. For this reason the ethylene was treated as ethane in calculating the rate constants. If this is unjustifiable the error introduced is small because the C_2 fraction is much smaller than the amount of methane.

The Arrhenius plots of the rate constants, k_1 and k_2, are given in figure 6. The rate constants used to make up the plots were all determined in the region of the pressure indicated and empirically corrected to this value. The straight lines correspond to:

$$\log_{10} k_1/\text{sec}^{-1} = 11.25 - (47200 \pm 1000/2.303RT)$$

$$\text{and} \quad \log_{10} k_2/\text{sec}^{-1} = 6.86 - (35000 / 2.303RT)$$

at 16 mm total pressure. No useful estimate of the probable error in the activation energy of reaction 2 can be made (3 to 5 kcal mole^{-1} is probably a fair figure). At 5 mm total pressure:

$$\log_{10} k_1/\text{sec}^{-1} = 11.03 - (47300/2.303RT)$$

The value of k_1 and A_1 at infinite pressure could only be determined from experiments over a far wider range of pressures than could be reached with the

TABLE 6 - THE EFFECT OF DIMETHYL ZINC CONCENTRATION ON THE VELOCITY CONSTANT (k_1)

temperature = 597°C pressure = 16.5 mm

run no.	t_c (sec)	$Zn(CH_3)_2$ (10^{-9} mole cm^{-3})	k_1 (sec^{-1})
9	1.13	7.43	0.208
15	0.97	12.38	0.214
14	0.98	25.30	0.212

TABLE 7 - THE EFFECT OF METHYL ZINC CONCENTRATION ON THE VELOCITY CONSTANT (k_2)

temperature = 783°C pressure = 16.0 mm

run no.	t_c (sec)	$ZnCH_3$ (10^{-9} mole cm^{-3})	k_2 (sec^{-1})
50	0.97	1.98	0.35
49	0.95	5.75	0.31
45	0.89	9.85	0.32

TABLE 8 - THE EFFECT OF CONTACT TIME ON THE VELOCITY CONSTANT (k_1)

temperature = 597°C

pressure = 16.5 mm			pressure = 6.6 mm		
run no.	t_c (sec)	k_1 (sec^{-1})	run no.	t_c (sec)	k_1 (sec^{-1})
14	0.98	0.212	12	1.44	0.158
5	4.73	0.218	8	6.30	0.154
1	6.74	0.206	3	10.85	0.135

apparatus used. Reaction 2 was apparently studied in its "second order" region; that is k_2 is directly proportional to the total pressure as is shown in figure 5. If toluene and methyl zinc are equally effective in energy transfer, then the rate constant may be written

$$\log_{10} k_2 \text{ / mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} = 13.36 - (35000/2.303RT).$$

D. Trimethyl Bismuth

The complete experimental results are given in table 9. They may be satisfactorily interpreted by the following reaction scheme:

$Bi(CH_3)_3$	=	$Bi(CH_3)_2 + CH_3$	(1)
$Bi(CH_3)_2$	=	$Bi\ CH_3 + CH_3$	(2)
$BiCH_3$	=	$Bi + CH_3$	(6)
$CH_3 + C_6H_5CH_3$	=	$CH_4 + C_6H_5CH_2$	(3)
$2\ CH_3$	=	C_2H_6	(4)
$2\ C_6H_5CH_2$	=	$(C_6H_5CH_2)_2$	(5)

Runs B, C, E and A' were all carried out at high temperatures, where the observed decomposition is close to 100% as measured both by the volume of methane and ethane produced (% decomposition = ($\frac{1}{3}$ moles methane + $\frac{2}{3}$ moles ethane) 100 ÷ moles trimethyl bismuth used) and by the quantity of undecomposed alkyl. It is thus established that three methyl radicals are released each time a molecule undergoes reaction 1. The analysis of the gaseous products of runs B and C shows that the amounts of hydrogen, ethylene, and C_3 and C_4 hydrocarbons formed are negligible. The conclusion that the quantity of gas produced is a satisfactory measure of the progress of the decomposition is further supported by run B'.

The rate constants for a number of runs with different contact times are given in table 10. The rate constant for run 5 has been adjusted to 382°C, the temperature of runs 32 and 30. These results show that the calculated rate

TABLE 9 - THE PYROLYSIS OF TRIMETHYL BISMUTH

run no.	temp. (°C)	toluene (mm)	t_c (sec)	CH_4	C_2H_6	$BiMe_3$	k_1 (sec^{-1})
				10^{-4} mole			
E a	584	16.1	1.16	7.22	18.70	14.90	-
C ac	548	16.1	1.26	7.10	18.20	14.50	-
B ad	526	16.1	1.29	7.95	17.50	14.40	-
1 a	430	16.1	1.40	9.70	14.80	13.80	2.12
A'	429	16.1	3.25	7.45	14.30	12.05	
C' e	409	16.1	3.78	6.12	10.90	9.25	.820
16	409	16.1	1.67	7.47	11.20	13.60	.795
4 a	409	16.1	1.42	6.15	9.26	12.10	.800
18	403	16.1	1.75	4.02	4.02	6.20	.597
17	402	16.1	1.78	6.10	8.85	12.20	.578
14	401	16.1	1.77	5.28	8.37	11.80	.570
15	400	16.1	1.77	6.18	9.62	14.10	.518
B'b	395	16.1	3.86	5.13	8.65	9.40	.410
12	392	16.1	1.77	4.72	7.77	14.10	.368
13	392	6.3	3.14	2.06	5.54	6.60	.347
27	392	16.1	1.80	4.36	5.50	10.70	.364
11	390	10.6	2.18	3.29	6.30	10.40	.327
10	389	11.0	2.12	3.04	5.35	9.70	.302
8	388	16.1	1.72	4.72	6.15	14.20	.296
3 a	387	16.1	1.54	3.45	5.15	12.80	.280
9	387	6.3	2.94	0.85	0.80	1.60	.244
33	387	16.1	0.69	2.32	1.83	11.20	.278
6	386	16.1	1.77	2.74	2.34	6.60	.264
7	386	16.1	1.71	1.44	0.77	2.73	.264
5	383	16.1	1.76	3.41	4.34	12.40	.222

Table 9 (continued)

run no.	temp. (°C)	toluene (mm)	t_c (sec)	CH_4	C_2H_6	$BiMe_3$	k_1 (sec^{-1})
				10^{-4} mole			
30	382	25.0	1.53	3.18	2.24	9.1	.217
31	382	6.3	3.14	2.78	8.55	14.20	.200
32	382	16.1	4.04	3.94	5.86	8.95	.217
28	380	16.1	1.79	2.86	3.18	10.50	.193
19	380	15.9	1.88	3.16	4.80	13.80	.196
20	378	16.1	1.87	3.14	4.25	13.90	.175
29	374	16.1	1.83	2.54	2.75	11.70	.142
2 a	369	16.1	1.56	1.80	2.41	13.50	.114
22	367	16.1	1.95	1.90	2.10	11.70	.0972
21	367	16.1	1.98	2.00	2.44	13.60	.0932
23	355	16.1	2.00	1.10	0.97	10.50	.0500
24	355	16.1	1.91	1.10	0.97	11.10	.0499
25	354	16.1	1.93	1.05	0.92	11.30	.0461
26	346	16.1	1.94	0.77	0.59	11.20	.0306

Duration of all runs 30 min.

a runs in packed reaction vessels

b colorimetric estimation of the undecomposed alkyl yields $k_1/sec^{-1} = 0.405$

c no C_3 or C_4 gases detectable

d $\sim 20\mu$ mole ethylene, $\sim 7\mu$ mole hydrogen

e k_1/sec^{-1} based on undecomposed alkyl identical to k_1/sec^{-1} calculated from analysis of the gaseous products

constant is independent of the contact time.

The results given in table 11 show that k_1 is independent of the concentration of trimethyl bismuth. The rate constant for run 18 has been adjusted to the indicated temperature.

For the runs shown in table 12 the reaction vessel was packed in the usual way thus increasing the surface to volume ratio by a factor of five. The rate constants for runs 2 and 3 have been adjusted to 367°C and 388°C respectively so that a direct comparison with runs 22 and 8 may be made. Over the temperature range studied k_1 is independent of the surface to volume ratio.

The two series of runs shown in table 13 indicate that above a total pressure of about 10 mm k_1 is independent of the total pressure in the reaction system. Runs 12, 27 and 13 were carried out at 392°C. The rate constants for runs 10 and 11 have been adjusted to this temperature. Similarly the rate constant for run 5 has been adjusted to 382°C.

The experiments may therefore be accepted as a measure of the rate of fission of the $(CH_3)_2$ Bi-CH_3 bond. The activation energy calculated from the slope of the line in figure 7, whose equation is

$$\log_{10} k_1/sec^{-1} = 13.9 - (43600 \pm 400/2.303RT),$$

is then equal to the strength of the bond.

E. Trimethyl Antimony

The complete experimental results are given in table 14. These results show that the pyrolysis of trimethyl antimony is homogeneous (runs 32, 49), but otherwise the decomposition is not simple. Even at the highest temperatures the yield of methane and ethane falls far below the amount that would be expected if all the alkyl decomposed. For instance, in run 29, only 73.6% of the possible gases were produced, but amounts of antimony corresponding to 98.5% decomposition were deposited in the reaction vessel. The discrepancy is not due to the formation

TABLE 10 - THE EFFECT OF CONTACT TIME ON THE VELOCITY CONSTANT (k_1) FOR TRIMETHYL BISMUTH

temperature = 382°C

run no.	t_c (sec)	k_1 (sec^{-1})
30	1.53	0.217
5	1.76	0.216
32	4.04	0.217

temperature = 387°C

run no.	t_c (sec)	k_1 (sec^{-1})
33	0.69	0.278
3	1.54	0.280

TABLE 11 - THE EFFECT OF TRIMETHYL BISMUTH CONCENTRATION ON THE VELOCITY CONSTANT (k_1)

temperature = 386°C

run no.	$Bi(CH_3)_3$ (10^{-9} moles cm^{-3})	k_1 (sec^{-1})
7	1.87	0.264
6	4.70	0.264
3	9.70	0.266

temperature = 402°C

run no.	$Bi(CH_3)_3$ (10^{-9} mole cm^{-3})	k_1 (sec^{-1})
18	4.30	.580
17	8.56	.578

TABLE 12 - THE EFFECT OF SURFACE TO VOLUME RATIO ON THE VELOCITY CONSTANT (k_1) FOR TRIMETHYL BISMUTH

temperature = 408.5°C

run no.	k (sec^{-1})
4a	0.800
16	0.795

temperature = 388°C

run no.	k (sec^{-1})
3a	0.295
8	0.296

temperature = 367°C

run no.	k (sec^{-1})
2a	0.103
22	0.097

a - runs in packed reaction vessel

TABLE 13 - THE EFFECT OF TOTAL PRESSURE ON THE VELOCITY CONSTANT (k_1) FOR TRIMETHYL BISMUTH

temperature = 392°C

run no.	pressure (mm)	k_1 (sec^{-1})
13	6.28	0.347
11	10.6	0.362
10	11.0	0.361
27	16.1	0.364
12	16.1	0.368

temperature = 382°C

run no.	pressure (mm)	k_1 (sec^{-1})
31	6.25	0.200
32	16.10	0.217
5	16.10	0.216
30	25.0	0.217

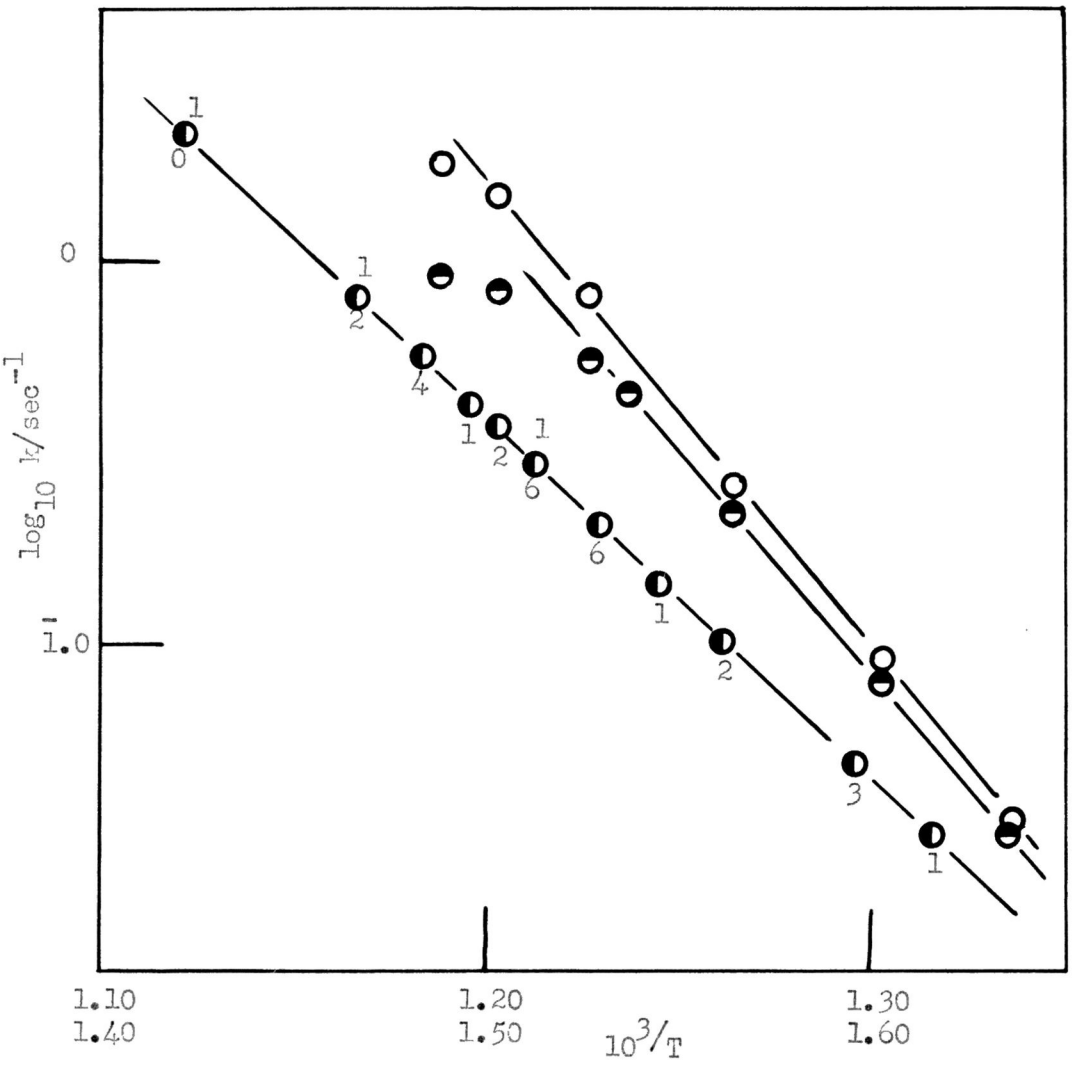

FIGURE 7 Arrhenius plots for the decomposition of trimethyl bismuth and trimethyl antimony.

○ Trimethyl antimony, k_m's based on metal analysis

◒ Trimethyl antimony, k_g's based on gas analysis

◐ Trimethyl bismuth, the figures beside the points indicate the number of runs averaged to obtain the value plotted; superscripts, runs in packed vessel; subscripts, runs in unpacked vessel.

The upper temperature scale refers to the runs with trimethyl antimony.

TABLE 14 - THE PYROLYSIS OF TRIMETHYL ANTIMONY

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	$SbMe_3$	k_g (sec^{-1})	k_m (sec^{-1})
				10^{-4} mole				
1	664	17.2	1.43	15.9	4.92	12.3	0.835	
2	625	17.2	1.50	13.8	3.28	9.85	0.770	
27 c	605	16.5	0.56	12.9	2.24	8.28	2.14	
28	603	16.5	1.38	21.6	6.25	16.0	0.905	
29	603	16.5	1.33	20.7	6.40	15.2	1.00	3.16
3	587	17.3	1.56	22.0	5.50	15.8	0.770	
26 d	582	16.5	0.57	13.2	2.07	8.09	2.18	
36	569	16.5	1.43	22.2	4.90	14.9	0.885	1.78
35	558	16.5	1.44	20.7	4.00	13.9	0.814	1.47
25 c	557	16.5	0.59	13.3	2.12	11.1	1.26	
19	540	16.5	1.64	3.33	0.164	1.74	0.752	
39	543	16.5	1.52	6.10	0.490	3.60	0.700	1.16
37	541	16.5	1.47	11.2	1.47	7.80	0.612	0.890
18	540	16.5	1.60	11.4	1.61	8.03	0.580	
31	542	16.5	1.45	17,3	3.45	14.8	0.545	
40 c	543	16.5	1.49	17.0	3.30	14.4	0.532	0.810
17	540	16.5	1.57	18.0	3.86	15.5	0.513	
4	541	16.5	1.66	18.5	3.94	15.6	0.501	
38 c	542	16.5	1.48	17.1	5.10	18.3	0.467	0.690
16 c	541	17.7	1.55	20.3	6.34	21.8	0.455	
30	536	16.5	1.43	15.4	2.94	14.9	0.447	
12	518	17.0	1.66	4.15	0.315	4.13	0.295	
43	518	16.5	1.56	4.65	0.425	5.90	0.275	
41	519	16.5	1.55	6.11	0.670	7.55	0.258	0.332

Table 14 (continued)

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	$SbMe_3$	k_{g-1} (sec^{-1})	k_{m-1} (sec^{-1})
				10^{-4} mole				
13	518	17.0	1.58	7.08	0.806	8.65	0.258	
24 c	516	16.5	0.63	5.02	0.735	17.4	0.210	
48	518	16.5	0.55	5.86	0.920	21.2	0.232	0.291
49 a	518	16.5	1.29	8.06	1.28	14.1	0.220	0.260
32	517	16.5	1.49	8.84	1.42	14.4	0.210	0.248
5	518	16.3	1.59	9.45	1.59	15.1	0.205	
47	518	6.3	2.59	5.02	2.20	11.6	0.121	0.142
44	516	16.5	1.63	12.0	2.78	24.6	0.164	0.182
46 b	519	29.0	1.22	19.7	2.99	33.2	0.245	0.282
42	519	16.5	1.53	13.4	3.28	27.9	0.179	0.215
14 e	518	17.0	1.67	7.91	1.89	16.7	0.160	
23	518	16.5	3.52	12.7	3.16	14.8	0.158	
15	518	17.0	1.56	17.0	4.98	40.7	0.158	
11	495	17.6	1.71	4.15	0.315	4.13	0.101	
9	495	17.5	1.79	2.94	0.264	7.85	0.089	
6	495	17.4	1.79	4.24	0.540	14.7	0.072	
33	496	15.5	1.59	4.40	0.600	17.3	0.073	0.083
10	495	17.5	1.78	6.17	1.08	25.8	0.063	
20	475	16.5	1.80	0.871	0.039	4.55	0.040	
21	475	16.5	1.79	1.43	0.130	9.60	0.033	
34	475	16.5	1.58	1.72	0.145	14.4	0.030	0.034
22	477	16.5	1.78	2.08	0.197	15.0	0.031	
7	475	17.6	1.82	1.99	0.192	16.6	0.026	
8	475	17.5	1.82	3.22	0.506	36.7	0.020	

Unless otherwise indicated duration of runs 30 min.

a run in packed reaction vessel
b ~20μ mole ethylene formed.
c Duration of runs 20 min.
d Duration of run 15 min.
e Duration of run 17 min.

of substances such as propane or butane for negligible quantities of these gases are produced. Nevertheless, for the purpose of further discussion it will be convenient to assume that each trimethyl antimony molecule that undergoes reaction yields three methyl radicals and an atom of antimony. The first order rate constants given in the table derived from measurements of the gases, k_g, and the metal, k_m, are based on this assumption.

