Studies in the thermal decomposition of metallic alkyls.

Michael G. Jacko
University of Windsor

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THE PYROLYSIS OF TRIMETHYL GALLIUM

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M. G. JACKO and S. J. W. PRICE

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ABSTRACT

The pyrolysis of trimethyl gallium has been studied in a toluene carrier flow system from 686° K to 983° K using total pressures from 6.1 mm to 31.1 mm. The progress of the reaction was followed by measuring the amount of methane, ethane, and ethylene formed. The rate constants decline rapidly if the toluene-to-alkyl ratio is decreased below 45. Part of this decrease has been shown to result from the loss of methyl radicals as ethylbenzene, propane, propylene, and xylenes. In an unseasoned vessel, the decomposition is markedly dependent on surface conditions. In the unpacked conditioned vessel, the reaction is 94% homogeneous in the first bond region and 97% homogeneous in the second bond region.

The decomposition occurs in two steps:

\[ \text{Ga(CH}_3\text{)}_3 \rightarrow \text{Ga(CH}_3\text{)}_2 + \text{CH}_3 [1] \]

\[ \text{Ga(CH}_3\text{)}_2 \rightarrow \text{Ga(CH}_3\text{)} + \text{CH}_3. [2] \]

The analysis of a black solid from the reaction zone is consistent with the formation of \((\text{GaCH}_3)^{\prime}\). Both rate constants depend on the total pressure in the system, the dependence of \(k_1\) being very slight. A least-squares analysis of the experimental results gives:

\[ \log_{10} k_1 \,(\text{sec}^{-1}) = 15.54 - \frac{59,500}{2.303RT} \]

\[ \log_{10} k_2 \,(\text{sec}^{-1}) = 7.94 - \frac{35,410}{2.303RT}. \]

INTRODUCTION

No previous kinetic studies of the thermal decomposition of trimethyl gallium have been reported. The heat of formation of trimethyl gallium has been obtained by the reaction of trimethyl gallium with iodine in benzene solution (1) and by the combustion of trimethyl gallium with oxygen (2). The mean gallium-carbon bond energies obtained from these studies are respectively 56.7±4 kcal/mole and 57.7±2 kcal/mole. In a recent review Long (3), using \(D(\text{CH}_3--\text{H}) = 102.5\) kcal/mole, has recommended a value of 57.5 kcal/mole.

EXPERIMENTAL

Materials

(a) Trimethyl Gallium

Trimethyl gallium was prepared by refluxing pure gallium with dimethyl mercury in an atmosphere of dry nitrogen, using mercuric chloride as catalyst (4). The fraction boiling at 56° C (uncorrected) was degassed by bulb-to-bulb distillation and stored under vacuum at −190° C. Melting point and vapor pressure data were in agreement with literature values (2).

(b) Toluene

(i) Toluene was prepared by the diazotization of o-toluidine followed by deamination with sodium hypophosphite. The organic layer was dried over anhydrous calcium chloride and fractionally distilled. The fraction boiling 109–110° C (uncorrected) was dried by refluxing over sodium under vacuum and degassed by bulb-to-bulb distillation.

(ii) Toluene from sulphonic acid (Eastman Organic, X325) has been found to be as suitable as that described above. It was dried by refluxing over sodium under vacuum and then degassed by bulb-to-bulb distillation.

Apparatus and Procedure

The experiments were carried out in a typical toluene carrier flow system in which the reaction zone was 195 cc. In the runs with the vessel packed with quartz tubing the surface area in the reaction zone was increased by a factor of 10 and its volume reduced to 145 cc. Pressures were measured using a mercury-di-octyl phthalate differential manometer designed to give a magnification of 10 to 1. The trimethyl gallium vapor was injected into the toluene stream through a capillary sealed to the barrel of a stopcock at the top.

1 Recipient of a National Research Council of Canada Studentship.

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1560
of the alkyl reser voir. The alkyl and toluene vessels were weighed at the end of each run to determine the amount of each used. In each experiment a pre-run of 4 to 6 minutes during which only toluene was passed was used to stabilize flow conditions. A similar post-run was used to remove all products from the reaction zone while conditions were still stabilized. In a few selected runs using the toluene from sulphonic acid, pre-runs were extended to 30 minutes. During the first 25 minutes the gaseous products were collected and measured. The rate constants obtained agreed with those obtained from the decomposition of toluene from o-toluidine (5). An acetone - dry ice trap removed toluene, ethylbenzene, dibenzyl, and similar products. The remaining products were transferred by a diffusion pump to a Le Roy still at −160°C to remove traces of toluene and hydrocarbons higher than C2. The remaining H2, CH4, C2H6, and C3H4 were transferred past a non-return valve to a gas burette with the aid of a Toeppler pump. After the gaseous mixture was measured, a sample was taken for chromatographic analysis.

The chromatographic analyses were carried out using a 2-m silica gel column at 40°C with a flow rate of approximately 20 cc/min. Internal standards were run with each set of analyses so that peak heights could be used. In a few selected runs, the contents of the acetone – dry ice trap were analyzed using a 2-m diisodecyl phthalate on diatomaceous earth column at 130°C with a flow rate of 28.5 cc/min. This method is sensitive to better than 0.0002 part ethylbenzene or xylenes in toluene.

Analysis of a black solid recovered from the reaction zone was carried out by admitting concentrated hydrochloric acid (12 N) to an evacuated bulb containing a weighed sample. After 6 hours' digestion at 78°C, the bulb was cooled to −190°C. The non-condensable products were collected and measured and a sample taken for chromatographic analysis. The mixture in the flask was filtered through a weighed sintered-glass crucible to determine the weight of the insoluble materials. The remaining solution was then twice evaporated to dryness and then analyzed for gallium by titration with 0.01 M potassium ferrocyanide using 3,3'-dimethylnaphthidine in the presence of a trace of ferricyanide as indicator (6).

RESULTS AND DISCUSSIONS

Selected experimental results are given in Tables I and II. Analysis of the data indicates that the thermal decomposition of trimethyl gallium does not occur by the simple release of three methyl radicals. It was found that even at 1075° K no more than two thirds of the theoretical quantity of methyl radicals could be accounted for. This is similar to the decomposition of trimethyl antimony (7) where the formation of (SbCH3)₃ was indicated. To test for the possible formation of a similar gallium polymer, a black deposit scraped from the reaction zone was analyzed as previously described. The results of this analysis indicated: 80% gallium (I) oxide, 12% carbon, and 8% gallium methyl. The carbon is probably due to the decomposition of the carrier in the high-temperature runs. Since limited quantities of air were admitted to the reaction vessel between certain runs to test for surface effects, the Ga₂O₃ could easily be formed from the reaction of O₂ with (GaCH₃)₃. Subsequently analyses were carried out on the contents of the acetone – dry ice trap and on the deposit in the furnace following each of a series of experiments. Under conditions such that less than one third of the theoretical yield of methyl radicals was observed, the gallium was found quantitatively in the acetone – dry ice trap. At temperatures above which two thirds decomposition occurred, the gallium was found quantitatively in the reaction vessel, as a thin, apparently non-metallic film. It therefore seems plausible that GaCH₃ does not decompose but deposits in the reaction vessel as (GaCH₃)₃.

The following mechanism is proposed:

\[
Ga(CH₃)₃ \rightarrow Ga(CH₃)₂ + CH₃ \quad [1]
\]
\[
Ga(CH₃)₂ \rightarrow Ga(CH₃) + CH₃ \quad [2]
\]
\[
π(GaCH₃) \rightarrow (GaCH₃)₃ \quad [3]
\]
\[
CH₃ + C₆H₆ \rightarrow C₆H₅-CH₂ \rightarrow C₆H₅-CH₂ + CH₄ \quad [4]
\]
\[
2CH₃ \rightarrow C₆H₆ \quad [5]
\]
\[
2C₆H₅-CH₂ \rightarrow (C₆H₅-CH₂)₂ \quad [6]
\]

The small amounts of ethylene formed were assumed to arise from the reactions

\[
CH₃ + C₆H₆ \rightarrow C₆H₅ + CH₄ \quad [7]
\]
\[
C₆H₅ \rightarrow C₆H₄ + H. \quad [8]
\]
**TABLE IA**

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<th>Temp. (°K)</th>
<th>Contact time (sec)</th>
<th>Total pressure (mm)</th>
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*Packed vessel runs.
†Moles H₂ approximately equal to moles C₂H₄.
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*Packed vessel runs. †Moles H₂ approximately equal to moles C₂H₄.

TABLE IB

JACKO AND PRICE: PYROLYSIS OF Ga(C₃H₅)₃
<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>Contact time (sec)</th>
<th>Total pressure (mm)</th>
<th>Length of run (min)</th>
<th>GaMe₂ (10⁻⁴ mole)</th>
<th>CH₄ (10⁻³ mole)</th>
<th>C₂H₆ (10⁻³ mole)</th>
<th>C₃H₈ (10⁻³ mole)</th>
<th>k₁ (sec⁻¹)</th>
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*Packed vessel runs.  
†Molar ratio.
It was apparent from the analysis of the data that the second methyl radical was not released immediately after the first. The pattern of \( \log k_4/k_b^{1/2} \) shown in Fig. 1 indicates that the release of the first two methyl groups might be similar to the successive decomposition of dimethyl zinc, first to zinc methyl and only at much higher temperatures to zinc plus a methyl radical \((8)\). The detailed calculations of \( k_1 \) and \( k_2 \) have therefore been carried out as for the decomposition of dimethyl zinc, assuming that below 820° K the decomposition of dimethyl gallium is not an important source of methyl radicals.

The mechanism further assumes that reaction \([9]\) is unimportant. The following evidence

\[
\text{CH}_3 + \text{C}_6\text{H}_6 \rightarrow \text{CH}_2 - \text{C}_6\text{H}_6 - \text{CH}_2\text{CH}_3
\]

indicates the validity of this assumption under the experimental conditions used for most runs. First, values of \( k_1 \) obtained at 817° K and 13.0 mm pressure using toluene-to-alkyl ratios between 45 and 120 show little variation. Similarly values of \( k_2 \) at 916° K and 13.0 mm using toluene-to-alkyl ratios between 45 and 120 show little variation. Previous experiments and calculations \((9)\) also indicate that under similar experimental conditions the loss of methyl radicals according to reaction \([9]\) is negligible. However, as shown in Fig. 2, the value of \( \log k_1 \) falls sharply when the toluene-to-alkyl ratio is decreased below 45. Values for \( k_2 \) are affected similarly. Additional gas chromatographic analyses have shown that the apparent falloff is due in part at least to the formation of propane, propylene, ethylbenzene, and xylene. Analysis for butanes could not be made at present but these are probably also formed.

The Arrhenius plots shown in Fig. 1 were plotted using \( k_1 \)'s obtained using toluene-to-alkyl ratios of 45 to 120. The simple linear nature of these plots supports the method of calculation used. The curves may be represented by:

\[
\begin{align*}
\log_{10} k_1 \text{ (sec}^{-1}) &= 15.54 - (59,500/2.303RT) \\
\log_{10} k_2 \text{ (sec}^{-1}) &= 7.94 - (35,410/2.303RT)
\end{align*}
\]

at 13.0 mm. No other plausible explanation of the results could be found.

The values of \( k_1 \) and \( k_2 \) were both extremely sensitive to the nature of the surface in the reaction zone. Admission of limited quantities of air to the conditioned vessel between
runs resulted in approximately a 100% increase in $k_1$ and a 200% increase in $k_2$ even after pumping over a 48-hour period. Approximately three runs were required to bring values of $k_1$ and $k_2$ back to those normally observed in the conditioned vessels. Using a conditioned packed vessel with a surface-to-volume ratio 12 times that of the unpacked vessel gave values of $k_1$ 2.0 times and values of $k_2$ 1.4 times those observed in the unpacked conditioned vessel. It would therefore appear that in the conditioned unpacked vessel, both first and second bond ruptures are predominantly homogeneous processes with a 6% heterogeneous contribution in the first bond region and a 3% contribution in the second bond region.

Both $k_1$ and $k_2$ depend upon the total pressure in the system, although the dependence of $k_1$ is very slight (Fig. 3). The dependence of $k_2$ is similar to that observed for dimethyl mercury and dimethyl cadmium (9). Therefore, based solely on unimolecular pressure effects, the value of $A_2$ would be expected to be of the order $10^{11}$–$10^{13}$ sec$^{-1}$. However,
the observed $A_2$, $8.71 \times 10^7$, is much lower than expected. This is presumably due to a change in multiplicity from triplet to singlet state as the second methyl radical is released from trimethyl gallium.

The pressure dependence of $\log \frac{k_i}{k_b}^{1/2}$ is shown in Fig. 4. The falloff with increasing pressure is similar to that previously observed (7, 8, 9) and may be attributed to the third-body requirements of reaction [5].

The experimental evidence although complex would indicate that the activation energies may be approximately related to $D((\text{CH}_3)_2\text{Ga}—\text{CH}_3)$ and $D((\text{CH}_3)\text{Ga}—\text{CH}_3)$. Taking the total strength of the three gallium–carbon bonds equal to 172.4 kcal/mole (3) gives $D(\text{Ga}—\text{CH}_3)$ equal to 77.5 kcal/mole.

ACKNOWLEDGMENT

This work has been supported by a grant from the National Research Council of Canada.