Comparison of the rate constants for runs 23 (t_c = 3.52 sec), 24 (t_c = 0.63 sec), and 48 (t_c = 0.55 sec) with runs carried out using the same alkyl concentration but intermediate contact times shows that the rate constant is not affected by a six-fold increase in contact time.

In figure 8 the logarithm of the rate constant is plotted as a function of the total pressure in the system. The experimental points are based on the rate constants for runs 44, 46 and 47 corrected to 518°C and an alkyl concentration 14.4×10^{-9} mole cm^{-3}. It can be seen from this figure that k_m and k_g are dependent upon the total pressure in the reaction system. The dependence is very similar to that shown by the dimethyl derivatives of the group II metals as can be seen from the following figures for the rate constants at 6 and 24 mm. pressure of toluene.

Alkyl	$Zn(CH_3)_2$	$Cd(CH_3)_2$	$Hg(CH_3)_2$	$Sb(CH_3)_3$
Temp. °C	597	552	543	518
k_{24}/k_6	2.0	2.0	1.9	2.1

This dependence is presumably due to the limiting effect of the rate of energy transfer. The greater complexity of trimethyl antimony is offset by its higher A factor. Hereinafter only those runs in which the toluene pressure was close to 16.5 mm. will be considered.

The apparent loss of methyl radicals in the products which is illustrated by the figures below is most simply interpreted by supposing that a polymer of the

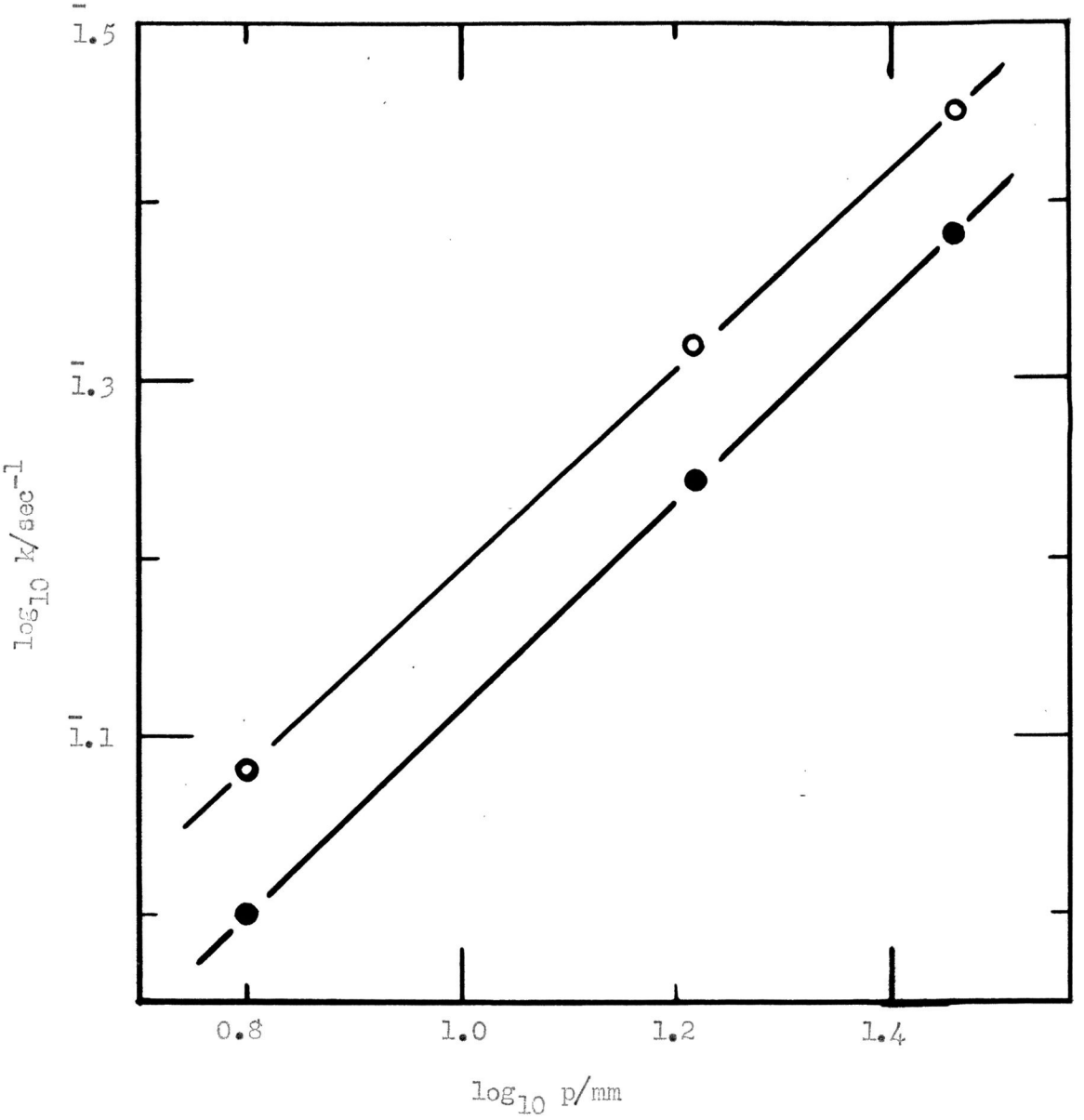

FIGURE 3 The variation of the rate constants for the decomposition of trimethyl antimony with pressure. Open circles, k_m based on metal analysis; full circles, k_g based on gas analysis. Temperature 518°C.

type $(SbMe)_n$ is produced

Run	29	36	37	48	32	34
Temp. °C	603	569	541	518	517	475
$\frac{\%\text{ decomposition (gas)}}{\%\text{ decomposition (metal)}}$	.75	.78	.82	.81	.87	.91

It is simplest to suppose that the polymer is formed from $SbCH_3$ radicals by a reaction of higher order than the first. This would explain the greater formation of the polymer at the higher temperatures, although the activation energy of reaction (6) is probably very low, because the radical concentration would then be highest. A tentative reaction mechanism may therefore be written as follows:-

$$Sb(CH_3)_3 = Sb(CH_3)_2 + CH_3 \quad (1)$$

$$Sb(CH_3)_2 = SbCH_3 + CH_3 \quad (2)$$

$$SbCH_3 = Sb + CH_3 \quad (5)$$

$$n\ SbCH_3 = (SbCH_3)_n \quad (6)$$

followed by the usual reactions of methyl radicals in the presence of toluene.

This mechanism does not explain the dependence of the overall rate constant, measured either by the gas produced or the metal deposited, on the initial concentration of the alkyl. The effect is illustrated in figure 9. It is difficult to see how reaction (1) could be less than first order, accordingly we must suppose that the trimethyl can be regenerated. This may be done by the disproportionation reaction (7) with low activation energy.

$$2Sb(CH_3)_2 = Sb(CH_3)_3 + SbCH_3 \quad (7)$$

At a given temperature the concentration of dimethyl antimony will be roughly proportional to a fractional power of the concentration of trimethyl antimony admitted to the system. The regeneration will probably be proportional to a power of the initial alkyl concentration higher than the first but lower than the second.

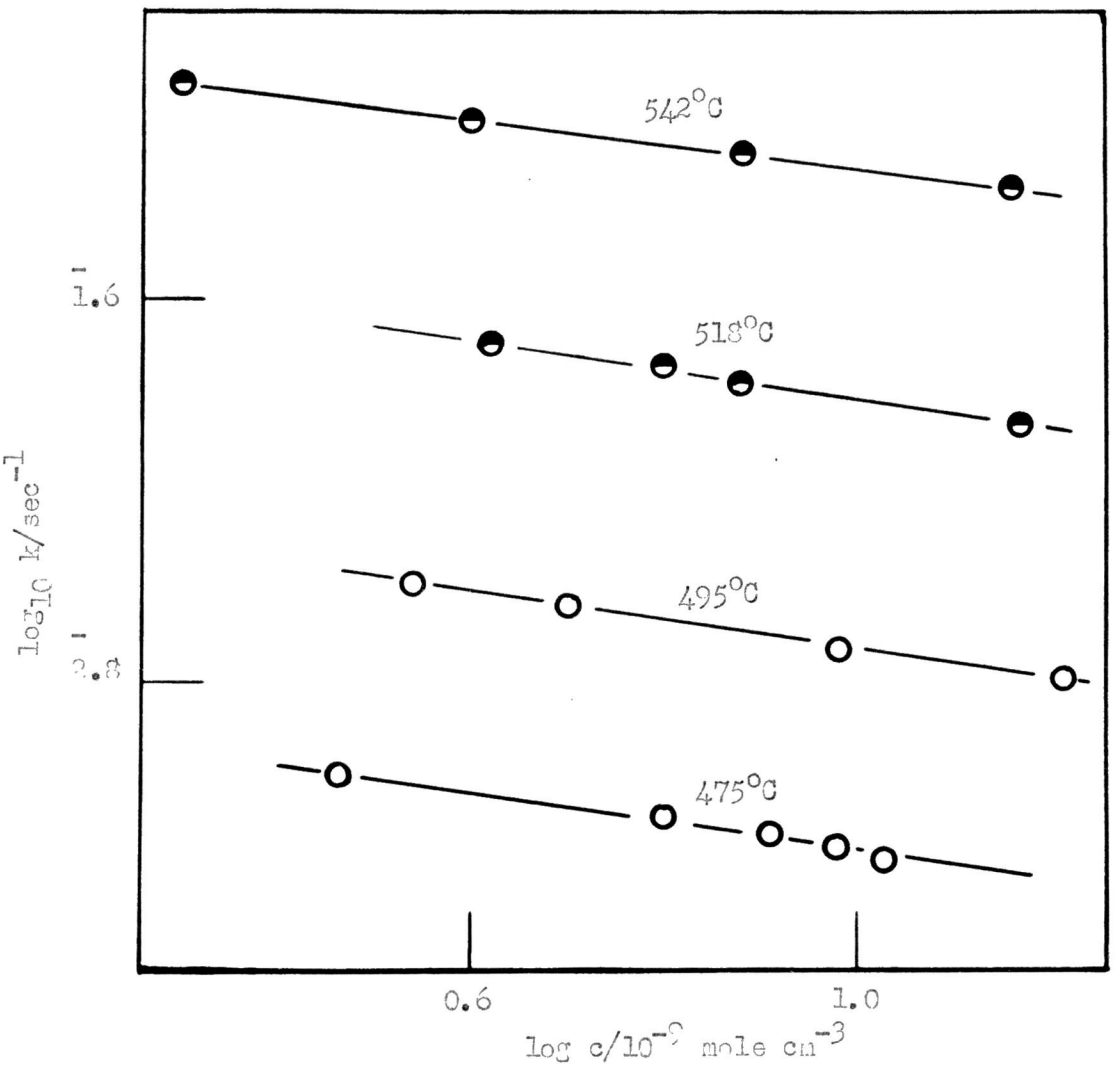

FIGURE 9 The variation of the first order rate constant for the decomposition of trimethyl antimony with alkyl concentration.

● km's based on metal analysis
○ kg's based on gas analysis

This mechanism accounts qualitatively for the observed effects. The complexities introduced by the flow conditions and the limited precision of the results makes it impractical to apply a detailed quantitative treatment.

If this mechanism is correct, values of k_1 should be obtained by measurements of the rate of metal production at zero alkyl pressure. Unfortunately the results do not lend themselves well to extrapolation to zero alkyl pressure. However, it can be seen that the plots of $\log_{10}k$ against $\log_{10}$ alkyl concentration at the different temperatures are nearly parallel. We may therefore be reasonably confident that the values of $\log k_1$ at zero alkyl concentration will run closely parallel to the values at a concentration of 7.6×10^{-9} mole cm^{-3}. The latter values have been plotted in the Arrhenius plot in figure 7. The Arrhenius plot based on gas analysis is also shown. The equations for the lines are

$$\log_{10}k_1/sec^{-1} = 15.2 - (57000/2.303\ RT) \quad \text{(metal)}$$

and

$$\log_{10}k_1/sec^{-1} = 14.1 - (53500/2.303\ RT) \quad \text{(gas)}$$

respectively.

F. Dimethyl Tin Dichloride

The complete experimental results are given in Table 15. They may be satisfactorily interpreted in terms of the following simple reaction scheme:

$$(CH_3)_2SnCl_2 = CH_3SnCl_2 + CH_3 \quad (1)$$

$$CH_3SnCl_2 = SnCl_2 + CH_3 \quad (2)$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \quad (3)$$

$$2CH_3 = C_2H_6 \quad (4)$$

$$2C_6H_5CH_2 = (C_6H_5CH_2)_2 \quad (5)$$

If the amount of ethane formed plus half the amount of methane is used as a measure of the amount of dimethyl tin dichloride decomposed, it is found that

96.8 and 98.0 per cent decomposition occurred in runs 1 and 2, respectively. This is good evidence that two methyls are released each time a molecule decomposes. Accordingly the first order rate constants were calculated on this basis.

The results of runs 10, 11 and 25 at 588° and of runs 20 and 26 at 567° show that the decomposition is homogeneous (table 16). Those of runs 3, 4, 5 and 6 show that the rate constant is independent of variations of the alkyl concentration between 1.01×10^{-9} and 4.36×10^{-9} mole cm^{-3} (table 17), and those of runs 10, 11, 23 and 24 show that it is independent of variations in the contact time from 0.66 to 3.21 sec. (table 18).

The rate constants depend slightly on the overall pressure of toluene as is shown by the following results, allobtained at 514.4°C.

Run	7	9	3	8
Toluene pressure/mm.	6.0	9.5	16.1	25.0
k/sec^{-1}	0.0795	0.0965	0.118	0.130

Accordingly, all the results obtained at about 16.1 mm. are adjusted to this pressure.

The Arrhenius plot of the rate constants for the overall decomposition at 16.1 mm. pressure is given in figure 10. The results have been fitted to the Arrhenius equation by the method of least squares. Hence

$$\log k/sec^{-1} = (13.52 \pm 0.01) - (56\,100 \pm 40/2.303\,RT)$$

The errors are most probable errors found by the normal statistical methods. The results are clearly very reproducible but it is likely that normal systematic errors which may be considerable are also involved. Unfortunately they cannot be satisfactorily estimated.

TABLE 15 - THE PYROLYSIS OF DIMETHYL TIN DICHLORIDE

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	Me_2SnCl_2	k_1 (sec^{-1})
				10^{-4} mole			
2 b	688	16.1	3.22	5.54	0.328	3.16	-
1 c	637	16.1	3.38	3.94	0.220	2.26	1.02
18	637	16.1	1.12	7.14	0.133	5.18	1.13
19	636	16.1	1.10	6.41	0.108	4.68	1.13
16	624	16.1	1.10	7.36	0.362	7.14	0.775
17	624	16.1	1.12	5.10	0.126	4.52	0.795
14	612	16.1	1.16	4.71	0.089	5.86	0.467
15	612	16.1	1.13	5.27	0.104	6.72	0.465
12	600	16.1	1.17	3.80	0.080	6.77	0.296
13	600	16.1	1.17	3.36	0.057	5.77	0.307
23	589	16.1	3.21	3.54	0.100	3.73	0.216
10	588	16.1	1.19	2.50	0.049	5.81	0.213
25 a	588	16.1	0.98	2.36	0.050	6.50	0.213
11	588	16.1	1.22	2.41	0.053	5.61	0.208
24	587	16.1	0.66	1.59	0.017	6.32	0.210
7	575	6.0	1.87	1.76	0.104	7.07	0.080
9	575	9.5	1.43	1.11	0.029	4.50	0.097
5	575	16.1	1.22	0.63	0.008	2.32	0.121
4	574	16.1	1.27	0.96	0.010	3.56	0.116
3	574	16.1	1.27	1.30	0.031	4.87	0.118
6	575	16.1	1.26	2.60	0.059	9.65	0.120
8	575	25.0	1.09	1.22	0.008	4.69	0.130
26 a	567	16.1	1.00	0.95	0.026	5.91	0.088
20	567	16.1	1.19	0.823	0.013	4.35	0.087
21	554	16.1	1.17	0.536	0.006	4.72	0.051
22	554	16.1	1.21	0.596	0.006	5.15	0.050

a runs in packed vessel; b 12 μ mole H_2; c 4 μ mole H_2

Duration of all runs 30 minutes.