REFERENCES

THE PYROLYSIS OF TRIMETHYLINDIUM

M. G. Jacko and S. J. W. Price
THE PYROLYSIS OF TRIMETHYLINDIUM

M. G. Jacko and S. J. W. Price
Department of Chemistry, University of Windsor, Windsor, Ontario
Received December 12, 1963

ABSTRACT

The pyrolysis of trimethylindium has been studied in a toluene carrier flow system from 550° K to 781° K using total pressures from 6.0 to 33.5 mm. The progress of the reaction was followed by measuring the amount of methane, ethane, ethylene, propene, and ethylbenzene formed and in a number of cases by direct indium analysis. The decomposition occurs in three steps:

\[
\begin{align*}
\text{In}(\text{CH}_3)_3 & \rightarrow \text{In}(\text{CH}_3)_2 + \text{CH}_4 \quad [1] \\
\text{In}(\text{CH}_3)_2 & \rightarrow \text{In}(\text{CH}_3) + \text{CH}_4 \quad [2] \\
\text{In}(\text{CH}_3) & \rightarrow \text{In} + \text{CH}_3 \quad [3]
\end{align*}
\]

At all temperatures reaction [2] follows rapidly after reaction [1]. Reaction [3] occurs at a measurable rate only at temperatures sufficiently high that reactions [1] and [2] are completed in a very small fraction of the contact time. At lower temperatures the \text{InCH}_3 produced deposits in the reaction zone as a white film of \text{(InCH}_3)_n.

Both \( k_1 \) and \( k_3 \) decline rapidly if the toluene-to-alkyl ratio is decreased below 150. In an unseasoned vessel, the decomposition is markedly dependent on surface conditions. In the unpacked conditioned vessel the reaction is at least 89% homogeneous in the first bond region and 97% homogeneous in the third bond region. Both \( k_1 \) and \( k_3 \) depend on the total pressure in the system, the dependence of \( k_1 \) being very slight. A least squares analysis of the experimental results gives:

\[
\log_{10} k_1 (\sec^{-1}) = 15.72 - (47,200/2.303RT) \\
\log_{10} k_3 (\sec^{-1}) = 10.91 - (38,700/2.303RT)
\]

at 13.0 mm. \( E_2 \) may be directly related to \( D[(\text{CH}_3)_2\text{In—CH}_3] \). A rough calculation based on unimolecular pressure effects indicates that \( D[\text{In—CH}_3] \) is probably about 2 kcal/mole greater than \( E_2 \).

INTRODUCTION

No previous kinetic studies of the thermal decomposition of trimethylindium have been reported.

A study of the reaction of triisobutylindium with 1-decene at 150° C for 100 hours (1) yielded tridecylindium and 83% isobutylene. The tridecylindium broke down further to yield only 64% free indium metal plus 1/2 CH\(_3\)--CH—C\(_8\)H\(_7\) and 3/2 CH\(_3\)--CH—C\(_8\)H\(_7\). The remaining indium was assumed to be in some polymeric form.

A kinetic study of the thermal decomposition of trimethylgallium has been reported (2). The rate constants obtained were extremely sensitive to the nature of the surface in the reaction zone. After a series of runs, the reaction zone became conditioned and reproducible results were obtained. The experimental results showed \( D_1 = 59.5 \) kcal/mole and \( D_2 = 35.4 \) kcal/mole. From a knowledge of the total bond energies, \( D_3 = 77.5 \) kcal/mole was calculated.

The thermal decomposition of trimethylindium is expected to be similar to that of trimethylgallium and the other neighboring methyl metallic alkyls that have been studied (3, 4, 5). The mean metal–carbon bond dissociation energy in trimethylindium has not been reported. However, from available data on the methyl compounds of groups IIb, IIIb, IVb, and Vb, a value for trimethylindium of \( E = 41 \pm 3 \) kcal/mole may be estimated.

1Recipient of a National Research Council of Canada Studentship.

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EXPERIMENTAL

Materials

(a) Trimethylindium was prepared by refluxing indium metal with dimethylmercury in an atmosphere of dry nitrogen using mercuric chloride as catalyst. After 8 days, the reaction flask was cooled to 0°C (vapor pressure of trimethylindium, 0.2 mm) and the unreacted dimethylmercury (vapor pressure, 17 mm) was distilled off. The crude trimethylindium was then distilled at 80.5°C and gave vapor pressure measurements consistent with literature values (6). It was stored under its own vapor pressure at −190°C.

(b) Toluene from sulphonic acid (Eastman Organic, X325) was dried by refluxing over sodium under vacuum and then degassed by bulb-to-bulb distillation.

Apparatus and Procedure

The experiments were carried out in a typical toluene carrier flow system in which the reaction zone was 195 cc. To test for surface effects the reaction vessel was packed with thin-walled quartz tubing of 2 mm O.D. The surface area in the reaction zone was increased by a factor of 10 and its volume reduced to 145 cc. Pressures were measured with a mercury-diocylphthalate differential manometer designed to give a magnification of 10 to 1.

Trimethylindium was added to the carrier stream by a variable split-stream U-tube pickup system. Before a run, 0.1 to 0.2 gram of the alkyl was distilled from a weighed vessel into the U-tube and the vessel reweighed to determine the exact quantity used. The entire sample in the U-tube was used in the run. The period of alkyl injection was preceded by a 5- to 10-minute flow of toluene to stabilize flow conditions and was followed by a 5- to 10-minute flow of toluene to remove all volatile products from the reaction zone.

An acetone-dry ice trap removed unreacted trimethylindium, toluene, ethylbenzene, dibenzyl, and similar products. The remaining products were transferred by a diffusion pump to a trap at −100°C (acetone-toluene sludge) to remove traces of toluene and hydrocarbons higher than C6. The remaining gaseous mixture was transferred past a non-return valve to a gas burette with the aid of a Toepler pump.

RESULTS AND DISCUSSION

The experimental results are given in Tables I and II. They may be discussed in terms of the following mechanism:

\[ \text{In(CH}_3\text{)}_3 \rightarrow \text{In(CH}_3\text{)}_2 + \text{CH}_3 \]  
\[ \text{In(CH}_3\text{)}_2 \rightarrow \text{In(CH}_3\text{)} + \text{CH}_3 \]  
\[ \text{In(CH}_3\text{)} \rightarrow \text{In} + \text{CH}_3 \]  
\[ n[\text{In(CH}_3\text{)}] \rightarrow [\text{In(CH}_3\text{)}]_n \]  
\[ \text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_4 \]  
\[ 2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \]

followed by the usual reactions of the benzyl radicals to produce dibenzyl or ethylbenzene.

The abstraction reaction \([a]\) is a composite reaction proceeding mainly as written but with a small percentage of abstraction from the ring. The ethylene and hydrogen observed in small amounts result from the reactions:

\[ \text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4 \]  
\[ \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H} \]  
\[ \text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]
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<tr>
<th>Temp. (°K)</th>
<th>Contact time (sec)</th>
<th>Total pressure (mm)</th>
<th>ln(CH$_2$)$_3$</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_4$</th>
<th>C$_6$H$_6$</th>
<th>φ — C$_2$H$_5$</th>
<th>$k_2$ (sec$^{-1}$)</th>
<th>$k_2/k_1$ (cc/mole sec)$^1$</th>
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<td>( \text{CH}_4 )</td>
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<td>( \text{C}_3\text{H}_8 )</td>
<td>( \phi - \text{C}_4\text{H}_10 )</td>
<td>( k_1 ) (sec(^{-1}))</td>
<td>( k_s/k_1 ) (cc/mole sec)</td>
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TABLE II

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<th>(k_a) (sec(^{-1}))</th>
<th>(k_m) (sec(^{-1}))</th>
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*Runs in an unconditioned vessel.

The values of \(k_a/k_r^{1/2}\) given in Tables 1A and 1B have been calculated using the equation

\[
k_a/k_r^{1/2} = \frac{[\text{moles CH}_{4}]}{[\text{moles C}_{2}\text{H}_{4} + \text{C}_{2}\text{H}_{6}]^{1/2}} \times \frac{1}{\sqrt{V^{1/2} / \text{toluene}}} \]

where \(V\) = volume of reaction zone, and \(t\) = length of run.

If in the decomposition of a compound of the type \(M(\text{CH}_{3})_n\), we have

\[
M(\text{CH}_{3})_n \rightarrow M(\text{CH}_{3})_{n-y} + y\text{CH}_{3} \quad [\text{I}]
\]

occurring over a temperature range \(T_1\) to \(T_2\) while

\[
M(\text{CH}_{3})_{n-y} \rightarrow M(\text{CH}_{3})_{n-y-z} + z\text{CH}_{3} \quad [\text{II}]
\]

occurs appreciably only above \(T_2\), we shall have a number of factors which will influence the value of \(k_a/k_r^{1/2}\). First, in a flow reaction, the temperature increases as the reaction zone is approached, therefore when the temperature in the reaction zone \(T_2\) is above \(T_2\), reaction [I] will occur partly in the tube leading to the reaction zone and will be complete in some small fraction of this zone. This has a dual effect on \(k_a/k_r^{1/2}\):

(i) reaction [I] is occurring at an average temperature above \(T_2\) but below \(T_3\), and

(ii) the volume over which reaction [I] occurs is no longer the total volume of the reaction zone.

The net effect is to hold the apparent observed value of \(k_a/k_r^{1/2}\) approximately constant as \(T\) increases. Actually, the net effect might be a slight decrease except for the fact that reaction [II] is occurring over the entire reaction zone at \(T_3\). Experimentally, for dimethylzinc,

\[
\text{Zn(CF}_{2})_2 \rightarrow \text{ZnCH}_{2} + \text{CH}_{3} \quad [\text{I}]
\]

\[
\text{ZnCH}_{2} \rightarrow \text{Zn} + \text{CH}_{3} \quad [\text{II}]
\]

the ratio shows a slight decrease above \(T_2\) (4). For trimethylgallium

\[
\text{Ga(CH}_{3})_3 \rightarrow \text{Ga(CH}_{3})_2 + \text{CH}_{3} \quad [\text{I}]
\]

\[
\text{Ga(CH}_{3})_2 \rightarrow \text{Ga(CH}_{3}) + \text{CH}_{3} \quad [\text{II}]
\]

where \(V\) = volume of reaction zone, and \(t\) = length of run.
the ratio continues to rise slightly (2). In any case, a sharp break in the \( k_a / k_r^{1/2} \) curve is observed.

The Arrhenius plot of \( k_a / k_r^{1/2} \) for the present work is shown in Fig. 1. In this case, the characteristic break occurs at 67% theoretical yield of methyl radicals indicating that below 670° K reaction [2] follows rapidly after reaction [1], but reaction [3] does not occur to any appreciable extent. Rate constants below this temperature \( (k_1) \) have therefore been calculated assuming that two methyl radicals are released for each trimethylindium undergoing reaction. Above 680° K all of the trimethylindium is converted to methylindium plus two methyl radicals in a very small fraction of the contact time. Rate constants in this region \( (k_3) \) have therefore been calculated assuming that the fraction of the third bond ruptured is given by:

\[
\frac{(\text{moles of methyl radicals}) - (2 \text{ moles trimethylindium})}{\text{moles of trimethylindium}}
\]

Although the break in the Arrhenius curve of \( k_a / k_r^{1/2} \) is indicative of the process outlined, independent tests have been made to verify the mechanism.

(i) In 18 runs, the contents of the acetone–dry ice trap located at the outlet of the furnace were analyzed for indium. If reaction [4] is responsible for the removal of \( \text{In(CH}_3\text{)} \), then above 670° K all the indium should be deposited in the reaction zone. Table II shows that over the entire third bond region only traces of indium reach the acetone–dry ice trap. Below this temperature the quantity of indium found in the trap was always in agreement with the proposed mechanism.

(ii) In 7 of the 18 runs listed in Table II a clean pyrex vessel was used. In each of these seven runs the indium content of the reaction zone was analyzed. The values of \( k_1 \) calculated assuming moles of indium in the reaction zone equal the moles of trimethylindium decomposed are shown in Fig. 1. The agreement with \( k_1 \) values in a seasoned vessel calculated assuming two methyl radicals released for each trimethylindium decomposed is excellent.
The rate constants for the reaction in a clean vessel based on gas analysis lie above the Arrhenius curve. The difference in extent of reaction based on metal analysis is a result of reaction on the unconditioned surface. The most probable surface reactions consistent with the experimental results are the surface decomposition of methylindium to give indium metal plus a methyl radical and the surface decomposition of trimethylindium. The first of these reactions leads to a decrease in the quantity of \((\text{InCH}_3)_n\) deposited in the reaction zone. Hence in an experiment in an unconditioned vessel in which 1.0 millimole of methylindium would have been deposited in the reaction zone in a conditioned vessel, addition of bromine vapor to the hot reaction vessel (637° K) while still under vacuum produced only 0.34 millimole of hydrogen bromide and a quantity of polymethylene qualitatively in agreement with the reaction

\[
2n\text{Br}_2 + (\text{InCH}_3)_n \rightarrow n\text{InBr}_3 + n(\text{CH}_2) + n\text{HBr}
\]

followed by the polymerization of the methylene radicals in cooler regions of the reaction vessel. The 0.66 millimole of methylindium apparently lost by surface decomposition was in good agreement with the additional methyl radicals detected in the gas analysis (0.58 millimole).

Starting with a clean vessel, both \(k_1\) and \(k_3\) decrease over several runs to a fixed minimum value in what is subsequently called a conditioned vessel. If air is admitted to the reaction vessel between runs, an additional two to three runs are required to recondition the surface of the reaction vessel. The percentage of heterogeneous reaction in the conditioned vessel was estimated by carrying out a series of runs in a packed vessel with a surface-to-volume ratio 12 times that of the unpacked vessel. Because of the large surface area, complete conditioning was probably not obtained, but after a series of runs \(k_1\) was reduced to about 2.2 times its value in the unpacked vessel and \(k_3\) to about 1.3 times its value in the unpacked vessel. Therefore, in the unpacked vessel used in this work, the reaction is at least 89% homogeneous in the first bond region and at least 97% homogeneous in the third bond region.

Both \(k_1\) and \(k_3\) depend on the total pressure in the system, although the dependence of \(k_1\) is very slight (Fig. 2). The slight pressure dependence of \(k_1\) is similar to that observed in the decomposition of trimethylgallium (2). As shown in Fig. 3, the pressure dependence

![Fig. 3. Comparison of the effect of pressure on the rate of thermal decomposition of InCH₃ and ZnCH₃.](image)

of the decomposition of methylindium is somewhat less than that of methylzinc (4). This is presumably due to the large temperature difference at which these decompositions occur.