TABLE 16 - THE EFFECT OF SURFACE TO VOLUME RATIO ON THE VELOCITY CONSTANT FOR DIMETHYL TIN DICHLORIDE

run no.	temp. (°C)	k (sec^{-1})	run no.	temp. (°C)	k (sec^{-1})
10	588.3	0.213	26 a	567.0	.0875
25 a	588.0	0.213	20	566.6	.0865
11	587.7	0.208			

a - runs in packed reaction vessel

TABLE 17 - THE EFFECT OF THE DIMETHYL TIN DICHLORIDE CONCENTRATION ON THE VELOCITY CONSTANT

run no.	temp. (°C)	Alkyl conc. (10^{-9} moles cm^{-3})	k (sec^{-1})
5	575.0	1.01	0.121
4	574.2	1.62	0.116
3	574.4	2.22	0.118
6	574.7	4.36	0.120

TABLE 18 - THE EFFECT OF CONTACT TIME ON THE VELOCITY CONSTANT FOR DIMETHYL TIN DICHLORIDE

run no.	temp. (°C)	t_c (sec)	k (sec^{-1})
23	589.0	3.21	0.216
11	587.7	1.22	0.208
10	588.3	1.19	0.213
24	587.0	0.66	0.210

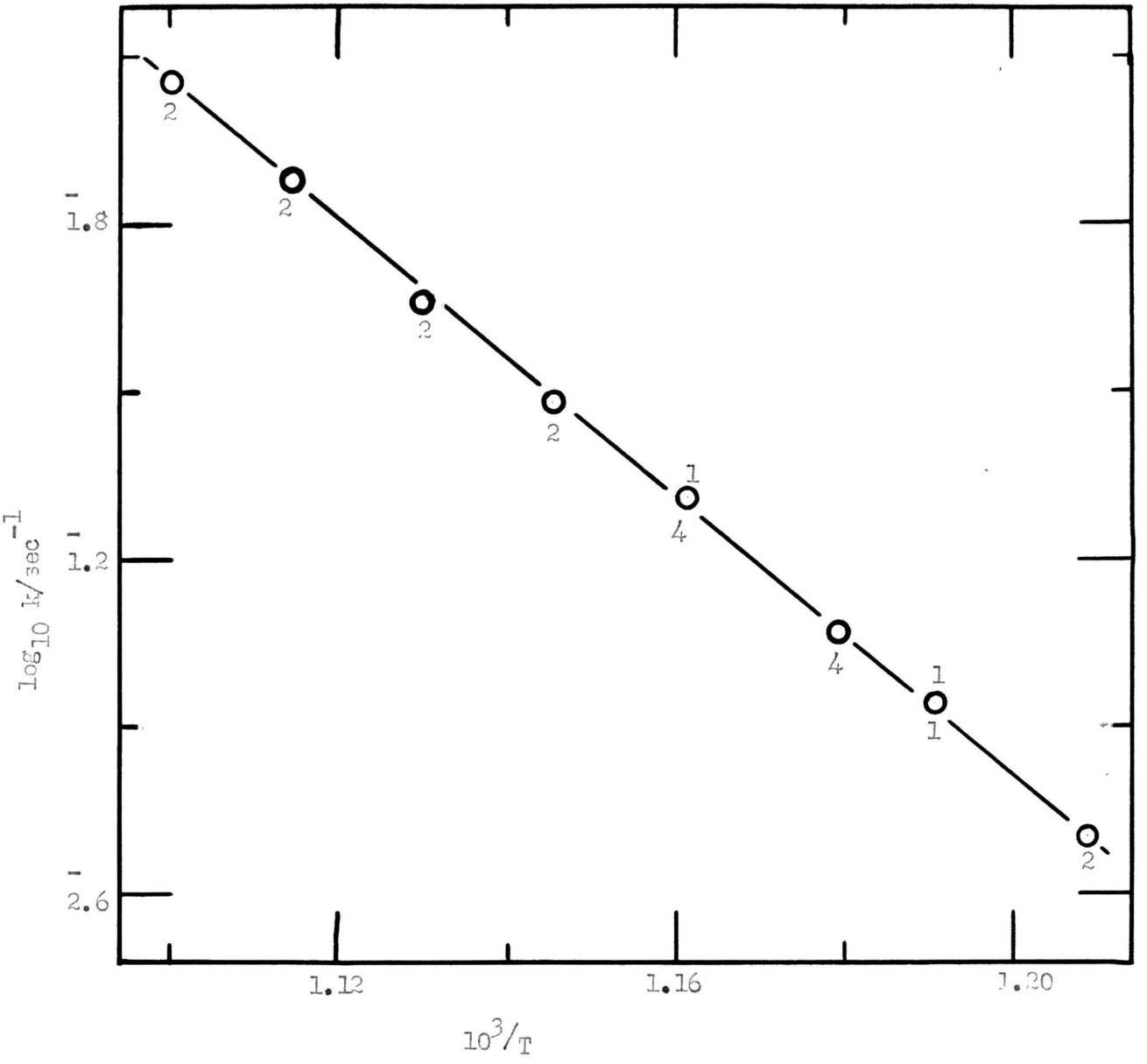

FIGURE 10 Arrhenius plot for the decomposition of dimethyl tin dichloride. The figures beside the points indicate the number of runs averaged to obtain the value plotted; superscripts, runs in packed vessel; subscripts, runs in unpacked vessel.

G. The Reaction of Methyl Radicals with Toluene

In the present work methyl radicals were produced by the thermal decomposition of metallic alkyls. Stable molecules were formed from these radicals by the reactions

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \qquad (3)$$

and

$$2\,CH_3 = C_2H_6 \qquad (4)$$

Assuming the radicals were produced at a constant rate

$$\frac{d(CH_4)}{dt} = R(CH_4) = k_3\,[CH_3]\,[C_6H_5CH_3]$$

and

$$\frac{d(C_2H_6)}{dT} = R(C_2H_6) = k_4\,[CH_3]^2$$

Hence

$$k_3/k_4^{\frac{1}{2}} = \frac{R(CH_4)}{R(C_2H_6)} \times \frac{1}{[\text{Toluene}]}$$

The values of $k_3/k_4^{\frac{1}{2}}$ in table 19 have been calculated from this expression. The rates of formation of the hydrocarbons were calculated from the total numbers of moles produced in a run. The expression that was used is

$$R(X) = \frac{(\text{total moles of X}) \times t_c}{V \times t} \text{ mole cm}^{-3}\text{ sec}^{-1}$$

where V is the volume of the reaction zone (cm^3), t is the duration of the run (sec) and t_c is the contact time. The concentration of toluene (moles cm^{-3}) was calculated on the assumption that within the reaction zone toluene behaves as an ideal gas.

The value of $k_3/k_4^{\frac{1}{2}}$ at any one temperature was found to be markedly dependent upon the total pressure in the reaction system. This is shown in figure 3 and figure 5 for values of the ratio obtained when the radical source was dimethyl mercury, dimethyl cadmium or dimethyl zinc. A similar effect was observed in the study of the other alkyls. The variation of the ratio with pressure must be ascribed to the variation in k_4 as k_3 should not depend upon

pressure under the experimental conditions used. The variation of k_4 with pressure has been observed in studies of the photolysis of acetone at lower temperatures but also at lower pressures (5, 29). This is in qualitative agreement with the prediction of the theory of unimolecular reactions (30).

An Arrhenius plot of $k_3/k_4^{\frac{1}{2}}$ is given in figure 11. The experimental points shown are representative values from table 19 corrected to 16 mm pressure. The straight line corresponds to:

$$\log_{10} (k_3/k_4^{\frac{1}{2}}) \text{ / mole}^{-\frac{1}{2}} \text{ cm}^{3/2} \text{ sec}^{-\frac{1}{2}} = 6.3 - (12900/2.303RT).$$

Assuming the activation energy of reaction 4 to be zero, and using the value of k_4 calculated by Shepp (4), gives

$$\log_{10} k_3 \text{ / mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} = 13.0 - (12900/2.303RT).$$

If $E_4 = 0$ at high pressures it should have a negative value (though probably a small one) under the present conditions. E_4 would certainly not be expected to be sufficiently low to reconcile the present values of $k_3/k_4^{\frac{1}{2}}$ with those determined at lower temperatures (31, 32). No explanation of the discrepancy between the low temperature results and those of the present work can be given. Three points of interest may however be noted. First, if the present results are empirically corrected to the total pressure used in the acetone -d_6 work (figure 11) the values of $k_3/k_4^{\frac{1}{2}}$ obtained at the lowest temperatures in the present work would be in reasonable agreement with the acetone -d_6 values. Second, correction of the low temperature curve obtained using the photolysis of dimethyl mercury as radical source to the pressure used in the acetone -d_6 work would increase the separation between the two curves. Third, the values of $k_3/k_4^{\frac{1}{2}}$ obtained in the present work are in excellent agreement with values calculated from a previous flow system study of mercury dimethyl (1).

TABLE 19 - THE RATIO $k_3/k_4^{\frac{1}{2}}$ OVER THE TEMPERATURE RANGE 346°C to 701°C

Radical Source - Dimethyl zinc

run no.	temp. (°C)	pres. (mm)	$k_3/k_4^{\frac{1}{2}}$
42	573	16.0	685
12	597	4.6	1600
11	597	5.8	2200
8	597	6.6	1610
3	597	7.2	1535
6	597	9.8	1233
13	597	10.0	1070
2	597	12.5	1134
5	597	16.0	1040
9	597	16.5	793
14	597	16.5	1080
15	597	16.5	1030
1	597	22.4	900
7	597	26.5	846
4	597	28.5	825
29	624	16.0	1450
31 a	624	16.2	1010
17	648	16.6	1760
40	658	16.3	1580
41	658	16.3	1790
21	672	5.3	3800
20	672	5.8	3600
19	672	16.3	2000
22	672	16.4	2150
18	672	16.8	2090
30 a	672	16.3	1880
32 a	672	16.1	1800
43	700	16.6	2500
33 a	701	16.1	1990
25	701	16.0	2140
24	701	16.5	2140
23	701	16.6	2300

Radical Source - Dimethyl Cadmium

run no.	temp. (°C)	pres. (mm)	$k_3/k_4^{\frac{1}{2}}$
30	469	18.6	260
37	469	19.3	305
32	469	19.9	245
28	490	17.5	350
36	490	19.3	326
33	501	18.5	350
40 a	508	19.0	356
39 a	517	18.9	380
35	522	17.6	550
34	524	16.5	510
27	524	18.3	430
9	552	5.2	910
24	552	5.8	1030
22	552	6.3	990
23	552	10.0	825
13	552	13.2	520
16	552	13.8	655
17	552	14.4	507
15	552	15.4	700
4	552	15.6	646
18	552	18.0	694
19	552	18.6	631
20	552	18.6	526
8	552	18.7	602
7	552	19.2	600
21	552	20.0	493
12	552	21.8	675
10	552	24.4	660
26	571	17.0	790
38	571	17.0	700

Radical Source - Dimethyl Mercury

run no.	temp. (°C)	pres. (mm)	$k_3/k_4^{\frac{1}{2}}$
9	465	16.1	192
10	466	16.1	180
8	483	16.2	263
7	505	16.2	365
6	531	16.3	510
18	543	4.4	975
17	543	10.3	674
4	542	16.0	579
3	543	16.1	581
19	543	25.5	430
2	560	16.1	625
1	560	17.0	519
14	562	16.1	692
16	562	16.1	745
15	562	16.5	693
13	573	16.1	668
12	585	16.2	834
5	585	16.5	682
11	608	16.0	833

Table 19 (continued)

Radical Source - Trimethyl antimony

run no.	temp. (°C)	pres. (mm)	$k_3/k_4^{\frac{1}{2}}$
34	475	16.5	248
21	475	16.5	216
20	475	16.5	238
8	475	17.5	237
7	475	17.6	234
22	477	16.5	259
6	495	17.4	308
9	495	17.4	302
10	495	17.5	321
11	495	17.6	398
33	496	16.5	322
24	516	16.5	413
44	516	16.5	424
32	517	16.5	428
47	518	6.3	550
43	518	16.5	410
48	518	16.5	351
49 a	518	16.5	414
5	518	16.3	440
23	518	16.5	428
12	518	17.0	413
13	518	17.0	442
14	518	17.0	444
15	518	17.0	428
41	519	16.5	428
42	519	16.5	440
46	519	29.0	377
30	536	16.5	533
17	540	16.5	550
18	540	16.5	530
19	540	16.5	482
4	541	16.5	556
16	541	16.5	564
37	541	16.5	550
31	542	16.5	555
38	542	16.5	461
39	543	16.5	512
40	543	16.5	561
25	557	16.5	675
35	558	16.5	640
36	569	16.5	621
26	582	16.5	805

Radical Source - Trimethyl bismuth

run no.	temp. (°C)	pres. (mm)	$k_3/k_4^{\frac{1}{2}}$
26	346	16.1	46.5
25	354	16.1	51.2
24	355	16.1	52.7
23	355	16.1	53.0
21	367	16.1	61.4
22	367	16.1	62.9
2 a	369	16.1	61.0
29	374	16.1	74.1
20	378	16.1	68.0
19	380	15.9	71.5
28	380	16.1	78.0
31	382	6.3	117
32	382	16.1	81.0
30	382	25.0	72.9
5	383	16.1	81.0
6	386	16.1	87.5
7	386	16.1	80.0
9	387	6.3	120
3 a	387	16.1	82.4
33	387	16.1	85.0
8	388	16.1	94.8
13	392	6.3	116
11	390	10.6	100.0
10	389	11.0	96.0
27	392	16.1	94.4
12	392	16.1	84.6
B'	395	16.1	87.6
15	400	16.1	101
14	401	16.1	101
17	402	16.1	104
18	403	16.1	101
4 a	409	16.1	113
16	409	16.1	115

Table 19 (continued)

Radical Source - Dimethyl tin dichloride

run no.	temp. (°C)	pres. (mm)	$k_3/k_4^{\frac{1}{2}}$
22	554	16.1	480
21	554	16.1	423
20	567	16.1	450
26 a	567	16.1	394
4	574	16.1	600
3	574	16.1	460
7	575	6.0	915
9	575	9.5	689
5	575	16.1	440
6	575	16.1	669
8	575	25.0	549
24	587	16.1	770
11	588	16.1	661
25 a	588	16.1	726
10	588	16.1	711
23	589	16.1	705
13	600	16.1	900
12	600	16.1	860
15	612	16.1	1060
14	612	16.1	1025
17	624	16.1	950
16	624	16.1	810
19	636	16.1	1300
18	637	16.1	1310

a - runs in packed reaction vessel

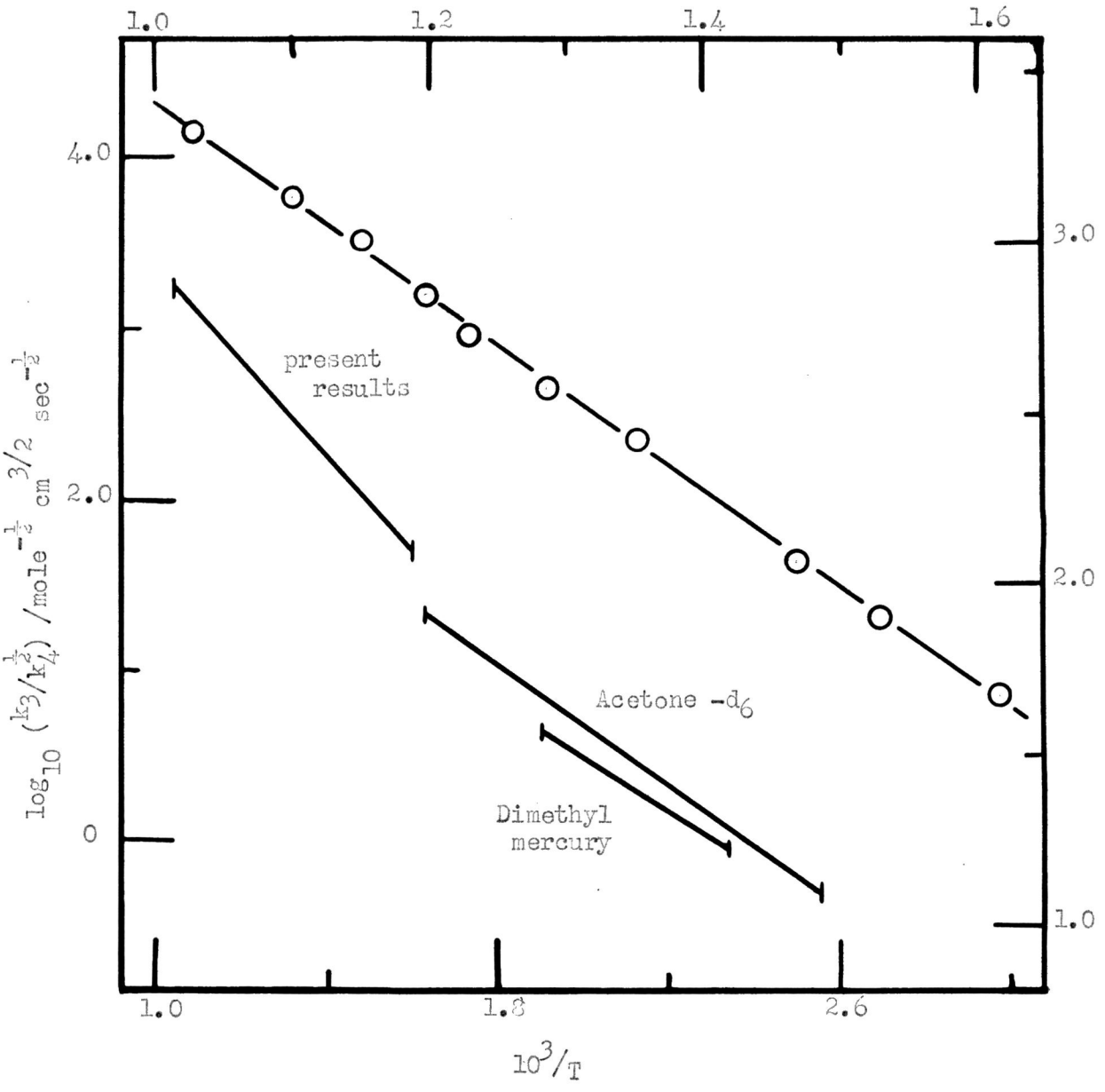

FIGURE 11 Arrhenius plot for the reaction of methyl radicals with toluene.

O Representative points including at least one value from each of the six alkyls studied.
Acetone - d_6 Trotman-Dickenson and Steacie (31)
$HgMe_2$ Rebbert and Steacie (32)
The top and righthand scales refer to the full plot of the present experimental results (upper curve).