The pressure dependence of \(k_a/k_r^{1/2}\) is shown in Fig. 4. The fall-off with increasing
pressure is similar to that previously observed (2-5) and may be attributed to the third body requirements of the methyl radical recombination reaction.

As shown in Fig. 5, the value of $k_1$ falls sharply when the toluene-to-alkyl ratio is decreased below 150. Values for $k_3$ are similarly affected. The Arrhenius curves shown in Fig. 1 were therefore plotted using only rate constants obtained in runs where the toluene-to-alkyl ratio was greater than 150. At 13.0 mm, the curves may be represented by:

$$\log_{10} k_1 \text{ (sec}^{-1}) = 15.72 - \left(\frac{47,200}{2.303R7}\right),$$

$$\log_{10} k_3 \text{ (sec}^{-1}) = 10.91 - \left(\frac{38,700}{2.303R7}\right).$$

The experimental evidence indicates that the activation energies may be approximately related to the bond strengths, although a rough estimate based on unimolecular pressure effects indicated that $D_3$ is about 2 kcal/mole greater than $E_3$. Thus $D[(CH_3)_2In—CH_3]$ equals 47.2 kcal/mole and $D[In—CH_3]$ equals 40.7 kcal/mole. The mean bond energy in trimethylindium is not known. However, comparison of neighboring methyl metallic alkyls indicate that $E(\text{In—CH}_3)$ in trimethylindium is probably 41±3 kcal/mole. Allowing limits of error of ±1 kcal/mole in $D_1$ and $D_3$ would give $D[(\text{CH}_3)\text{In—CH}_3]$ equal to 35±5 kcal/mole, a value consistent with the proposed mechanism.

ACKNOWLEDGMENTS

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REFERENCES

STUDIES IN THE THERMAL DECOMPOSITION OF METALLIC ALKYLs

BY

MICHAEL G. JACKO

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario
1964
THIS THESIS HAS BEEN EXAMINED AND APPROVED BY:

[Signatures]
The metal-carbon bond strengths for some of the metals in Groups IIb, IVb, and Vb have been determined. The object of this work was to study the metal-carbon bond strengths of the Group IIIb metals - gallium, indium, and thallium.

The thermal decompositions of trimethylgallium, trimethylindium, and trimethylthallium have been studied in a toluene carrier gas flow system. The methyl derivatives of these metals were chosen so that the reactions of the radicals released on decomposition might be as simple as possible. The overall progress of the decompositions was followed by measuring the amount of methane, ethane, ethylene, propane, and ethylbenzene formed, and in a number of cases by direct metal analysis.

In an unseasoned vessel, the thermal decompositions were dependent on the surface conditions. In an unpacked conditioned vessel, trimethylgallium was 9% heterogeneous, dimethylgallium 4%, trimethylindium 10%, methylindium 3%, and trimethylthallium 14%.

All rate constants depended on the total pressure in the system. The pressure dependence for the decompositions of the trimethyls was slight, but increased for the dimethyl and monomethyl forms.

The break in the curve of the Arrhenius plot of $\frac{k_a}{k_r}$
indicated consecutive reactions; the second bond was not immediately released after the first if this break occurred at 33% theoretical yield of methyl radicals (as in trimethylgallium); the third bond was not immediately released after the second if this break occurred at 67% theoretical yield of methyl radicals (as in trimethylindium); no break indicated that the second and third bonds ruptured rapidly after the first. Independent tests were carried out to verify these mechanisms.

From theoretical considerations, it was shown that the experimental activation energy may be approximately related to the bond strengths.

In the thermal decomposition of trimethylgallium, the first two metal-carbon bond energies were determined directly and the third was determined by difference:

\[ \Delta \overline{E}_{(\text{CH}_3)\text{Ga-CH}_3} = 59.5 \text{ kcal/mole} \]
\[ \Delta \overline{E}_{(\text{CH}_3)\text{Ga-CH}_3} = 37.2 \text{ kcal/mole} \]
\[ \overline{E}_{\text{Ga-CH}_3} = 75.8 \text{ kcal/mole} \]

In the thermal decomposition of trimethylindium, the first and third metal-carbon bonds were determined directly and the second was determined by difference:

\[ \Delta \overline{E}_{(\text{CH}_3)\text{In-CH}_3} = 47.2 \text{ kcal/mole} \]
\[ \Delta \overline{E}_{(\text{CH}_3)\text{In-CH}_3} = 27.4 \text{ kcal/mole} \]
\[ \overline{E}_{\text{In-CH}_3} = 40.0 \text{ kcal/mole} \]

In the thermal decomposition of trimethylthallium, only the first bond could be determined:

\[ \Delta \overline{E}_{(\text{CH}_3)\text{Tl-CH}_3} = 26.4 \text{ kcal/mole} \]
ACKNOWLEDGEMENTS

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-Michael G. Jacks
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>11</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>viii</td>
</tr>
<tr>
<td>TABLE OF NOMENCLATURE</td>
<td>x</td>
</tr>
</tbody>
</table>

**Chapter**

**I. INTRODUCTION**

- General Introductory Remarks.......................... 1
- Some Previous Studies by the Toluene Carrier Technique........ 9

**II. THEORETICAL CONSIDERATIONS**

- Theory of the Metal-Carbon Bond.................. 11
- Properties of Metallic Alkyls.................. 16
- The Group IIIb Metals.......................... 20
- Metallic Alkyls of Group IIIb................. 22
- Mean Bond Energies by Calorimetric Methods.......................... 23
- Bond Dissociation Energies by the Kinetic Method.................. 27
- Pressure Dependence of Bond Dissociation Energies.................. 31
- The Toluene Carrier Gas Technique.............. 35
- Kinetics of Unimolecular Decompositions.................. 37
- Kinetics of Methyl Extraction.................. 39

**III. EXPERIMENTAL**

- Preparation of Materials.................. 42
Chapter Page

Apparatus.............................. 45
Experimental Technique..............54

IV. EXPERIMENTAL RESULTS

The Pyrolysis of Trimethylgallium.... 58
The Pyrolysis of Trimethylindium..... 76
The Pyrolysis of Trimethylthallium... 91

V. DISCUSSION

Reaction of Methyl Radicals with
Toluene...................................... 106
The Toluene Carrier Technique......... 109
The Pyrolysis of Trimethylgallium..... 110
The Pyrolysis of Trimethylindium..... 112
The Pyrolysis of Trimethylthallium.... 113
Suggestions for Further Work........... 114