DISCUSSION

A. METHYL-METAL BOND ENERGIES

The available bond dissociation energies and mean bond energies of covalent methyl-metal bonds are given in table 20. Values for the methyl derivatives of the non-metals of groups IV to VII are included for comparison. Group I and all the A subgroups of the periodic table have been omitted. In group I, excepting the special case of hydrogen, only lithium, copper and gold form methyl derivatives that may possibly be covalent in nature. The lithium compound is very involatile and is probably polymeric. Trimethyl gold has been prepared but decomposes in ether solution at -40°C to -35°C yielding metallic gold, ethane and some methane. Methyl copper is somewhat more stable but decomposes in boiling ether with the formation of metallic copper, methane and ethane. No determination of the bond strengths in these compounds has been reported. All attempts to isolate methyl derivatives of the elements of groups IIA to VIIA inclusive have failed.

All mean bond energies shown in table 20 have been calculated from the appropriate heat of formation at 25°C, the heat of atomization of the central element, and the following data. $D(CH_3 - H) = 102.5$ kcal mole^{-1} (33), ΔH_f^o (H) = 52.089 kcal mole^{-1} (34), and ΔH_f^o (CH_4) = -17.889 kcal mole^{-1} (34). The stated limits of error assume the above three values to be exact. That is, only errors in the heat of atomization of the central atom and in the heat of formation of the alkyl have been taken into consideration in assigning limits of error to the mean bond energy.

The compounds are discussed in turn, starting with those of group II elements and working through to those of group VII elements. Within each group the compounds are considered in order of increasing atomic number of the central

TABLE 20 - MEAN BOND ENERGIES AND BOND DISSOCIATION ENERGIES OF M - CH_3 BONDS

Group II	Group III	Group IV	Group V	Group VI	Group VII
Be (4)	B (5)	C (6)	N (7)	O (8)	F (9)
	E 88.9 ± 2	E 85.4	E 71.4	E 84.4	D_1 109.8
		D_1 78.0		D_1 76.3	
				D_2 92.5	
Mg (12)	Al (13)	Si (14)	P (15)	S (16)	Cl (17)
	E 61.9 ± 3.5		E 65.3 ± 1.0	E 62.6	D_1 81.1
				D_1 73.6	
				D_2 51.6	
Zn (30)	Ga (31)	Ge (32)	As (33)	Se (34)	Br (35)
E 41.5 ± 0.2	E 57.7 ± 1.3		E 51.5 ± ?		D_1 67.8
D_1 47.2 ± 1.0			D_1 54.0 ± 3		
D_2 35					
Cd (48)	In (49)	Sn (50)	Sb (51)	Te (52)	I (53)
E 33.1 ± 0.3		E 53.4 ± 4	E 49.7 ± 6		D_1 53.5
D_1 45.8 ± 1.0		D_1 56.1 ± .04	D_1 57.0 ± ?		
D_2 20.4 ± 1.3					
Hg (80)	Tl (81)	Pb (82)	Bi (83)		
E 28.6 ± 0.1		E 36	E 33.8 ± 6		
D_1 51.0 ± 1.0			D_1 43.6 ± 0.4		
D_2 6.1 ± 1.1					

KEY

Central atom (atomic number) in MX_n

$$E = \frac{D_1 + \ldots\ldots + D_n}{n}$$

$$D_x = D\,(Me - MX_{n-x})$$

unless stated in text X = CH_3

all values - kcal $mole^{-1}$

atom. Since a number of mercury alkyls and aryls have been investigated a special section on these compounds is included in the discussion of group II.

Dimethyl Zinc

The heat of formation of dimethyl zinc has been determined by two sets of investigators. Hartley, Pritchard and Skinner (35) determined the heat of formation of liquid dimethyl zinc from the heat of hydrolysis of this compound in aqueous etherial solution and from the heat of reaction of dimethyl zinc with aqueous sulphuric acid. The values obtained were 6.6 kcal $mole^{-1}$ and 5.5 kcal $mole^{-1}$ respectively. They assume that the heat of formation calculated from the reaction in etherial solution is too large due to partial solution of the gaseous products. Similarly the heat of formation calculated from the reaction in sulphuric acid is said to be too small because of side reactions. The best value is estimated at ΔH_f^o ($ZnMe_2$, liq.) = 6.3 ± 1 kcal $mole^{-1}$. Using the heat of vapourization calculated from the equation of Thompson and Linnett (36), 6.8 kcal $mole^{-1}$, gives ΔH_f^o ($ZnMe_2$, g) = 13.1 ± 1 kcal $mole^{-1}$.

Long and Norrish (37) have determined the heat of formation of liquid dimethyl zinc from the heat of combustion of this compound in a static bomb. Difficulty was encountered in obtaining complete combustion, only one of five experiments being completely satisfactory. They calculate ΔH_f^o ($ZnMe_2$, liq.) = 6.5 ± .04 kcal $mole^{-1}$ corresponding to ΔH_f^o ($ZnMe_2$, g) = 13.3 ± .04 kcal $mole^{-1}$. The error quoted is based solely on the estimated error in the heat of combustion.

Using the Long and Norrish value for the heat of formation of gaseous dimethyl zinc and a value of 31.1 ± 0.2 kcal $mole^{-1}$ for the heat of atomization of zinc (37) gives $D(CH_3\ Zn\text{-}CH_3) + D(CH_3 - Zn)$ = 82.9 ± 0.3 kcal $mole^{-1}$.

No previous determination of the bond dissociation energies in dimethyl zinc have been reported. Assuming the activation energies determined at 16 mm

pressure to be a measure of the dissociation energies

$$D\ (CH_3Zn - CH_3) = D_1 = 47.2 \pm 1 \text{ kcal mole}^{-1}$$

and $$D\ (CH_3 - Zn) = D_2 = 35 \text{ kcal mole}^{-1}.$$

Hence $$D_1 + D_2 = 82.2 \text{ kcal mole}^{-1}.$$

The agreement between the kinetic estimate and the thermochemical estimate is meaninglessly good as an overall error of approximately ± 5 kcal should probably be associated with the kinetic result.

Dimethyl Cadmium

The heat of formation of liquid cadmium dimethyl has been determined by Long and Norrish to be 18.9 ± 0.7 kcal mole^{-1} (37). Using more recent data and correcting a slight error in the original calculation, Laurie and Long have recalculated this value to be 19.6 kcal mole^{-1} (38). Carson, Hartley and Skinner have also determined the heat of formation of this alkyl. From the heat of reaction of dimethyl cadmium with sulphuric acid these workers calculate ΔH_f^o ($CdMe_2$, liq.) = 16.7 ± 0.2 kcal mole^{-1} (39, 35). This value is accepted in the present work. Combining it with the molar heat of vapourization of dimethyl cadmium, 9.15 kcal mole^{-1} (40), and the heat of atomization of cadmium, 27.0 ± 0.2 kcal mole^{-1} (37), gives $D\ (CH_3Cd - CH_3) + D\ (CH_3 - Cd)$ = 66.15 ± 0.4 kcal mole^{-1}.

Including the present work three studies of the pyrolysis of dimethyl cadmium have now been reported. The first of these studies appeared in 1953 (41). The reaction was carried out in a static system. A marked effect of surface to volume ratio was observed but no attempt to sort out the homogeneous components of the reaction was made. The activation energy for the overall reaction may be calculated to be 28 kcal mole^{-1}. No significance can be attached to this value.

Following publication of the present flow system results the third study of dimethyl cadmium was reported. Despite the difficulties reported by Heller and Taylor (41) this study by Laurie and Long (38) was carried out in a static system. As might have been anticipated the rate constant of the reaction was found to depend upon the surface to volume ratio. The reaction was therefore studied at one temperature using various surface to volume ratios. The rate constant of the homogeneous reaction was estimated by extrapolation to zero surface to volume ratio. A similar procedure could have been carried out at other temperatures and the activation energy and A factor calculated in the usual way. However, Laurie and Long felt that the limited accuracy of their results did not warrant the work involved. The activation energy was therefore estimated from the rate constant for the homogeneous reaction at 258°C and an A factor based upon analogy with the present work on dimethyl cadmium and previous work on dimethyl mercury (42, 1). The activation energy calculated in this way is 43.5 ± 1.4 kcal $mole^{-1}$. This result is probably too low. The present result is 45.8 ± 1 kcal $mole^{-1}$ at 16 mm pressure. Because precise information on the pressure dependence of the activation energy is lacking the value obtained at 16 mm has been left uncorrected. However it is probably a minimum value and perhaps should be as high as 47-48 kcal $mole^{-1}$. The work of Laurie & Long was carried out at sufficiently high pressures that the observed activation energy should be very close to the high pressure limit.

In view of the fact that Laurie and Long have estimated the rate constant of the homogeneous reaction by an extrapolation to zero surface to volume ratio the disagreement of their work with that of Heller and Taylor should perhaps be noted. Based on analysis of the gaseous products Heller and Taylor's results show that an increase in surface to volume ratio by a factor of 5.5

decreases the rate constant by 75% (41). Working in the same temperature region, using the same type of reaction vessel and packing (pyrex), and approximately the same total pressure of reactant Laurie & Long (38) report an increase in surface to volume ratio by a factor of two causes an increase in the rate constant of 60%. The rate constants of Laurie & Long are calculated from the amount of undecomposed alkyl. Since some solid products are formed in the decomposition a small difference might be expected in the two sets of results. It should not be large enough to account for the opposite effect of surface to volume ratio.

Accepting the experimental activation energy obtained in the present work as a measure of D ($CH_3Cd - CH_3$) and using the thermochemical sum of the two methyl-cadmium bonds derived earlier gives

$$D\ (CH_3Cd - CH_3) = 45.8 \pm 1 \text{ kcal mole}^{-1}$$

$$\text{and} \quad D\ (CH_3 - Cd) = 20.4 \pm 1.3 \text{ kcal mole}^{-1}$$

Mercury Compounds

The mean bond energies and bond dissociation energies of a number of mercury alkyls and aryls are given in table 21. The discussion of individual compounds follows the order given in the table.

(a) Dimethyl mercury - Two satisfactory determinations of the heat of formation of dimethyl mercury have been made. Hartley, Pritchard and Skinner give ΔH_f^o ($HgMe_2$, g) = 22.4 ± 2 kcal mole^{-1} based on the heat of bromination of the alkyl (43). Combustion in a static bomb (44) has given the same result but the limits of error claimed are much narrower (± 0.1 kcal mole^{-1}). ΔH_f^o (Hg, g) has been accurately determined to be 14.54 kcal mole^{-1} (34). Hence D ($CH_3Hg - CH_3$) + D ($CH_3 - Hg$) = 57.14 ± 0.1 kcal mole^{-1}.

The activation energy for the thermal decomposition of dimethyl

TABLE 21 - MEAN BOND ENERGIES AND BOND DISSOCIATION ENERGIES IN MERCURY ALKYLS AND ARYLS

Compound	E kcal mole^{-1}	D_1 kcal mole^{-1}	D_2 kcal mole^{-1}
Dimethyl mercury	28.6 ± 0.1 a	51.0 ± 1.0	6.1 ± 1.2
Diethyl mercury	24.3 ± 2.1	42.5 ± 2.0	6.0 ± 6.2
Di-isopropyl mercury	20.2 ± 3.5	(20.2 ± ?) b	
Di-n-propyl mercury	24.7 ± 2.0	(23.6 ± 0.5) b	
Phenyl mercury chloride	42.9 ± 1.5	59.3 ± 3.0	-
Phenyl mercury bromide	40.0 ± 1.5	63.0 ± 2.0	-
Diphenyl mercury	30.2 ± 5.0	(34 ± 2) b	

a Limits of error based on error in heat of combustion only.

b One half of the experimental activation energy for the overall decomposition into a mercury atom and two methyl radicals.

mercury has been determined in four investigations. Two of these have been carried out using static systems (42, 45). The reaction is homogeneous and below approximately 333°C follows first order kinetics (42). Above this temperature the order appears to increase; at 342°C the reaction is apparently 1.5 order. At all temperatures the reaction products are complex. In addition to C_1 and C_2 gases an oily or solid film and a fine carbon deposit are often observed. The percentage decomposition has therefore been determined in both cases by measuring the quantity of undecomposed alkyl. Laurie and Long (42) obtain 51.3 ± 0.5 kcal $mole^{-1}$ for the activation energy of the first order reaction. Yeddanapalli et al.(45) studied the reaction at only three temperatures, one of which was in the "1.5 order" region. Calculation of the first order rate constants from results at 305.5°C and 323.5°C leads to a value of 50.4 kcal $mole^{-1}$ for the activation energy. Obviously little significance can be attached to this value.

The decomposition of dimethyl mercury in a flow system particularly in the presence of toluene is a much cleaner reaction than that obtained in static systems. Extensive work by Gowenlock, Polanyi and Warhurst (1) has shown that substantial agreement is obtained between the amount of mercury formed and the quantity of gaseous products. The decomposition is largely homogeneous and over the entire temperature range used obeyed first order kinetics. The calculated activation energy was 51.5 ± 2 kcal $mole^{-1}$ at 10 mm. A partial pressure of 3.15 mm of toluene was used. The value obtained in the present work is 50.1 ± 1 kcal $mole^{-1}$ at 16 mm.

The value given in tables 20 and 21 for the bond dissociation energy of the first methyl-mercury bond, 51 ± 1 kcal $mole^{-1}$, is the mean of the two flow system results and the static system value of Laurie & Long. Hence D (CH_3 - Hg) = 6.1 ± 1.1 kcal $mole^{-1}$.

(b) Diethyl mercury - The sum of the two metal-carbon bond energies

in diethyl mercury has been determined in two investigations. From the heat of reaction of the alkyl with iodine and with bromine the heat of formation of liquid dimethyl mercury has been calculated to be 9.9 ± 1.7 kcal mole^{-1} (46). Using ΔH vap.($HgEt_2$) = 10.1 kcal mole^{-1} (36) and ΔH_f^o (Et) = 25.3 ± 2 (47) gives D (EtHg - Et) + D (Et - Hg) = $D_1 + D_2$ = 45.1 ± 6 kcal mole^{-1}. Combustion of the alkyl in a static bomb calorimeter has given a value ΔH_f^o ($HgEt_2$, liq.) = 6.5 ± 0.2 kcal mole^{-1} (44). This corresponds to $D_1 + D_2$ = 48.5 ± 4.2. These limits of error do not take into account possible errors in the heat of vapourization of the alkyl.

The thermal decomposition of diethyl mercury has been investigated in a flow system at 10 mm total pressure (2). A partial pressure of approximately 3 mm of toluene was used. The remainder of the carrier gas was nitrogen. The reaction was first order and homogeneous. The activation energy, which may be associated with D (EtHg - Et), was 42.5 ± 2 kcal mole^{-1}. Combining this with the sum of $D_1 + D_2$ obtained from combustion experiments, 48.5 ± 4.2 kcal mole^{-1}, gives D (Et - Hg) = 6.0 ± 6.2 kcal mole^{-1}.

(c) <u>Di-isopropyl mercury</u> - The only satisfactory determination of the heat of formation of di-isopropyl mercury is that of Mortimer, Pritchard and Skinner (48). The value obtained was ΔH_f^o ($Hg(iso\text{-}Pr)_2$, g) = 8.4 ± 2.3 kcal mole^{-1}. The value which may be calculated from early heat of combustion work (37), ΔH_f^o ($Hg(iso\text{-}Pr)_2$, g) = 21.5 kcal mole^{-1}, is much too high. Assuming the dissociation energy of a secondary C - H bond in propane to be 93.9 ± 2 kcal mole^{-1} (49) gives ΔH_f^o (iso-Pr) = 17.1 ± 2 kcal mole^{-1}. Hence using Mortimer, Pritchard and Skinner's value for the heat of formation of di-isopropyl mercury gives 40.3 ± 7 kcal mole^{-1} for the sum of the two mercury-carbon bond energies.

The thermal decomposition of di-isopropyl mercury has been studied in a flow system at a total pressure of approximately 7.4 mm using nitrogen as a

carrier gas (50). The decomposition is first order and homogeneous. The rate constant may be represented by the expression

$$\log_{10} k / \text{sec}^{-1} = 16.2 - (40{,}400/2.303RT).$$

The apparent near equality of the observed activation energy and the sum of the two metal-carbon bond energies coupled with the fact that the A factor is larger than that normally associated with a unimolecular decomposition into two radicals has led to the suggestion that the initial process is a split into three fragments.

(d) Di-n-propyl mercury - The heat of formation of di-n-propyl mercury has been determined from measurements of the heat of halogenation of the alkyl (48), ΔH_f^o ($Hg(n\text{-}Pr)_2$, g) = 10.33 ± 2.0 kcal mole^{-1}. Using D ($CH_3CH_2CH_2$ - H) = 99.4 ± 1 kcal mole^{-1} (49), ΔH_f^o (n-Pr) = 22.6 ± 1 kcal mole^{-1} and hence the sum of the two mercury-carbon bond dissociation energies is 49.4 ± 4 kcal mole^{-1}. Early work on the heat of combustion of the alkyl is in fair agreement with this result (37).

The thermal decomposition of di-n-propyl mercury has been studied by a method similar to that used in the investigation of di-isopropyl mercury (51). The reaction rate was observed to be pressure dependent below 7 mm. As in the case of the iso-propyl alkyl the decomposition was observed to be a first order, homogeneous, and non-chain reaction. The rate constant may be represented by

$$\log_{10} k / \text{sec}^{-1} = 15.52 - (47{,}100/2.303RT).$$

As in the case of di-isopropyl mercury it was again postulated that the observed process was an initial split into three fragments.

(e) Phenyl mercury chloride - The only value available for the sum of the methyl-mercury and chlorine-mercury bond dissociation energies is 85.8 ± 3 kcal mole^{-1} (52). This assumes D (Ph - H) = 102 kcal mole^{-1}.

The thermal decomposition of phenyl mercury chloride has been studied in a flow system using a total pressure of 10 mm of which approximately

4 mm was toluene, the remaining carrier gas being nitrogen (2). Substrate pressures of $1 - 10 \times 10^{-2}$ mm were used. The reaction was first order and homogeneous. The rate constant is given by

$$\log_{10} k / sec^{-1} = 13.0 - (59{,}300 \pm 3{,}000/2.303RT).$$

The initial process in the decomposition is assumed to be a split into phenyl and mercury chloride. The activation energy may therefore be equated to the dissociation energy of the mercury-phenyl bond, D_1. Estimation of D_1 from thermochemical data has given a value of 64 ± 6 kcal $mole^{-1}$ (53).

(f) Phenyl mercury bromide - Assuming D (Ph - H) = 102 kcal $mole^{-1}$, the sum of the mercury-phenyl and mercury-bromine bond dissociation energies is 79.9 ± 3 kcal $mole^{-1}$ (52).

A kinetic study of this alkyl has been carried out by the same method employed for phenyl mercury chloride (2). The rate constant is given by

$$\log_{10} k / sec^{-1} = 14.3 - (63{,}000 \pm 2{,}000/2.303RT).$$

The rate determining step is again the splitting off of the phenyl group. Hence the dissociation energy of the phenyl-mercury bond is 63 ± 2 kcal $mole^{-1}$. This bond dissociation energy has also been estimated from thermochemical data (53). The value obtained is 62.0 ± 6 kcal $mole^{-1}$, the large limits of error being mainly due to uncertainty in the heat of formation of the phenyl radical.

(g) Diphenyl mercury - The heat of formation of diphenyl mercury has been determined by several groups of workers (44, 46, 53, 54). Chernick, Skinner and Wadso (53) have reviewed the values for ΔH_f° ($HgPh_2$, cryst.) and propose 66 ± 2.5 kcal $mole^{-1}$ as the best value. Using 26.95 kcal $mole^{-1}$ for the heat of sublimation of diphenyl mercury (55) gives ΔH_f° ($HgPh_2$, g) = 93 ± 2.5 kcal $mole^{-1}$. The heat of formation of the phenyl radical may be taken as 69.4 ± 4 kcal $mole^{-1}$ (53). The sum of the two mercury-phenyl bond dissociation energies is therefore 60.3 ± 10 kcal $mole^{-1}$.

The thermal decomposition of diphenyl mercury has been studied in a flow system using a total pressure of approximately 10 mm (2). Nitrogen containing a partial pressure of 2 mm of toluene was used as carrier gas. The rate constant for the reaction is given by

$$\log_{10} k / sec^{-1} = 16.0 - (68,000 \pm 4,000/2.303RT).$$

The initial step in the decomposition is assumed to be a split into a mercury atom and two phenyl radicals. Hence the activation energy should be equal to the sum of the mercury-phenyl bond dissociation energies. The agreement with the thermochemical value is not good but it does lie within the stated limits of error.

Trimethyl boron

Skinner and Smith (56) give ΔH_f^o (BMe_3, g) = -28.4 ± 3 kcal mole^{-1} based on the heat of combustion of the alkyl reported by Long and Norrish (37). Using ΔH_f^o (B, g) = 140.9 ± 2 kcal mole^{-1} (56) gives 88.9 ± 2 kcal mole^{-1} for the mean methyl-boron bond energy.

Trimethyl aluminium

From the heat of combustion of the alkyl in a static bomb calorimeter the value ΔH_f^o ($AlMe_3$, g) = -13.3 ± 0.1 kcal mole^{-1} has been calculated (37). The calculation assumes that at 25°C trimethyl aluminium vapour exists as a dimer and that D (Me_3Al - $AlMe_3$) = 20.2 kcal mole^{-1}. The error quoted in the heat of formation is based solely on the uncertainty in the heat of combustion. If ΔH_f^o (Al, g) = 75 ± 10 kcal mole^{-1} (34) then the mean methyl-aluminium bond energy is 61.9 ± 3.5 kcal mole^{-1}.

The thermal decomposition of trimethyl aluminium has been studied in a static system using pressures of 10 mm to 85 mm as measured at room temperature (57). The reaction is largely homogeneous but appears to follow 1.5 order kinetics. It is impossible to derive any useful estimate of D (Me_2Al - Me)

from this work.

Trimethyl gallium

From heat of combustion experiments Long and Sackman have calculated ΔH_f^o ($GaMe_3$, liq.) = -17.6 ± 3 kcal mole^{-1} (58). Using ΔH_f^o (Ga, g) = 65.8 ± 0.5 kcal mole^{-1} (59) they give 57.7 ± 1.3 kcal mole^{-1} for the mean methyl-gallium bond energy.

Tetramethyl carbon

The heat of formation of neopentane is -39.67 kcal mole^{-1} (28). Therefore accepting 171.7 kcal mole^{-1} as the heat of atomization of carbon (28) gives 85.4 kcal mole^{-1} for the mean methyl-carbon bond energy in this compound.

An estimate of D (Me_3C - Me) may also be made. Stevenson's electron impact experiments lead to a value of D (Me_3C - H) = 90 kcal mole^{-1} (49). Using ΔH_f^o (Me_3CH) = -32.2 kcal mole^{-1} (28) gives ΔH_f^o (Me_3C) = 5.8 kcal mole^{-1}. Hence D(Me_3C - Me) = 78.0 kcal mole^{-1}.

Tetramethyl tin

The value ΔH_f^o ($SnMe_4$, g) = -13.6 ± 10 kcal mole^{-1} has been reported (60). Using ΔH_f^o (Sn, g) = 70.0 ± 2 kcal mole^{-1} (61) leads to a value of 53.4 ± 4 kcal mole^{-1} for the mean methyl-tin bond energy.

This mean bond energy may also be estimated indirectly. The reported heat of formation of tetraethyl tin (37) leads to a value of 52.8 kcal mole^{-1} for the mean ethyl-tin bond energy. Hence E(Me - Sn) - E(Et - Sn) = 0.6 kcal mole^{-1}. By analogy with the group IIB alkyls this difference would be expected to be 6 ± 2 kcal mole^{-1}. The discrepancy between this value

	ΔH_f^o	$D_1 + D_2$	ΔH_f^o	$D_1 + D_2$	ΔH_f^o	$D_1 + D_2$
$ZnMe_2$	13.3	82.9 $CdMe_2$	25.9	66.2 $HgMe_2$	22.4	57.1
$ZnEt_2$	13.0 (37,35)	68.7 $CdEt_2$	24.5 (35)	53.1 $HgEt_2$	16.6	48.5
ΔE		7.1		6.6		4.3

ΔE = E (Me - M) - E (Et - M), all values expressed in kcal mole^{-1}

and the directly calculated difference of 0.6 kcal $mole^{-1}$ may of course arise from several sources. The analogy between the group II compounds and those of tin may not be valid. The heat of formation of either tetramethyl tin or tetraethyl tin or of both may be in error. If the analogy is valid and if the reported heat of formation of tetraethyl tin is correct then the mean bond energy in tetramethyl tin should be some 3 - 7 kcal $mole^{-1}$ greater than the directly calculated value of 53.4 ± 4 kcal $mole^{-1}$. Therefore although the directly calculated value is used in Table 20 it should be accepted with reserve.

Waring and Horton have investigated the pyrolysis of tetramethyl tin in a static system (3). They reported that above 80 mm the reaction followed first order kinetics and had an activation energy of 82.4 ± 1.2 kcal $mole^{-1}$. The A factor was given as $10^{21.92}$. Both free radical and molecular elimination mechanisms were postulated but it was assumed that the reaction proceeded predominantly by the latter. The results have been recalculated on the basis of a free radical chain mechanism which is assumed to lead to a value of 1.5 for the order of the overall reaction (62). The activation energy thus calculated is 75.9 kcal $mole^{-1}$.

In the present work the thermal decomposition of dimethyl tin dichloride has been shown to have an overall activation energy of 56.1 ± .04 kcal $mole^{-1}$. This may be associated with the dissociation energy of the first methyl carbon bond in the dichloride and should not differ greatly from D (Me_3Sn - Me). The observed activation energy is therefore tentatively used in table 20 as a measure of the dissociation energy of the first methyl-tin bond in tetramethyl tin. It would appear that whatever the reaction mechanism for the thermal decomposition of tetramethyl tin in a static system may be, the overall activation energy can not be associated with the dissociation energy of the first methyl-tin bond.

Tetramethyl lead

The heat of formation of gaseous tetramethyl lead has been reported as 3.2 ± 3 kcal mole^{-1} (60). This value is almost certainly too low. The heat of formation of tetraethyl lead has recently been determined using a rotating bomb calorimeter, ΔH_f° (PbEt, g) = 26.3 ± 0.6 kcal mole^{-1} (63, 64). If this is combined with the heat of formation of the ethyl radical and the heat of atomization of lead, 46 kcal mole^{-1} (65), the mean bond energy of the ethyl-lead bond is found to be 30.2 kcal mole^{-1}. By analogy with the dimethyl and diethyl alkyls of group IIB it would therefore appear that the mean methyl-carbon bond in tetramethyl tin should be approximately 36 ± 3 kcal mole^{-1}. This corresponds to ΔH_f° ($PbMe_4$, g) = 32 kcal mole^{-1}, some 29 kcal mole^{-1} greater than the value of Lippincott and Tobin (60). The reported value for the heat of formation of tetramethyl lead has therefore been disregarded. The value given in table 20 is that estimated from the heat of formation of tetraethyl lead.

Trimethylamine

Long and Sackman have reviewed thethermochemistry of trimethylamine. They give as a "best" value ΔH_f° (NMe_3, g) = -4.1 kcal mole^{-1} (66). If 112.6 kcal mole^{-1} is accepted as the heat of atomization of nitrogen (67) the mean methyl-nitrogen bond energy is 71.4 kcal mole^{-1}.

Trimethylphosphine

From heat of combustion experiments in a static bomb calorimeter Long and Sackman obtained ΔH_f° (PMe_3, g) = -23.2 ± 2 kcal mole^{-1} (66). Using 75.18 ± 1 kcal mole^{-1} for the heat of atomization of phosphorus (34) gives a value of 65.3 ± 1 kcal mole^{-1} for the mean methyl-phosphorus bond energy.

Trimethyl arsenic

The heat of formation of trimethyl arsenic has been determined by

Long and Sackman (68), ΔH_f^o ($AsMe_3$, g) = 3.7 ± 1.2 kcal mole^{-1}. The heat of atomization of arsenic is rather uncertain. The National Bureau of Standards (34) recommend a value of 60.64 kcal mole^{-1}. However, the value of D (As_2 - As_2) used in calculating this result is probably too low (69). Therefore the mean methyl-arsenic bond energy calculated using the National Bureau of Standards' values, E (Me - As) = 51.5 ± ? kcal mole^{-1}, can probably be considered as a minimum value.

The thermal decomposition of trimethyl arsenic in a static system has been studied (70). Preliminary experiments were carried out in which it was shown that although the gaseous products accounted for only 70-75% of the carbon, a linear relation existed between the percentage decomposition and the pressure increase in the system. Using the pressure increase as a measure of the extent of reaction the decomposition was shown to be first order and homogeneous. Unfortunately little reliance can be placed on the latter conclusion as the method of packing the reaction vessel was unsatisfactory. The overall rate constant is reported as

$$\log_{10} k / \text{sec}^{-1} = 12.77 - (54{,}600/2.303RT).$$

No error limits are given in the published results. From an Arrhenius plot of the results the uncertainty in the activation energy has been estimated at ± 3 kcal mole^{-1}. The value given for the activation energy appears slightly high and it is recommended that 54.0 ± 3 kcal mole^{-1} is a better figure.

The pyrolysis of trimethyl antimony is so complex, even when studied by the toluene carrier technique, that it is difficult to believe the pyrolysis of trimethyl arsenic in a static system is straightforward. Acceptance of the overall activation energy as a measure of D (Me_2 As - Me) should be rather tentative.

Trimethyl antimony

The heat of formation of trimethyl antimony has been calculated from the heat of combustion in a static bomb (24), ΔH_f^o ($SbMe_3$, g) = 9.2 ± 3.1 kcal $mole^{-1}$. The heat of atomization of antimony is given by the National Bureau of Standards (34) as 60.8 kcal $mole^{-1}$. This value may well be in error by ± 15 kcal $mole^{-1}$. Therefore the mean methyl-antimony bond energy is 49.7 ± 6 kcal $mole^{-1}$. Consideration of the mean bond energies of the M - CH_3 bonds of the group V elements indicate that this value may be too high (66).

No previous kinetic study of trimethyl antimony has been reported. The present results are not entirely satisfactory but it seems reasonable to assume that the observed activation energy should be close to D (Me_2Sb - Me). Hence the value 57.0 kcal $mole^{-1}$ is tentatively advanced for this dissociation energy. No useful estimate of the possible error in this result can be given.

Trimethyl Bismuth

Combustion experiments have led to the value ΔH_f^o ($BiMe_3$, g) = 45.8 ± 1.7 kcal $mole^{-1}$ (23). The value of ΔH_f^o (Bi, g) has been given as 49.7 kcal $mole^{-1}$ (34) but unfortunately as in the case of antimony considerable doubt exists as to the accuracy of this result. Errors of up to ± 15 kcal $mole^{-1}$ are likely. The evidence which indicated that ΔH_f^o (Sb, g) is probably lower than the current value indicates that the reverse may be true for ΔH_f^o (Bi, g) (66). Hence the derived mean bond energy, E (Bi - Me) = 33.8 ± 5.6 kcal $mole^{-1}$, may be considered as a minimum value. Long and Sackman (66) give 36.7 kcal $mole^{-1}$ as a possible alternative value for E (Bi - Me) but still favour the lower result.

The present work is the only kinetic study of trimethyl bismuth. The reproducibility of the results is good and the overall accuracy seems very satisfactory. The activation energy has been determined in a region in which the rate constant is independent of the total pressure in the system. The value

obtained for the activation energy may be accepted as a measure of the dissociation energy of the first methyl-bismuth bond. Hence D (Me_2Bi - Me) = 43.6 ± 0.4 kcal $mole^{-1}$.

Since the minimum sum of the three methyl-bismuth bond dissociation energies is 101.4 kcal $mole^{-1}$, D (Bi - Me) + D (MeBi - Me) = $D_3 + D_2$ must be greater than, or equal to, 57.8 kcal $mole^{-1}$. It is therefore possible to make some tentative deductions about D_2 and D_3. It was found that the rate of decomposition of zinc methyl was given by

$$\log_{10} k / sec^{-1} = 6.8 - (D/2.303RT) \text{ at 16 mm.}$$

k was found to be proportional to the overall pressure. Hence if it was assumed that toluene molecules established an energetic equilibrium on each collision with zinc methyl, the results could be expressed as

$$\log_{10} k / mole^{-1}\ cm^3\ sec^{-1} = 13.36 - (D/2.303RT)$$

This A factor is very close to that which would be expected for the decomposition of a diatomic molecule in a region in which its rate is proportional to the pressure. It is therefore reasonable to assume that A_3 for the decomposition of methyl bismuth is also 13.36 $mole^{-1}\ cm^3\ sec^{-1}$.

Now at 389°C $\log_{10}k_1 = -0.5$. Since there is no evidence that any of the methyl bismuth fails to decompose, $\log_{10}k_3$ must be $> +0.5$. If A_3 = 13.36 $mole^{-1}\ cm^3\ sec^{-1}$, then $E_3 = D_3 < 19.2$ kcal $mole^{-1}$. Hence $D_2 > 38.6$ kcal $mole^{-1}$. If D_2 were substantially greater than 38.6 kcal $mole^{-1}$, k_2 would be less than k_1 for A_1 is reasonably high. It is therefore likely that ΔH_f^0 (Bi, g) is not much greater than 49.7 kcal $mole^{-1}$.

Dimethyl ether

The heat of formation of gaseous dimethyl ether may be taken as -44.3 kcal $mole^{-1}$ (34). Using ΔH_f^0 (O) = 59.5 kcal $mole^{-1}$ (71) gives D (MeO - Me) + D (Me - O) = 168.8 kcal $mole^{-1}$.

Gray has calculated ΔH_f^o (CH_3O, g) = -0.5 kcal mole^{-1} (72). Therefore D (MeO - Me) = 76.3 kcal mole^{-1}.

Dimethyl sulphide

The heat of formation of gaseous dimethyl sulphide may be taken as -6.9 kcal mole^{-1} (34). Using ΔH_f^o (S, g) = 53.25 kcal mole^{-1} (34) gives D (MeS - Me) + D (Me - S) = 125.2 kcal mole^{-1}.

The heat of formation of the methyl sulphide radical has been estimated from the appearance potential of CH_3S^+ in dimethyl sulphide and in dimethyl disulphide (73). Hence D (CH_3S - CH_3) = 73.6 kcal mole^{-1}. By difference D (CH_3 - S) = 51.6 kcal mole^{-1}.

Methyl fluoride

The heat of formation of methyl fluoride may be taken as -59 $\pm$ 2 kcal mole^{-1} (74). Using 18.3 kcal mole^{-1} (34) for the heat of atomization of fluorine gives D (CH_3 - F) = 109.8 kcal mole^{-1}.

Methyl chloride

The heat of formation of methyl chloride may be taken as -19.6 kcal mole^{-1} (34). Using 29.0 kcal mole^{-1} (34) for the heat of atomization of chlorine gives D (CH_3 - Cl) = 81.1 kcal mole^{-1}.

Methyl bromide

The heat of formation of methyl bromide may be taken as -8.6 $\pm$ 0.5 kcal mole^{-1} (43). Using 26.7 kcal mole^{-1} (34) for the heat of atomization of bromine gives D (CH_3 - Br) = 67.8 kcal mole^{-1}. The value obtained from the pyrolysis of methyl bromide in a toluene carrier flow system is 67 kcal mole^{-1} (75).

Methyl iodide

The heat of formation of methyl iodide may be taken as 4.5 kcal mole^{-1} (43). Using 25.5 kcal mole^{-1} (34) for the heat of atomization of iodine gives D (CH_3 - I) = 53.5 kcal mole^{-1}.

B. SUGGESTIONS FOR FUTURE WORK EMPLOYING THE TOLUENE CARRIER TECHNIQUE

By referring to table 20 it is obvious that the covalent methyl derivatives of a considerable number of metals remain to be studied. However, the number of these to which the toluene carrier technique may be applied with reasonable hope of success is rather limited.

Dimethyl beryllium may be prepared and is sufficiently volatile for study in a flow system, vap. pres. 0.6 mm at 100°C and 5 mm at 130°C (76). However D (MeBe - Me) is likely to be too large to be studied by the toluene carrier technique. Dimethyl magnesium would appear to be too involatile to be studied in a flow system.