BIBLIOGRAPHY............................ 117

VITA AUCTORIS........................... 120
<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The Pyrolysis of Dimethylgallium</td>
<td>59</td>
</tr>
<tr>
<td>2. The Pyrolysis of Trimethylgallium</td>
<td>60</td>
</tr>
<tr>
<td>3. The Pyrolysis of Dimethylgallium and Trimethylgallium (Packed Vessel Runs)</td>
<td>61</td>
</tr>
<tr>
<td>4. Variation of k with $\text{Ctol/Calk}$</td>
<td>68</td>
</tr>
<tr>
<td>5. Pressure Dependence of Metal Dimethyils</td>
<td>73</td>
</tr>
<tr>
<td>6. The Pyrolysis of Methylindium</td>
<td>77</td>
</tr>
<tr>
<td>7. The Pyrolysis of Trimethylindium</td>
<td>78</td>
</tr>
<tr>
<td>8. The Pyrolysis of Methylindium and Trimethylindium (Packed Vessel Runs)</td>
<td>79</td>
</tr>
<tr>
<td>9. Runs with Indium Analyses</td>
<td>82</td>
</tr>
<tr>
<td>10. Variation of k with $\text{Ctol/Calk}$</td>
<td>90</td>
</tr>
<tr>
<td>11. The Pyrolysis of Trimethylthallium (in a Unpacked Unconditioned Vessel)</td>
<td>92</td>
</tr>
<tr>
<td>12. The Pyrolysis of Trimethylthallium (in a Packed Unconditioned Vessel)</td>
<td>93</td>
</tr>
<tr>
<td>13. The Pyrolysis of Trimethylthallium (in a Unpacked Conditioned Vessel)</td>
<td>94</td>
</tr>
<tr>
<td>14. The Pyrolysis of Trimethylthallium (in a Packed Conditioned Vessel)</td>
<td>96</td>
</tr>
<tr>
<td>15. Runs with Thallium Analyses</td>
<td>99</td>
</tr>
<tr>
<td>16. Metal-Methyl Bond Strengths</td>
<td>116</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Formation of the sp$^3$ Hybrid Orbital</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Potential Energy Curve for a Unimolecular Decomposition into two Radicals</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>Schematic Diagram of the Toluene Carrier Flow System used in this Work</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>Injection System for a Volatile Metallic Alkyl</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>Pick-up System for Metallic Alkyls of Low Volatility</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Placement of Heating Windings in the Furnace Construction</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>A Typical Temperature Profile</td>
<td>51</td>
</tr>
<tr>
<td>8</td>
<td>Arrhenius Plots of Rate Constants for the Decomposition of Trimethylgallium and Dimethylgallium and the Reaction of Methyl Radicals with Toluene</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>Variation of Rate Constants with the Molar Ratio of Toluene-to-Alkyl</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>Variation of Rate Constants with Pressure for Trimethylgallium and Dimethylgallium</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td>Variation of Rate Constants of Various Dimethyl Metals with Pressure</td>
<td>74</td>
</tr>
<tr>
<td>12</td>
<td>Variation of $k_a/k_r$ with Pressure</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>Arrhenius Plots for the Decomposition of Methylindium and Trimethylindium and the Reaction of Methyl Radicals with Toluene</td>
<td>81</td>
</tr>
<tr>
<td>14</td>
<td>Variation of Rate Constants with Pressure for Trimethylindium and Methylindium</td>
<td>86</td>
</tr>
</tbody>
</table>
15. Variation of Rate Constant with Pressure for Methyl Metals ............................................... 87
16. Variation of $k_a/k_r^{1/2}$ with Pressure ............ 88
17. Variation of Rate Constants with Molar Ratio of Toluene-to-Alkyl ......................... 89
18. Arrhenius Plot for the Reaction of Methyl Radicals with Toluene ......................... 98
19. Arrhenius Plots for the Decomposition of Trimethylthallium ................................. 101
20. Variation of $k_a/k_r^{1/2}$ with Pressure .......... 104
21. Variation of Rate Constant with Pressure for Trimethylthallium ............................. 104
22. Arrhenius Plot for the Reaction of Methyl Radicals with Toluene ......................... 108

ix
## TABLE OF NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-Exponential Factor of the Arrhenius Equation</td>
</tr>
<tr>
<td>A, B, C</td>
<td>Moments of Inertia of a Molecule</td>
</tr>
<tr>
<td>D</td>
<td>Bond Dissociation Energy</td>
</tr>
<tr>
<td>E</td>
<td>Arrhenius Activation Energy</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Arrhenius Activation Energy at the high Pressure Limit</td>
</tr>
<tr>
<td>E</td>
<td>Mean Bond Energy</td>
</tr>
<tr>
<td>h</td>
<td>Planck's Constant</td>
</tr>
<tr>
<td>K</td>
<td>Transmission Coefficient</td>
</tr>
<tr>
<td>k'</td>
<td>Boltzmann's Constant</td>
</tr>
<tr>
<td>k</td>
<td>Rate Constant</td>
</tr>
<tr>
<td>$k_\infty$</td>
<td>Rate Constant at the High Pressure Limit</td>
</tr>
<tr>
<td>m</td>
<td>Mass of a Molecule</td>
</tr>
<tr>
<td>n</td>
<td>Number of Atoms in a Molecule</td>
</tr>
<tr>
<td>n'</td>
<td>Number of Effective Oscillators in a Molecule</td>
</tr>
<tr>
<td>R</td>
<td>Gas Constant</td>
</tr>
<tr>
<td>R₁</td>
<td>Free Radical Group</td>
</tr>
<tr>
<td>T</td>
<td>Absolute Temperature</td>
</tr>
<tr>
<td>(\Delta H_f)</td>
<td>Standard Heat of Formation at 25° C</td>
</tr>
<tr>
<td>v</td>
<td>Vibrational Frequency</td>
</tr>
<tr>
<td>(\Theta)</td>
<td>Parameter Related to the Amplitude Factor</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Symmetry Number</td>
</tr>
</tbody>
</table>

x
CHAPTER I

INTRODUCTION

**General Introductory Remarks**

The dissociation energy, $D_{R_1-R_2}$, of a bond $R_1-R_2$ is the change in energy at the absolute zero in the ideal gas state, $E_0^0$, for the reaction:

$$R_1R_2 \longrightarrow R_1 + R_2$$

with the products being in their ground state.

The bond dissociation energy is the most direct measure of the strength of a bond, and therefore of the stability of the chemical combination between the two atoms or radicals from which it is formed. Theoretical Chemistry is concerned with chemical information from general principles, ultimately from physical laws governing the behaviour of nuclei and electrons. Energy quantities are perhaps the most accessible numerical quantities we can hope to calculate for chemical systems, and it could be maintained that the most specific energy quantities are dissociation energies. The fact that it has been possible to account qualitatively for the chemical binding and quantitatively for the dissociation energies of hydrogen and other simple molecules is important evidence that Theoretical Chemistry is on the right path. The present objective is to expand Theoretical Chemistry. To have reliable experimental values of bond
dissociation energies is to have a useful touchstone to test our theoretical ideas on chemical binding. More specifically, the objective of the present research is to give reliable experimental values of dissociation energies for some metal-carbon bonds.

Bond dissociation energies can in general be determined in a variety of methods, among the most common are the following: thermal equilibrium methods, electron impact methods, spectroscopic methods, photochemical methods, and kinetic methods (static and flow systems). However, the methods that can be employed satisfactorily to determine metal-carbon bond dissociation energies in metallic alkyls are rather limited. The radicals produced in the initial dissociation are too reactive to allow the use of any thermal equilibrium method. Although spectroscopic methods are capable of giving the most accurate values for dissociation energies of simple molecules, they cannot be used for polyatomic metallic alkyls because of the complexity of their spectra. Electron impact methods give only the upper limit of the dissociation energy and are complicated due to the large number of atoms present in the metallic alkyl molecule. The determination of bond dissociation energies by photochemical methods are reliable only if the mechanism of absorption of radiation and the subsequent decomposition can be established; the result will be a maximum bond dissociation energy.