The methyl-boron bond is much too strong to be studied in a toluene carrier system. Trimethyl aluminium might be suitable but the experiments would have to be carried out in a temperature region in which an appreciable quantity of toluene would decompose. The accuracy of the results would therefore depend on the accuracy of the correction for the decomposition of toluene. It would be tempting to study dimethyl aluminium chloride rather than the trimethyl derivative in order to avoid possible complex reaction of the type observed in the study of trimethyl antimony. However, the first methyl-aluminium bond in the monochloride is likely to be even stronger than the corresponding bond in trimethyl aluminium. Hence the correction for the decomposition of toluene would probably be prohibitively large. The trimethyl compounds of gallium, indium and thallium may all be suitable for study. All three are readily prepared and have suitable vapour pressures (77). It is possible that the same complexities observed with trimethyl antimony might appear in the studies of the gallium and indium compounds. In the case of gallium it should be feasible, if necessary, to study dimethyl gallium chloride.

The behaviour of the group IV alkyls may not be simple. From

studies of stannous chloride and stannic chloride the following bond strengths have been estimated (78):

$$D\ (Cl_3Sn - Cl) = 76 \text{ kcal mole}^{-1} \qquad D\ (Cl_2Sn - Cl) = 42 \text{ kcal mole}^{-1}$$

$$\frac{D\ (ClSn - Cl) + D\ (Sn - Cl)}{2} = 97 \text{ kcal mole}^{-1}$$

Separate estimates of D (ClSn - Cl) and D (Sn - Cl) are not available. However, it would seem likely that the rupture of the $Cl_3Sn - Cl$ bond would not be the rate determining step of the overall decomposition of the four bonds. If this pattern of bond strengths carries over to the tetramethyl derivatives of the group IV metals, the decomposition of these compounds even in the presence of toluene would not be simple. Hence in the present work dimethyl tin dichloride was used in preference to the tetramethyl derivative. Dimethyl germanium dichloride should also be suitable for study but dimethyl lead dichloride would probably be too involatile. Trimethyl lead chloride could probably be used but it offers no obvious advantage over the tetramethyl compound.

The reinvestigation of the first methyl-antimony bond dissociation energy using dimethyl antimony chloride might prove worthwhile. The dimethyl compound may be readily prepared and should have a convenient vapour pressure, boiling point 155-160°C (77).

Nothing appears to be known about the dimethyl derivatives of selenium, tellurium and polonium. However, from their position in table 20 it is likely that all three alkyls would be suitable for study by the toluene carrier technique.

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543. *The Pyrolysis of* tert.-*Butyl Formate.*

By E. Gordon, S. J. W. Price, and A. F. Trotman-Dickenson.

The thermal decomposition of *tert.*-butyl formate into *iso*butene and formic acid has been studied in a static system at temperatures between 230° and 300° c. The decomposition is homogeneous and obeys first-order kinetics in its early stages; the rate constant is given by

$$\log_{10} k(\text{sec.}^{-1}) = 11{\cdot}1 - (34{,}600/2{\cdot}303RT)$$

The elimination of formic acid is probably a molecular process, as the addition of *cyclo*hexene has a very small effect on the rate. The rate of this reaction is reasonably related to the rates of similar decompositions.

Determinations of the rate constants of the decompositions of ethyl, *iso*propyl, and *tert.*-butyl chlorides, bromides, and acetates have all been reported in the literature.[1] No measurements have been reported on the decompositions of *tert.*-butyl formate although the ethyl and *iso*propyl derivatives have been investigated. The object of the present study was to fill this gap.

Experimental

Materials.—The *tert.*-butyl formate was specially prepared for use in this investigation by Dr. C. Barkenbus (University of Kentucky) according to his method.[2] The material was thoroughly degassed and stored in solid carbon dioxide. It was found that at temperatures appreciably above room temperature and in the absence of a drying agent the liquid rapidly decomposed, apparently into *iso*butene and formic acid. The *cyclo*hexene, which was also degassed, was freed from peroxides by shaking it with acidic ferrous sulphate solution.

Apparatus.—The decomposition was studied in a 385-c.c. Pyrex bulb attached to a conventional vacuum system by heated tubing; the total dead space was approximately 13 c.c. The empty bulb had a surface : volume ratio of 0·9 cm.$^{-1}$; when it was packed with fire-polished Pyrex tubing the ratio was 3·0 cm.$^{-1}$. The bulb was contained in a mercury-vapour jacket, whose temperature could be controlled readily by varying the pressure under which the mercury boiled. The temperature of the jacket was determined by reference to standard tables of the vapour pressure of mercury. The reaction was studied by following the change in pressure in the reaction vessel on a mercury manometer.

Procedure.—Runs were started by admitting a suitable quantity of the formate to the reaction vessel from the storage bulb; in some runs *cyclo*hexene was also added. Readings of the pressure in the vessel were then recorded at convenient intervals. Rate constants were determined from first-order plots of the logarithms of the pressure changes against time, based on the assumption that complete reaction corresponded to a doubling of the pressure. The logarithmic plots were strictly linear for the first 70—80% of the reaction at the higher temperatures but thereafter tended to curve slightly. No induction periods were observed.

Results and Discussion

tert.-Butyl formate was presumed to yield formic acid and *iso*butene as the primary products of the decomposition. This presumption is based upon the known ease with which these products are formed in the liquid in the presence of a trace of acid and upon the analogy with the decompositions of the other formates. It was difficult to check this by analysis, because of the rapidity with which the liquid decomposed. Several experiments were done with a trap system in which the formate and formic acid were condensed in a trap cooled in solid carbon dioxide and the *iso*butene in a trap cooled in liquid oxygen.

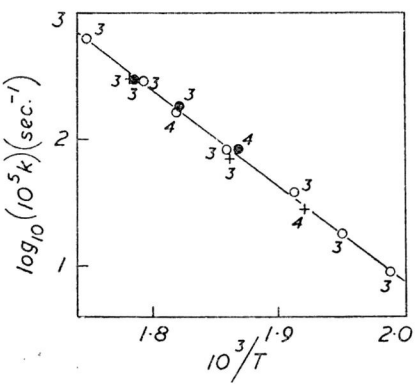
The *iso*butene was then transferred back into the reaction system and its pressure measured. The percentage decomposition based on the formation of *iso*butene was then calculated. The results of a series of runs at 251° were :

Percentage decomposition by pressure rise	11·4	19·0	30·0	41·0
Percentage decomposition by *iso*butene	7·9	14·4	30·0	39·0

The method of analysis was not very satisfactory, but there appears to be little doubt as to the nature of the decomposition. Runs which were followed for many half-lives never yielded a pressure greater than twice the initial pressure. This is evidence that the formic acid does not decompose at these low temperatures.

The linearity of the logarithmic plots demonstrated the first-order nature of the decomposition which was confirmed by runs with different initial pressures of the formate between 3·8 and 10·3 cm. No systematic trend or variation of the rate constants outside the limit of experimental error was observed.

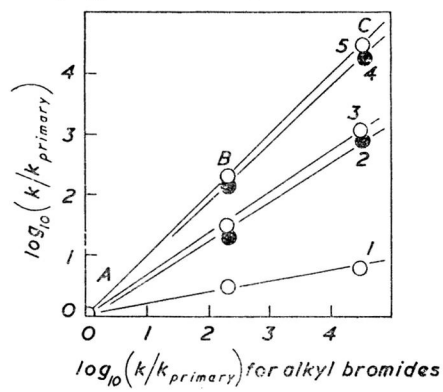
FIG. 1. *Arrhenius plot for the thermal decomposition of* tert.*-butyl formate.*



○ Unpacked vessel. ● Packed vessel. + Unpacked vessel with the addition of *cyclo*hexene.

The figures by the circles indicate the number of runs averaged to obtain each point.

FIG. 2. *The relation between the rates of the molecular decompositions of various ethyl,* iso*propyl, and* tert.*-butyl derivatives.*



A, Ethyl. *B*, *iso*Propyl. *C*, *tert.*-Butyl.

1, Hydrides. 2, Formates. 3, Acetates. 4, Chlorides. 5, Bromides.

Fig. 1 is an Arrhenius plot of the rate constants for the thermal decomposition. The best straight line was calculated by the method of least squares giving equal weight to each run : the points shown in the Figure are the mean values obtained at each temperature. The results are best expressed by

$$\log_{10} k(\text{sec.}^{-1}) = 11{\cdot}1 - [(34{,}600 \pm 900)/2{\cdot}303\boldsymbol{R}T]$$

Two facts showed the decomposition to be homogeneous. First, no conditioning of the reaction vessel was needed before reproducible results were obtained. Second, packing the reaction vessel did not affect the rate constants, as is shown in Fig. 1 where the mean results obtained in the packed vessel are plotted.

The absence of an induction period and the negligible effect of packing the vessel indicate that the decomposition is molecular and does not involve free radicals. This was confirmed by adding *cyclo*hexene to the system; 20—50% of *cyclo*hexene appeared to reduce the rate of decomposition very slightly, but the lowering was of the same order as the experimental scatter. The results obtained with *cyclo*hexene are also shown in Fig. 1.

The activation energy of this decomposition is markedly lower than those for the decomposition [3] of ethyl (44·1 kcal. mole^{-1}) and of *iso*propyl formate (44·0 kcal. mole^{-1}). However, it is often more enlightening to compare the variation of the rate constants of a

series of reactions rather than their A factors and activation energies. Such a comparison is made for several series of ethyl, *iso*propyl, and *tert.*-butyl esters in Fig. 2. All of these decompositions are thought to be molecular. The rate constants are corrected to 380° and are expressed in terms of the rate constant of the ethyl ester which has been assigned the value unity. In the figure the logarithms of the rate constants are plotted against the logarithms of the rate constants for the decomposition of the ethyl, *iso*propyl, and *tert.*-butyl bromides. The line labelled " hydrides " represents the rate constants for the decompositions of ethyl bromide, *n*-propyl bromide, and *iso*butyl bromide. It is evident that the same factors control the rates of each series of reactions.

We are greatly indebted to Dr. C. Barkenbus for the sample of the *tert.*-butyl formate and to the British Petroleum Company for a grant.

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[1] For full references see Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, and Maccoll and Thomas, *Nature*, 1955, **176**, 392.
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749. *The Thermal Decomposition of* cyclo*Pentyl Bromide.*

By S. J. W. Price, R. Shaw, and A. F. Trotman-Dickenson.

The thermal decomposition of *cyclo*pentyl bromide into *cyclo*pentene and hydrogen bromide has been studied in a static system at temperatures between 300° and 360° c. The decomposition is homogeneous and obeys first-order kinetics in its early stages; the rate constant is given by

$$k = 10^{11.9}\exp(-41{,}400/\boldsymbol{R}T)\ \text{sec.}^{-1}$$

The elimination of hydrogen bromide is probably a molecular process, as the addition of *cyclo*hexene has no effect upon the rate.

During the past few years the thermal decomposition of many aliphatic bromides has been investigated, chiefly by Maccoll and his collaborators.[1,2] The majority of these bromides, in the presence of an inhibitor, decompose by a four-centre molecular elimination mechanism into hydrogen bromide and an olefin. One of the compounds which has been found to react in this way is *cyclo*hexyl bromide.[3] The rate constant for its decomposition is given by the Arrhenius equation

$$k = 10^{13.5}\exp(-46{,}100/\boldsymbol{R}T)\ \text{sec.}^{-1}$$

The investigation of the decomposition of *cyclo*pentyl bromide was undertaken in the hope that a knowledge of the rate factors, A and E in the Arrhenius equation, would throw light on the features of molecules which determine the rates of molecular elimination reactions. In particular, it was thought that the different degrees of flexibility of the carbon rings might influence the rates.

Experimental

Materials.—The *cyclo*pentyl bromide was a gift from the Michigan Chemical Company. It was degassed and purified by bulb-to-bulb distillation. No significant quantities of impurity could be detected by vapour-phase chromatography. The *cyclo*hexene, which was similarly degassed, was freed from peroxides by shaking with acid ferrous sulphate solution.

Apparatus.—The decomposition was studied in a bulb of 385 c.c. capacity attached to a conventional vacuum-system by tubing with a total dead space of approx. 13 c.c. The bulb was contained in a mercury-vapour jacket, whose temperature could be readily controlled by varying the pressure under which the mercury boiled. The temperature of the jacket was determined by reference to standard tables of the vapour pressure of mercury. The reaction was studied by following the change in pressure in the reaction vessel on a mercury manometer. It was found that the hydrogen bromide formed did not appreciably attack the mercury during a run, for the reaction vessel was separated from the manometer by about 30 cm. of 2-mm. capillary tubing.

Procedure.—Runs were started by admitting a suitable quantity of the bromide to the reaction vessel from a storage bulb; in some runs a quantity of *cyclo*hexene was also added. Readings of the pressure in the vessel were then recorded at convenient intervals. At the end of some of the runs the quantity of hydrogen bromide formed was determined analytically. It was found that inexplicably erratic and high results were usually obtained when the unseparated products were titrated with alkali, so the following procedure was adopted. First, the products were condensed in a side bulb, and the hydrogen bromide was separated by low-temperature distillation. Its amount was then determined by pressure measurements and by dissolving the gas in water and titrating the solution for hydrogen and halide ions. The results of the three determinations were always in excellent agreement. When a proper correction was made for the dead space it was found that the analytical results agreed well with degrees of decomposition deduced from the pressure measurements.

Rate constants were determined in the usual way from first-order plots of the logarithms of the pressure changes against time. The logarithmic plots were strictly linear for the first third of the reaction but thereafter tended to curve. The curvature was probably caused by the increasing importance of the back reaction. The rate constants for a few runs were calculated from the full expression for a first-order reaction opposed by a second-order reaction. The rate constants obtained in this way differed by only about 10% from those calculated by applying the equation for a simple first-order reaction to the observations made during the first third of the decomposition. All the rate constants reported here were determined by the less tedious procedure.

All runs showed short induction periods. Their lengths corresponded roughly to the time needed for 2—3% of the bromide to decompose. The presence of *cyclo*hexene appeared to shorten the induction periods slightly.

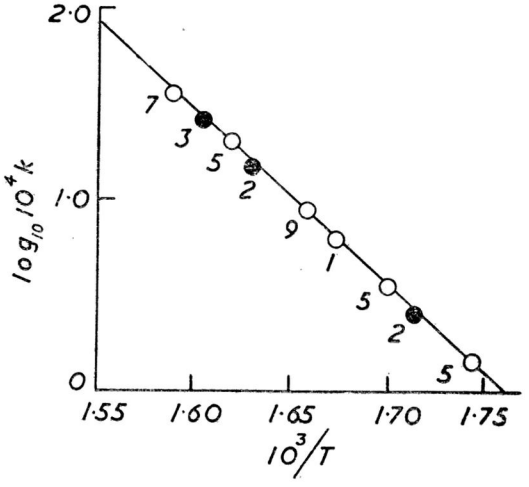
Results and Discussion

Preliminary runs in a clean-walled reaction vessel gave first-order rate constants which decreased slowly but steadily from run to run. Maccoll and his collaborators observed similar behaviour with other bromides and attributed the effect to heterogeneous processes. They therefore seasoned their reaction vessels by decomposing allyl bromide in them. This remedy proved effective for *cyclo*pentyl bromide also. It was used after any occasion on which air had been admitted to the reaction vessel. Incidentally, Maccoll's rate constant [4] for the decomposition of allyl bromide was confirmed.

The first-order nature of the decomposition was demonstrated by studying it with various initial pressures of *cyclo*pentyl bromide. The results obtained for a typical series of runs, all corrected to 356·5°, were as follows :

Initial pressure (mm.)	38·0	49·6	59·6	79·5	94·0	105·0	107·5
10^3k (sec.$^{-1}$)	3·48	3·48	3·39	3·66	3·53	3·80	3·78

The very small effect on the rate constant of the addition of *cyclo*hexene can be seen from the following Table, in which the observed rate constants are compared with those



Arrhenius plot for the thermal decomposition of cyclo*pentyl bromide.*

○ Unpacked reaction vessel.
● Packed reaction vessel.

The figures by the circles indicate the number of runs averaged to obtain each point.

calculated from the Arrhenius equation. The variations in the rates are of the same order as the experimental error.

*cyclo*Hexene (mm.)	20·0	30·0	10·0	9·0	40·0
*cyclo*Pentyl bromide (mm.)	60·0	72·5	64·0	48·2	38·0
Temp.	300·7°	315·2°	331·3°	344·5°	365·5°
k (obs.)/k (calc.)	1·05	0·95	1·02	0·98	0·91

Seven runs were carried out with the reaction vessel packed with Pyrex tubing so that the surface/volume ratio was increased from 0·9 to 2·0 cm.$^{-1}$. The results of these runs are distinctively plotted alongside the other results in the Figure. It can be seen that there is no evidence for any heterogeneous contribution to the reaction in an aged vessel.

The results of all the runs are shown on an Arrhenius plot in the Figure. The Arrhenius equation was derived by a least-squares treatment of the results for all the individual runs. The results are best expressed by the equation :

$$k = 10^{11\cdot9}\exp(-41{,}400/\boldsymbol{R}T)\ \text{sec.}^{-1}$$

Our experiments indicate that this is the rate constant for the homogeneous gas-phase molecular elimination of hydrogen bromide from *cyclo*pentyl bromide.

The rate constant for this decomposition at 380° (0·010 sec.$^{-1}$) is very slightly greater than that (0·008 sec.$^{-1}$) for the similar decomposition of *cyclo*hexyl bromide. This conclusion is of interest in view of a recent important suggestion [5] that the rate constants for the molecular elimination of hydrogen bromide from aliphatic bromides should run parallel to the rate constants for the elimination of bromide ions from the bromides by the S_N1 mechanism. No measurements on the rates of the S_N1 reactions of *cyclo*pentyl and *cyclo*hexyl bromide have been reported. It has been found,[6] however, that the S_N1 reaction of 1-methyl*cyclo*pentyl chloride in 80% aqueous ethanol at 25° is 125 times more rapid than the corresponding reaction of 1-methyl*cyclo*hexyl chloride. Evidently the parallelism between the rates of the S_N1 reactions and the molecular eliminations breaks down in this instance. Probably the cause is the different natures of the strains in the two types of transition states.

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[1] Harden and Maccoll; *J.*, 1955, 2454, and ref. 4.
[2] For similar reactions, see Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.
[3] Green and Maccoll, *J.*, 1955, 2449.
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METAL-CARBON BONDS

PART 1.—THE PYROLYSES OF DIMETHYL MERCURY AND DIMETHYL CADMIUM

METAL-CARBON BONDS

PART 1.—THE PYROLYSES OF DIMETHYL MERCURY AND DIMETHYL CADMIUM

BY S. J. W. PRICE AND A. F. TROTMAN-DICKENSON
Chemistry Dept., The University, Edinburgh

Received 12th February, 1957

The thermal decompositions of dimethyl mercury and dimethyl cadmium have been studied by the toluene-carrier technique between 465° and 608° C, and 469° and 571° C, respectively. The progress of the reactions were followed by measuring the hydrogen, methane, ethylene and ethane formed. The results obtained with dimethyl mercury may be expressed by

$$\log_{10} k/\text{sec}^{-1} = 13{\cdot}1 - (50{,}100 \pm 1000/2{\cdot}303\ \boldsymbol{RT}) \text{ at 16 mm},$$

in excellent agreement with previous determinations and with dimethyl cadmium by

$$\log_{10} k/\text{sec}^{-1} = 11{\cdot}9 - (45{,}800 \pm 1000/2{\cdot}303\ \boldsymbol{RT}) \text{ at 18 mm}.$$

In both cases k was markedly dependent upon the total pressure. The activation energies may be equated with the heats of reactions (1):

$$X(CH_3)_2 = XCH_3 + CH_3. \quad (1)$$

Hence, by thermochemistry, the heat of reaction

$$XCH_3 = X + CH_3 \quad (2)$$

is 7·2 kcal mole^{-1} for mercury and 21 kcal mole^{-1} for cadmium.

Little is known of the dissociation energies of the metal–carbon bonds in the metallic alkyls. This paper describes an attempt to determine the dissociation energies of the bonds in dimethyl mercury and dimethyl cadmium by a kinetic method. It is hoped that information on other compounds will be reported in later papers. The reasons for selecting these compounds for study may be briefly stated. Methyl derivatives were selected so that the reactions of the radicals released on decomposition might be as simple as possible. Furthermore there exists a considerable body of reliable information on methyl reactions. The mercury compound was selected because it has been the subject of a comprehensive study by a very similar method [1] to the one employed in the present work. There is excellent agreement between the results obtained in the two investigations. Dimethyl cadmium was selected because of its great similarity to dimethyl mercury.

EXPERIMENTAL

MATERIALS

DIMETHYL MERCURY was prepared from mercuric chloride and methyl magnesium iodide.[2] The crude product was dried ($CaCl_2$) and twice fractionated. The fraction boiling at 91·8° C (corrected) was stored under vacuum at room temperature. Analysis by gas chromatography showed a maximum of 0·1 % impurity.

DIMETHYL CADMIUM was prepared by the action of anhydrous cadmium chloride on methyl magnesium iodide.[3] The chloride was added from a conical flask connected to the reaction vessel by a short length of 1-in. diam. rubber tubing. The crude product was twice fractionated and the fraction boiling at 70·4° C at 240 mm was stored under vacuum at − 183° C.

TABLE 1.—THE PYROLYSIS OF DIMETHYL ZINC

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	H_2	$ZnMe_2$	k_1 (sec^{-1})
				10^{-4} mole				
1	597	22·4	6·74	14·40	0·73	—	18·2	0·246
2	597	12·5	9·00	11·70	1·25	—	17·1	0·179
3	597	7·2	10·85	9·46	2·41	—	17·3	0·139
4	597	28·5	4·91	13·50	0·40	—	17·4	0·280
5	597	16·0	4·73	11·00	0·57	—	17·9	0·218
6	597	9·8	5·66	9·34	0·94	—	16·8	0·187
7	597	26·5	3·53	10·70	0·27	—	17·1	0·273
8	597	6·6	6·30	8·58	1·50	—	18·0	0·154
9	597	16·5	1·13	3·72	0·04	—	18·3	0·208
11	597	5·8	1·50	4·04	0·13	—	18·2	0·170
12	597	4·6	1·44	2·76	0·19	—	19·1	0·146
13	597	10·0	1·17	3·60	0·13	—	18·4	0·190
14	597	16·5	0·98	12·36	0·61	—	72·0	0·212
15	597	16·5	0·97	6·32	0·16	—	35·5	0·214
17	648	16·6	0·94	12·00	0·20	0·10	19·0	0·988
18	672	16·8	0·89	16·60	0·28	0·15	20·0	1·94
19	672	16·3	0·90	16·20	0·31	0·15	19·6	1·92
20	672	5·8	1·11	13·85	0·65	0·10	19·5	1·29
21	672	5·3	1·15	13·60	0·70	0·10	19·2	1·26
22	672	16·4	0·91	15·80	0·25	0·15	18·1	2·10
23	701	16·6	0·86	18·20	0·30	0·30	18·5	4·12
24	701	16·5	0·86	17·10	0·31	0·30	17·7	3·75
25	701	16·0	0·87	18·10	0·37	0·30	18·5	4·12
29	624	16·0	0·93	4·90	0·05	—	13·9	0·47
30 [a]	672	16·3	0·75	14·00	0·26	0·10	18·4	1·90
31 [a]	624	16·2	0·84	7·30	0·28	—	21·1	0·517
32 [a]	672	16·1	0·78	14·50	0·32	0·10	18·9	1·89
33 [a]	701	16·1	0·74	17·40	0·39	0·20	18·8	3·40
40	658	16·3	1·06	12·55	0·29	0·15	17·0	1·27
41	658	16·3	0·99	12·10	0·21	0·15	17·0	1·27
42	573	16·0	1·10	1·18	0·01	—	12·9	0·090
43	700	16·6	0·90	17·30	0·23	0·30	17·1	3·60
								k_2 (sec^{-1})
26	730	16·6	1·01	19·9	0·44	0·60	18·2	0·147
27	730	16·3	1·04	19·9	0·47	0·60	18·7	0·122
34 [a]	755	16·8	0·72	21·6	0·56	3·00	19·7	0·200
35 [a]	793	16·8	1·28	25·8	1·40	4·10	19·4	0·420
36 [a]	793	16·4	0·73	23·3	0·90	6·90	19·1	0·450
37 [a]	825	16·0	0·71	25·3	1·02	11·90	18·7	0·670
38	827	16·0	0·90	24·7	0·97	11·90	17·8	0·590
39	762	16·3	0·88	19·5	0·49	2·70	16·7	0·250
44	758	16·1	0·89	19·1	0·60	2·20	17·2	0·210
45 [c]	783	15·8	0·89	27·8	1·52	4·70	20·6	0·320
47	783	6·3	0·60	20·4	0·80	2·60	17·7	0·146
48 [b]	783	9·5	1·27	22·5	1·03	3·20	17·2	0·196
49	783	15·8	0·95	25·8	0·77	5·70	16·9	0·303
50	783	16·2	0·97	7·96	0·31	3·04	5·7	0·350
51 [c]	825	16·2	0·91	16·85	0·71	8·95	11·2	0·660

[a] runs in packed reaction vessels

[b] complete analysis (10^{-4} mole) CH_4: 22·5; C_2H_6: 0·31; H_2: 3·20; C_2H_4: 0·72;

[c] run 20 min;

t is the contact time.

The quantities given in the table are total (uncorrected) amounts of products.

The XCH_3 radical formed by the other two alkyls decomposed so rapidly that it could be assumed that two methyl radicals were formed from each molecule that underwent reaction (1). However, it was soon found that this assumption was not tenable for dimethyl zinc. It appeared that even as high as 670° C reaction (2) did not occur to any great extent under the prevailing conditions. Only above 730° C was reaction (2) an important source of methyl radicals. Accordingly the decompositions of dimethyl zinc and methyl zinc were treated as successive reactions. At the highest temperatures all the dimethyl zinc was converted to methyl zinc in a very small fraction of the contact time. The rate of decomposition of methyl zinc could then readily be determined; the only interference came from the decomposition of the toluene carrier. At low temperatures the decomposition of methyl zinc was negligible and the decomposition of dimethyl zinc could be simply treated as a unimolecular reaction yielding one methyl radical. At intermediate temperatures the appropriate treatment for successive reactions of comparable rate had to be applied. The detailed methods of calculating were as follows.

(*a*) THE HIGH TEMPERATURE RANGES (k_2)

The amount of CH_4 produced was found by analysis of the $CH_4 + H_2$ fraction, a correction then had to be applied for the CH_4 produced by the decomposition of the toluene carrier. This correction was obtained from Szwarc's [4] expression for the rate constant

$$\log_{10} k/\text{sec}^{-1} = 13{\cdot}5 - (77500/2{\cdot}303\,\boldsymbol{R}T),$$

assuming that the ratio of $[H_2]/[CH_4]$ produced was in the ratio of 1·5/1. An experiment on the pyrolysis of pure toluene at 783° C yielded a value of k in good agreement with this expression; the ratio $[H_2]/[CH_4]$ was exactly 1·5/1. The percentage decomposition of methyl zinc was then equal to

$$\frac{(\text{corrected moles of methane} + 2 \times \text{moles of ethane}) \times 100}{\text{moles of dimethyl zinc used}} - 100.$$

First-order rate constants were calculated from these percentage decompositions. This calculation implies that the dimethyl zinc is converted to methyl zinc immediately it enters the reaction zone.

(*b*) THE LOW TEMPERATURE RANGE (k_1)

k_1 was calculated from the usual formula for successive unimolecular reactions:

$$CH_4 + 2C_2H_6 = Zn(CH_3)_2 \text{ used} \left\{ 2 - \frac{k_1}{k_1 - k_2} [\exp(-k_1 t) + \exp(-k_2 t)] \right\}.$$

The equation was solved for k_1 by the method of successive approximations. The values obtained were not very sensitive to the value selected for k_2 as the percentage decomposition of the $ZnCH_3$ was of the order of 1 % at 597° C, 3 % at 648° C and 6 % at 710° C.

The method of calculation depends upon the assumption that the zinc methyl radicals which do not decompose do not react in any other way while within the decomposition reaction zone. Presumably they eventually form stable saturated molecules in some cooler portion of the apparatus. No alternative assumption that was in accordance with the experimental findings and involved plausible reactions could be discovered.

The ratios $k_3/k_4^{\frac{1}{2}}$ were determined in the usual way assuming that the reactions took place uniformly throughout the reaction zone.

The rate constants k_1, k_2 and the ratio $k_3/k_4^{\frac{1}{2}}$ were found to be markedly dependent upon the total pressure in the reaction system, as shown in fig. 1. This was not due to any heterogeneous reaction. Packing the vessel with silica tubing

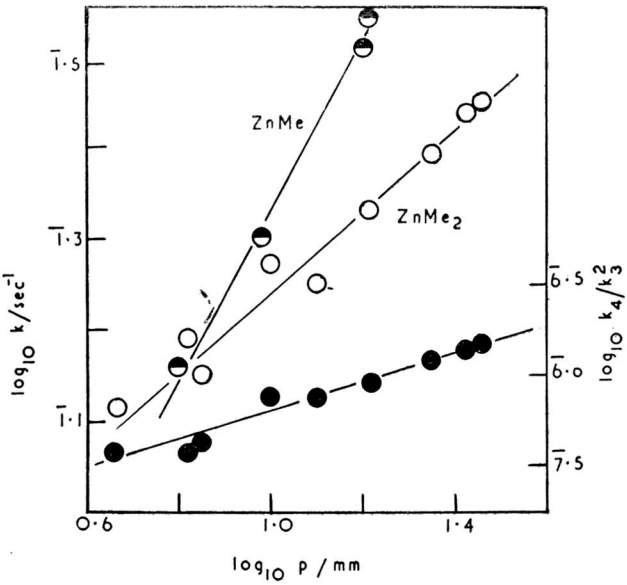
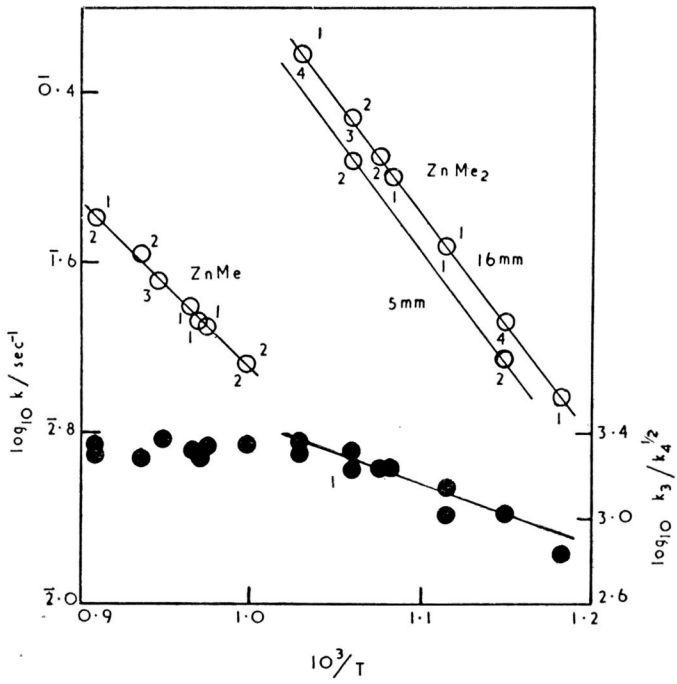


FIG. 1.—The variation of the rate constants with pressure. Open circles: the decomposition of dimethyl zinc (597° C); ◓ the decomposition of methyl zinc (783° C); full circles: k_4/k_3^2 (597° C).



FIK. 2.—Arrhenius plots for the decomposition of dimethyl and methyl zinc and the reaction of methyl radicals with toluene. The figures beside the points indicate the number of runs averaged to obtain the value plotted; superscripts, runs in a packed vessel; subscripts, runs in an unpacked vessel; full circles: $k_3/k_4^{\frac{1}{2}}$.

so as to increase the surface-volume ratio by a factor of five had no appreciable effect on the rates as is shown in fig. 2. So that the rate constants might be comparable, all that were determined in the region of 16 mm pressure were corrected empirically to 16 mm pressure. The resulting values of the rate constants, together with four determined at 5 mm pressure, are plotted on an Arrhenius diagram (fig. 2). At 16 mm total pressure:

$$\log_{10} k_1/\text{sec}^{-1} = 11{\cdot}25 - (47200 \pm 1000/2{\cdot}303\, \boldsymbol{R}T)$$

$$\log_{10} k_2/\text{sec}^{-1} = 6{\cdot}86 - (35000/2{\cdot}303\, \boldsymbol{R}T),$$

and at low temperatures

$$\log_{10} (k_3/k_4)/\text{mole}^{-\frac{1}{2}}\,\text{cm}^{\frac{3}{2}}\,\text{sec}^{-\frac{1}{2}} = 6{\cdot}30 - (13000/2{\cdot}303\, \boldsymbol{R}T).$$

At 5 mm total pressure:

$$\log_{10} k_1/\text{sec}^{-1} = 11{\cdot}03 - (47300/2{\cdot}303\, \boldsymbol{R}T).$$

The values of k_1 and A_1 at infinite pressure could only be determined from experiments over a far wider range of pressures than could be reached with our apparatus. Reaction (2) was apparently studied in its "second-order" region; that is, k_2 is directly proportional to the total pressure as is shown in fig. 1. If toluene and zinc methyl are equally effective in energy transfer, then the rate constant may be written

$$\log_{10} k_2/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 13{\cdot}36 - (35000/2{\cdot}303\, \boldsymbol{R}T).$$

The values of $k_3/k_4^{\frac{1}{2}}$ obtained at high temperatures are clearly not consistent with those at lower temperatures. The reliability of both sets of determinations of the rate constants is doubtful because of the difficulty of defining the reaction zone. However, the low-temperature results and the variation with pressure are in excellent agreement with those obtained with dimethyl mercury and dimethyl cadmium.[1]

The tests which can be applied in a flow system to demonstrate the adequacy of a mechanism are rather limited. This is especially so when, as in the present case, the rates of the unimolecular reactions are partially determined by the rate of energy transfer. Those tests which were applicable confirmed the mechanism.

From the quantity of methane (corrected) and ethane formed it was deduced that 98 % of the possible number of methyl radicals were released in passing dimethyl zinc through the system at 812° C with a contact time of 6 sec. The proportion that may be derived from the rate constants given above is 98·5 %. This is direct evidence that reaction (6)

$$C_6H_5CH_2 + CH_3 = C_6H_5C_2H_5 \qquad (6)$$

is unimportant. As a further check the contact time was varied by approximately a factor of ten in one series of runs (1-15).

The rather large quantities of hydrogen formed at the higher temperatures were not all the products of the unimolecular decomposition of toluene. It is possible that they were formed by the decomposition of benzyl radicals and of dibenzyl. A small quantity is probably formed by the decomposition of ethane into ethylene and hydrogen. For this reason the ethylene was treated as ethane in calculating the rate constants. If this is unjustifiable the error introduced is small because the C_2 fraction is much smaller than the amount of methane.

The apparent activation energy of a unimolecular reaction is a function of the pressure at which it is determined if the rate of the reaction is itself a function of pressure. However, for small molecules the difference between the activation energies determined in the "second-order" region and at high pressures is not great. Until more information is available it is reasonable to suppose that the activation energies found at 16 mm differ little from the high-pressure values. These activation energies may be equated with the heats of reaction if the back

reactions (combination of atoms and radicals) have no activation energies. On this assumption the following values of the bond strengths may be obtained:

$$D(CH_3 - ZnCH_3) = D_1 = 47{\cdot}2 \pm 1 \text{ kcal mole}^{-1},$$

$$D(Zn - CH_3) = D_2 = 35 \text{ kcal mole}.$$

No useful estimate of the probable error of the second value can be made (3 to 5 kcal mole^{-1} is probably a fair figure).

Hence $$D_1 + D_2 = 82 \text{ kcal mole}^{-1}.$$

This quantity may also be derived from the heat of formation of dimethyl zinc [5] (— 13·3 kcal mole^{-1}), of the zinc atom [6] and of the methyl radical (based upon $D(CH_3 - H) = 102{\cdot}5$ kcal mole^{-1}). From these quantities

$$D_1 + D_2 = 82{\cdot}9 \text{ kcal mole}^{-1}.$$

The agreement with the kinetic estimate is meaninglessly good as errors of ± 4 kcal mole^{-1} should be assigned to both figures. However, they do indicate that when dimethyl zinc decomposes, the zinc atom is released in its ground state.