Mean bond energies of metallic alkyls can be determined
by calorimetric methods. Calorimetric methods include the measurements of heats of hydolysis, heats of halogenation, combustion in static-bomb calorimeters, and combustion in rotating-bomb calorimeters.

Activation energies from 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 for recombination is small, the experimental activation energy determined will be a good approximation to the bond dissociation energy. The complexity of reactions in static systems is such that unambiguous interpretation of the result is almost impossible. The interpretation of results from experiments in flow systems has been much more satisfactory. Hydrogen was the first carrier used in flow systems to act as a radical scavenger and could be used over a very long temperature range; however the separation of the gaseous products from the hydrogen was difficult and required measurements by difference. The toluene carrier flow system, although limited for very high temperature work, offers the most satisfactory method for reducing the complexity of the reaction and gives satisfactory results.

Some Previous Studies by the Toluene Carrier Technique

The metal-carbon bond strengths of the Group IIb metals zinc, cadmium, and mercury have been determined by the toluene carrier technique (a kinetic method) and the
mean metal-carbon bond energies have been determined by calorimetry. The correlation of the results of these two methods is best exemplified by comparing the total bond energies obtained by the thermal decomposition of dimethylzinc \( \text{[1]} \) and the mean bond energy obtained from studies of the heat of reaction of dimethylzinc with water in ether solution \( \text{[2]} \).

From the heat of formation of dimethylzinc, the bond strengths \( D^\text{CH}_3\text{Zn-CH}_3 \) and \( D^\text{Zn-CH}_3 \) were calculated equal to 82.9 kcal/mole (assuming \( D^\text{CH}_3\text{-H} \) = 102.5 kcal per mole), and thus \( \overline{E} = 41.5 \text{ kcal/mole} \). The thermal decomposition of dimethylzinc in the toluene carrier flow system proceeds by the following mechanisms:

\[
\begin{align*}
\text{Zn(CH}_3\text{)}_2 & \rightarrow \text{Zn(CH}_3\text{)} + \text{CH}_3 \\
\text{Zn(CH}_3\text{)} & \rightarrow \text{Zn} + \text{CH}_3
\end{align*}
\]

Reaction (2) occurs at much higher temperatures than reaction (1) such that at high temperature reaction (1) occurs in a very small fraction of the contact time and reaction (2) can readily be determined. If the activation energies of these two reactions are equated to the metal-carbon bond strengths, \( D_1 = 47.2 \), \( D_2 = 35 \), and \( D_1 \) plus \( D_2 \) equal 82.2 kcal/mole. \( D_2 \) has a probable error of about 4 kcal/mole due to the large decomposition of the carrier.

Both steps of the decomposition have rate constants that are markedly dependent on the total pressure in the system. The apparent activation energy of a unimolecular reaction is a function of the pressure at which it is
determined if the reaction itself is a function of pressure.
Taking pressure dependency into consideration, both $D_1$ and $D_2$ are probably 2 kcal/mole higher than the experimental activation energies; consequently the agreement between the kinetic and calorimetric methods is meaninglessly good. However, this agreement indicates that when dimethylzinc decomposes completely, the zinc atom is released in the ground state.

In the thermal decomposition of dimethylcadmium, the mechanism is different from that of dimethylzinc in that the second methyl radical was released immediately after the first, and its rate could not be measured kinetically. From the heat of formation of dimethylcadmium obtained by calorimetric methods, $D\text{\textgreek}{\text{CH}_3\text{Cd}-\text{CH}_3}$ plus $D\text{\textgreek}{\text{Cd}-\text{CH}_3}$ equal 66.8 kcal/mole. The experimental activation energy was related to the first metal-carbon bond strength such that $D_1 = 45.8$ kcal/mole at 16 mm (pressure dependent region). $D_1$ is probably about 2 kcal/mole larger than the experimental activation energy, and thus $D_2$ may be assigned a value equal to 19 kcal/mole.

From thermochemistry, the two metal-carbon bonds of dimethylmercury have a combined strength of 57.3 kcal/mole. However, the precise mechanism and assignment of energies to each individual bond is apparently inconclusive. $D_1$ can probably be assigned a minimum value of 50 kcal/mole.

The metal-carbon bond strengths of the Group Vb metals bismuth, antimony, and arsonic have been determined by
calorimetry while only the metal-carbon bonds of bismuth and antimony have been studied by the toluene carrier technique.

The observed thermal decomposition of trimethylbismuth was straightforward $\text{[6]}$; in runs where the observed decomposition was close to 100%, the measured amounts of methane and ethane produced were in agreement with the analysis of the undecomposed metallic alkyl. Thus three methyl radicals were released each time a trimethylbismuth molecule decomposed and the following mechanism was proposed:

\[
\begin{align*}
\text{Bi(CH}_3\text{)}_3 & \rightarrow \text{Bi(CH}_3\text{)}_2 + \text{CH}_3 \quad (3) \\
\text{Bi(CH}_3\text{)}_2 & \rightarrow \text{Bi(CH}_3\text{)} + \text{CH}_3 \quad (4) \\
\text{Bi(CH}_3\text{)} & \rightarrow \text{Bi} + \text{CH}_3 \quad (5)
\end{align*}
\]

where both reactions (4) and (5) proceed immediately after reaction (3). The experimental activation energy was related to the strength of the first metal-carbon bond of trimethylbismuth, $D_{\text{Bi-CH}_3} = 44.0$ kcal/mole at 16 mm (pressure independent region). From the heat of formation of trimethylbismuth $\Delta H_f$, the sum of the three metal-carbon bond strengths was 101.4 kcal/mole (if $D_{\text{CH}_3-R}$ = 102.5 kcal/mole). The value for the sum ($D_2 + D_3$) of the second and third metal-carbon bond strengths was 57.8 kcal/mole.

On the other hand, the observed thermal decomposition of trimethylantimony was not simple $\text{[6]}$; at higher decompositions gaseous products corresponding to 74% decomposition were produced while amounts of antimony corresponding to 98% decomposition were deposited in the reaction zone.
This discrepancy was not due to the formation of substances such as hydrogen, ethylene, or propylene, for negligible quantities of these gases were produced. The apparent loss of methyl radicals was most simply interpreted by assuming that a polymer of the type \((\text{SbCH}_3)_n\) was produced. Nevertheless, for the purposes of further discussion it was convenient to assume that for each trimethylantimony molecule undergoing decomposition three methyl radicals were released. The first order rate constant based on gas analysis \(k_g\) approached the rate constant based on metal analysis \(k_m\) at low decompositions (0.179 and 0.215, respectively) but diverged at high decompositions (1.00 and 3.16, respectively). This corresponds to 91% agreement (based on percent decomposition) at low decompositions and only 75% agreement at high decompositions.