The results which have been obtained from our studies of the pyrolysis of the dimethyl compounds of the group 2 metals may be summarized as follows:

	D_1	$D_1 + D_2$ kcal mole^{-1}	D_2	D(X—H)[6]
$Hg(CH_3)_2$	50	57·3 *	7	9
$Cd(CH_3)_2$	46	66·8 *	21	16
$Zn(CH_3)_2$	47	82 (82·9) *	35	20

* from thermochemistry assuming $D(CH_3—H) = 102{\cdot}5$ kcal mole^{-1}.

The difference between the values of D_1 and D_2 for the compounds of the metal of group 2 has already been discussed by Skinner.[7] Gowenlock, Polanyi and Warhurst [8] have considered in detail the strengths of the bonds in dimethyl mercury. A full discussion of the present results may be postponed until experimental work is available on the alkyls of other metals.

It is interesting to note that for cadmium and zinc $D(X—CH_3)$ is greater than $D(X—H)$ whereas the bonds formed by methyl radicals are usually 10 to 20 kcal mole^{-1} weaker than the equivalent bonds formed by hydrogen atoms. There seems some evidence that the same reversal of strength occurs for $D(CH_3—CO)$, 20 kcal mole^{-1} [9] and $D(H—CO)$, 14 kcal mole^{-1}; [10] there is, however, considerable doubt about the second figure.[11]

We are indebted to the British Petroleum Company for a grant.

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METAL-CARBON BOND
PART 2—THE PYROLYSIS OF DIMETHYL ZINC

METAL-CARBON BONDS

PART 2.—THE PYROLYSIS OF DIMETHYL ZINC

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The thermal decomposition of dimethyl zinc has been studied by the toluene carrier technique between 573° and 827° C. The progress of the reaction was followed by measuring the hydrogen, methane, ethylene and ethane formed. The decomposition occurs in two steps

$$Zn(CH_3)_2 = ZnCH_3 + CH_3 \quad (1)$$

followed by

$$ZnCH_3 = Zn + CH_3 \quad (2)$$

$$\log_{10} k_1/\text{sec}^{-1} = 11{\cdot}25 - (47200 \pm 1000/2{\cdot}303\,\boldsymbol{RT}) \text{ at 16 mm},$$

$$\log_{10} k_2/\text{sec}^{-1} = 6{\cdot}8 - (35000/2{\cdot}303\,\boldsymbol{RT}) \text{ at 16 mm}.$$

Both rate constants are markedly dependent on the pressure in the system. The activation energies may be equated with the bond strengths, hence $D_1 = 47{\cdot}2$, $D_2 = 35$, $D_1 + D_2 = 82$ kcal mole^{-1}. Thermochemistry yields $D_1 + D_2 = 82{\cdot}9$ kcal mole^{-1}.

The first paper in this series [1] described the thermal decomposition of dimethyl mercury and dimethyl cadmium. The present paper on the decomposition of dimethyl zinc completes the study of the alkyls of suitable group 2 metals. No previous investigation of this pyrolysis has been reported.

EXPERIMENTAL

MATERIALS

Dimethyl zinc was prepared by the reaction of methyl iodide with a freshly prepared zinc-copper couple.[2, 3] Traces of methyl iodide were removed from the crude product by passing the vapour five times over a fresh portion of the couple at 150° C. A fraction boiling between 46·4° and 46·5° C at 758 mm was collected. Three weighed samples were decomposed with air + water or air alone and the residual methyl iodide determined by gas chromatography. Not all the methyl iodide was removed but it amounted to considerably less than 1 % of the samples. The alkyl was stored under vacuum at − 196° C.

APPARATUS

The apparatus and procedure were essentially the same as those employed in part 1.[1]

RESULTS AND DISCUSSION

The complete experimental results are given in table 1. Their satisfactory interpretation depends upon the selection of the correct mechanism for the system.

It was expected that the mechanism for the decomposition of dimethyl zinc would be very similar to that for the decomposition of dimethyl mercury and dimethyl cadmium:

$$Zn(CH_3)_2 = ZnCH_3 + CH_3 \quad (1)$$

$$ZnCH_3 = Zn + CH_3 \quad (2)$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \quad (3)$$

$$2CH_3 = C_2H_6 \quad (4)$$

$$2C_6H_5CH_2 = (C_6H_5CH_2)_2. \quad (5)$$

TOLUENE was purified by passing sulphur-free toluene twice through a quartz tube at 870° C and 25 mm pressure. The product was then fractionated and thoroughly degassed before use.

APPARATUS

The experiments were carried out in a typical toluene-carrier flow system [4] in which the reaction zone was 155 cm^3. In the runs with the vessel packed with quartz tubing the surface area in the zone was increased by a factor of five and its volume reduced to 127 cm^3. The reaction products were separated in a standard low-temperature trap system and measured in a gas burette. The hydrogen was estimated by oxidation in a copper oxide tube. The ethylene content of the ethane was determined by gas chromatography (we are much indebted to Mr. J. Falconer for these analyses).

Except as noted in the tables, the flow of alkyl lasted for 30 min during each run, preceded and followed by 5-min flow of toluene alone. Contact times were calculated on the assumption that the ideal gas law was obeyed by all substances within the reaction zone. The rate constants were calculated from the usual first-order equation.

RESULTS AND DISCUSSION

A possible mechanism for the decomposition of the metallic alkyls in the presence of toluene is as follows: [1]

$$X(CH_3)_2 = XCH_3 + CH_3 \quad (1)$$

$$XCH_3 = X + CH_3 \quad (2)$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \quad (3)$$

$$2CH_3 = C_2H_6 \quad (4)$$

$$2C_6H_5CH_2 = (C_6H_5CH_2)_2. \quad (5)$$

The results contained in tables 1 and 2 may be discussed in terms of this mechanism, in which it is assumed that reaction (2) is very much faster than reaction (1).

According to the mechanism the number of moles of ethane + half the number of moles of methane formed during a run should be equal to the number of moles of the alkyl which have decomposed. Using this measure of the progress of the

TABLE 1.—THE PYROLYSIS OF DIMETHYL MERCURY

run no.	temp. (° C)	contact time (sec)	toluene (mm)	$HgMe_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)
1 [a]	560	1·35	17·0	4·55	5·46	0·38
2 [a]	560	1·37	16·1	12·00	12·50	1·57
3 [a]	543	1·39	16·1	14·90	11·50	1·49
4 [a]	542	1·44	16·0	12·90	10·06	1·15
5 [a]	585	1·33	16·5	13·40	15·50	2·06
6 [a]	531	1·41	16·3	15·30	8·82	1·09
7 [a]	505	1·45	16·2	15·20	3·90	0·39
8 [a]	483	1·52	16·2	14·20	1·60	0·12
9 [a]	465	1·51	16·1	16·20	0·71	0·04
10 [a]	466	1·52	16·1	14·60	0·69	0·05
11 [c]	608	·405	16·0	3·42	4·49	0·19
12 [b, c]	585	·425	16·2	6·71	7·50	0·48
13 [c]	573	·459	16·1	7·80	6·59	0·58
14 [c]	562	·435	16·1	10·30	6·80	0·56
15 [c]	562	·426	16·5	10·40	7·12	0·58
16 [c]	562	·425	16·1	21·10	12·40	1·61
17	543	1·72	10·3	15·60	10·30	2·30
18	543	2·28	4·4	12·10	6·36	2·70
19 [c]	543	1·13	25·5	14·10	12·00	1·16

[a] H_2 1 ± 0·5 %; C_2H_4; *ca.* 0·5 % of C_1 and C_2 fractions;
[b] H_2 nil; [c] length of run 20 min.

TABLE 2.—THE PYROLYSIS OF DIMETHYL CADMIUM

run no.	temp. (° C)	contact time (sec)	toluene (mm)	$CdMe_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)
1	552	0·93	15·6	1·52	0·88	0·11
4	552	1·10	15·6	18·70	12·60	1·55
7	552	1·30	19·2	9·20	8·90	0·57
8	552	1·02	18·7	48·80	28·50	6·70
9	552	1·23	5·2	27·40	10·80	5·64
10	552	1·03	24·4	9·66	10·50	0·41
12	552	0·59	21·8	25·60	15·90	1·15
13	552	0·74	13·2	17·20	8·60	1·28
15	552	0·63	15·4	26·60	14·40	1·74
16	552	0·68	13·8	21·60	11·10	1·55
17 *d*	552	0·83	14·4	14·90	8·40	1·34
18	552	1·72	18·0	19·30	18·60	2·22
19	552	1·73	18·6	19·30	17·80	2·31
20	552	0·62	18·6	16·30	8·85	0·87
21	552	1·37	20·0	3·78	3·94	0·16
22	552	2·13	6·3	18·10	10·90	3·48
23	552	1·71	10·0	19·90	15·40	3·70
24	552	2·08	5·8	22·20	12·30	6·06
26	571	1·38	17·0	17·30	19·00	2·70
27	524	1·43	18·3	14·40	6·83	0·68
28	490	1·47	17·5	23·00	3·64	0·32
30 *c*	469	1·72	18·6	24·90	2·20	0·17
32	469	5·55	19·9	14·90	3·62	0·47
33 *a*	501	5·57	18·5	14·30	8·34	1·65
34	524	3·47	16·5	19·60	14·80	3·30
35	522	4·03	17·6	10·70	9·60	0·93
36	490	5·05	19·3	21·20	8·48	2·16
37	469	6·60	19·3	20·00	5·30	0·87
38 *c*	571	0·64	17·0	22·22	17·80	2·23
39 *b*	517	3·42	18·9	19·10	12·80	2·17
40 *b*	508	3·00	19·0	24·20	10·70	1·97

a complete analysis CH_4 82·6 %; C_2H_6 15·9 %; H_2 0·8 %; C_2H_4 0·7 %;
b packed vessel; *c* H_2 1·25 ± 0·25 % of C_1 fraction; *d* length of run 20 min.

reactions it was found that the decomposition of dimethyl cadmium obeys first-order kinetics at a constant total pressure in the system (see runs 7, 8, 19, 20, 21, 30, 32, 37). In general in this work less attention was paid to the details of the dimethyl mercury decomposition. The experiments were primarily carried out to check the finding of Gowenlock, Polanyi and Warhurst [1] and to extend them slightly. Experiments with dimethyl cadmium in the packed reaction vessel indicated that the decomposition was homogeneous, as the packing caused no appreciable change in the first-order rate constant.

The proposed mechanism for the decomposition will only be valid if reaction (6)

$$CH_3 + C_6H_5CH_2 = C_6H_5CH_2CH_3 \qquad (6)$$

can be neglected as a possible means by which methyl radicals might be removed from the system. k_6 has not been measured so there is no direct evidence on this point. Two facts, however, have been established, neither of which is compatible with reaction (6) being very important in this system. First, the rate constants for reaction (1), as derived, are independent of the rate of release of methyl radicals into the system; this has been checked by using various pressures of dimethyl cadmium while keeping the other conditions constant. Secondly, a run carried out at 595° C with a contact time of 5·6 sec produced methane and ethane in quantities corresponding to 98·7 % decomposition of the alkyl; this showed that no methyl radicals were removed by side reactions. Furthermore,

the A factor of reaction (6) may be calculated from the results of Szwarc [5] and reasonable estimates of the entropies of the methyl and benzyl radicals made.[6] Hence it is found that $A_6 = 10^{9\cdot5}$ mole^{-1} cm^3 sec^{-1} which is the maximum possible value of k_6. A reaction with such a low rate constant cannot compete successfully with reactions (3) or (4).

The rate constants for the decompositions depend markedly on the total pressure in the reaction system. This is shown in fig. 1. The reactions are being investigated under conditions such that the rate of energy transfer is not sufficient to maintain the high pressure rate constant. This is to be expected for molecules containing only three heavy atoms. Accordingly the majority of the runs with each alkyl were done near one pressure and corrected to this selected pressure by making use of the empirically determined relation between the rate constants and the pressure.

Values of $k_3/k_4^{\frac{1}{2}}$ were derived from the quantities of methane and ethane formed and the pressure of toluene. It was found that this ratio also depended upon pressure as is shown in fig. 1. The variation must be ascribed to the variation in k_4 as k_3 should not depend upon pressure. This variation of k_4 with pressure has been observed in studies of the photolysis of acetone at lower temperatures but also at lower pressures.[7, 8] This is in qualitative agreement with the predictions of the theory of unimolecular reactions.[9]

Arrhenius plots of the rate constants are given in fig. 2. The straight lines correspond to:

$$\log_{10} k_1/\text{sec}^{-1} = 13\cdot1 - (50\,100 \pm 1000/2\cdot303\,\boldsymbol{RT})$$

for dimethyl mercury at 16 mm pressure;

$$\log_{10} k_1/\text{sec}^{-1} = 11\cdot9 - (45\,800 \pm 1000/2\cdot303\,\boldsymbol{RT})$$

for dimethyl cadmium at 18 mm pressure;

$$\log_{10} (k_3/k_4^{\frac{1}{2}})/\text{mole}^{-\frac{1}{2}}\,\text{cm}^{\frac{3}{2}}\,\text{sec}^{-\frac{1}{2}} = 6\cdot4 - (13\,500/2\cdot303\,\boldsymbol{RT}).$$

The results with dimethyl mercury are in excellent agreement with those of earlier workers.

The consequences of studying the reactions at pressures at which the rates are a function of pressure must be examined before certain conclusions can be drawn from these results. High-pressure A factors cannot be deduced; the true A factors may be up to ten times the A factors in these Arrhenius equations. Activation energies depend much less markedly upon pressure. The activation energies at high pressures are unlikely to be more than 1 kcal greater than those given here. $E_4 = 0$ kcal mole^{-1} at high pressures, consequently it should have a negative value (though probably a small one) under the present conditions. E_4 would certainly not be expected to be sufficiently low to reconcile the present values of $k_3/k_4^{\frac{1}{2}}$ with those determined at lower temperatures.[10, 11] Probably the values given here are not very reliable because of difficulties associated with the precise definition of the reaction volume.

The sum of the bond strengths in these metallic alkyls may be calculated from their heats of formation and that of the methyl radical. There is still some doubt as to the precise strength of the C—H bond in methane. $D(CH_3—H)$ may, however, be conveniently taken to be 102·5 kcal mole^{-1}; no error need then be assigned to this value; if it is subsequently shown to be wrong the present calculations may readily be adjusted. If the measured activation energies are equated with the dissociation energies of the first methyl-carbon bonds (D_1), the following table may be compiled:

alkyl	$\Delta Hf°$(gas) kcal mole^{-1}	$D_1 + D_2$ kcal mole^{-1}	D_1 kcal mole^{-1}	D_2 kcal mole^{-1}
$Hg(CH_3)_2$	22·4	57·3 [11, 12]	50·1	7·2
$Cd(CH_3)_2$	25·2	66·8 [13]	45·8	21·0

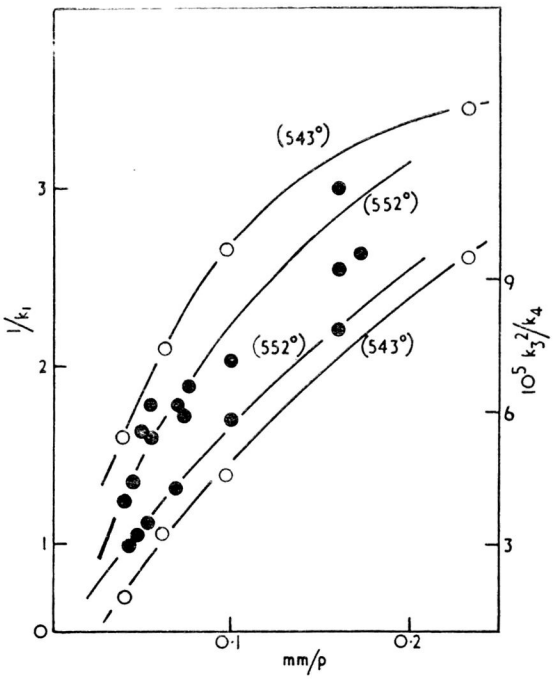

FIG. 1.—The variation of the rate constants with pressure. The right-hand scale refers to the two lower curves. The full points were obtained in the study of dimethyl cadmium.

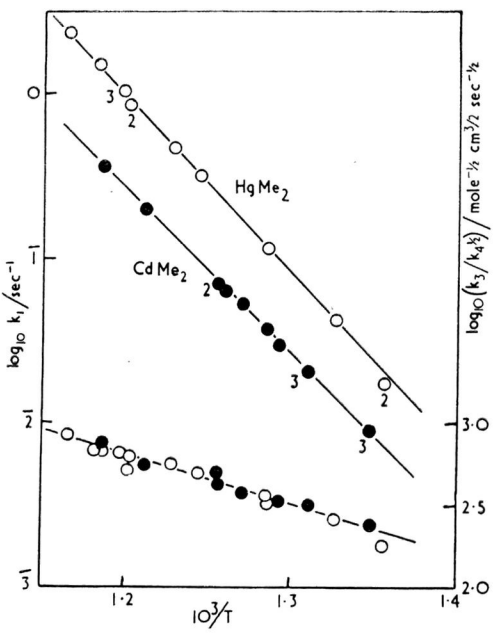

FIG. 2.—Arrhenius plots for the decomposition of dimethyl mercury and dimethyl cadmium, and the reaction of methyl radicals with toluene. The figures beside the point indicates the number of runs averaged to obtain the plotted value. The values for the decomposition of dimethyl cadmium have been displaced downwards by 0·5 log units.

In constructing this table two assumptions are tacitly made. First, that the metal atom released in the decomposition is in its ground electronic state. Secondly, that the addition of a methyl radical to a metal atom (reaction 2) is a process with zero energy of activation. Either or both of these assumptions may be invalid. D_2 may therefore be regarded as a minimum value. These values of $D(X—CH_3)$ are high compared with the known values of $D(X—H)$, that is 9 for mercury and 16 kcal mole^{-1} for cadmium.[14] A full discussion of the significance of these results may be postponed until more metallic alkyls have been investigated.

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