The activation energies from the Arrhenius equations derived from the metal and gas analyses are 57.0 and 53.5 kcal/mole, respectively. The activation energy based on the metal analyses was assumed to be the more probable estimate for the first metal-carbon bond strength of trimethylantimony, \(D_1^{\text{Sb-CH}_3} = 57.0\) kcal/mole. From the heat of combustion of trimethylantimony \(\Delta_f^\circ\text{Sb-CH}_3\), a value of 149.1 kcal/mole for the sum of the three metal-carbon bonds of trimethylantimony was found. Thus \(\overline{E} = 49.7\) kcal/mole and the first metal-carbon bond strength equal to 57.0 kcal/mole seems reasonable.

From the heat of formation of trimethylarsenic, the
total strength of the three metal-carbon bonds equals \(154.4\) kcal/mole \([9]\). Since the pyrolysis of trimethylantimony was so complex even when studied by the toluene carrier technique, it was difficult to believe that the pyrolysis of trimethylarsenic in a static system was straightforward. Probably little reliance could be placed on the suggestion that the overall activation energy of \(54.6\) kcal/mole observed by Ayscough and Emeleus \([10]\) was equal to the strength of the first metal-carbon bond of trimethylarsenic.

Of the Group IVb metals, a tin compound, dimethyltin dichloride, is the only compound of this group that has been studied by the toluene carrier technique. The decomposition of this compound was straightforward and the products were tin dichloride plus two methyl radicals. The experimental activation energy was equated to the strength of the first metal-carbon bond giving \(D_C{\text{Cl}}_2\text{CH}_3\text{Sn-CH}_3 = 56.1\) kcal/mole at \(16\) mm (pressure independent region) \([6]\). This bond dissociation energy is close to but greater than the mean bond energy of the metal-carbon bonds in tetramethyltin which have been reported to be \(53.5\) kcal/mole \([11]\). It is expected that the strength of the first metal-carbon bond in tetramethyltin will be greater than \(53.5\) but less than \(56.1\) kcal/mole. This is predicted by the observation that the redistribution of stannic halides with stannic alkyls was exothermic. The metal-carbon bonds in alkyl mercuric halides were found to be considerably stronger than the bonds in the corresponding dialkyls \([12]\) as in
the series:

\[ D^\text{ClHg-CH}_3 = 63.4 \text{ kcal/mole} \]
\[ D^\text{BrHg-CH}_3 = 60.7 \text{ kcal/mole} \]
\[ D^\text{IHg-CH}_3 = 59.0 \text{ kcal/mole} \]
\[ D^\text{CH}_3\text{Hg-CH}_3 = <57.3 \text{ kcal/mole}. \]

Introduction to the Present Research

Comparatively little was known about the metal-carbon bond strengths in the alkyls of the Group IIIb metals gallium, indium, and thallium. The object of the present research has been the determination of the strengths of the metal-carbon bonds of trimethylgallium, trimethylindium, and trimethylthallium. The trimethlys of these metals were so chosen because the bond ruptures should involve the simple release of methyl radicals.

No previous kinetic studies of the thermal decomposition of trimethylgallium, trimethylindium, or trimethylthallium have been reported.

The heat of formation of trimethylgallium has been obtained by the reaction of trimethylgallium with iodine in benzene solution \[ \text{^13} \], and by the heat of combustion of trimethylgallium with oxygen in a static-bomb calorimeter \[ \text{^14} \]. The mean gallium-carbon bond energies obtained by these studies were \( 56.7 \pm 4 \text{ kcal/mole} \) and \( 57.7 \pm 2 \text{ kcal/mole} \), respectively. In a recent review Long \[ \text{^15} \], using \[ D^\text{CH}_3\text{H-H} = 102.5 \text{ kcal/mole} \], has recommended a value of \( 57.5 \text{ kcal/mole} \).
A study of the reaction of tri-isobutylindium with 1-decene at 150° C for 100 hours yielded tridecylindium and 83% isobutylene $\left[{16}\right]$. The tridecylindium broke down further to yield only 64% free indium metal plus one-half mole $\text{CH}_2=\text{CH-C}_9\text{H}_{17}$ and three-halves moles $\text{CH}_3\text{CH}_2-\text{C}_8\text{H}_{18}$. The remaining indium was assumed to be in some polymeric form.

The mean metal-carbon bond energy of trimethylindium has not been reported. However, from the available data on the metal methyl compounds of Groups IIb, IIIb, IVb, and Vb, a value for trimethylindium of $E = 41 \pm 3$ kcal/mole was estimated. From incomplete studies on the heat of reaction of trimethylindium with bromine in chloroform solution, the mean indium-carbon bond strength indicated by these studies is $38.2$ kcal/mole $\left[{17}\right]$. This tentative experimental value will be used in further calculations in this work.
CHAPTER II
THEORETICAL CONSIDERATIONS

Theory of the Metal-Carbon Bond

The polarity or degree of ionic character of a bond not only influences the physical properties of the compound in accordance with the well-known characteristics of ionic and covalent compounds, but also markedly influences the chemical reactivity of the compound. In general, bond partners carry a difference of electrical charge relative to each other and this serves as a dipole that attracts and orientates neighbouring reagents. The intensity of attraction may be expected to influence the rate of reaction, and the direction of orientation will govern the products that are formed.

The carbon atom with its $2s^2$ electrons and $2p^2$ electrons in the outermost orbitals available for chemical binding, does not ordinarily employ them in these particular forms in chemical reactions. Instead, these four electrons in three orbitals (each p electron is in a separate orbital) are redistributed into four new hybrid orbitals, all equivalent in energy and tetrahedrally distributed in space; the s electrons are not distinguishable from the p electrons as would be expected because of the $2s^22p^2$ distribution, nor do we find two undirected s orbitals and two $90^\circ$ p
orbitals. The hybrid situation comes about by the 'promotion' of one of the 2s electrons to the third p orbital (unoccupied until now), followed by the interaction of the remaining s orbital with the three p orbitals to produce the sp$^3$ hybrid as shown in Fig. 1. This figure shows a schematic representation of the interaction of wave-mechanical expressions governing electron probability; the net effect is a lengthening and enlargement of one lobe of the p orbital and the marked shrinkage of the other. The resulting four elongated lobes are directed outwards from the origin towards the corners of a tetrahedron. If these four lobes overlap with the spherical orbitals of four hydrogen atoms, bonding results and the tetrahedral molecule methane is produced.

Fig. 1: Formation of an sp$^3$ Hybrid Orbital.
The promotion of an s electron to a higher energy p orbital in order to begin this process requires energy, but the energy is recovered in the process of chemical combination to form the stable tetrahedral product. The chief advantage of a hybridized atomic orbital is its high directional character, which according to the principle of maximum overlapping $\langle 18 \rangle$, should yield a stronger bond.

Certain general features of bond strengths follow from such considerations. In the first place, s bonds are almost always weak (excluding $H_2$ because of the inherent stability due to a completed orbital). This is because two similar s orbitals on adjacent atoms cannot possibly overlap to any great degree because of the spherically symmetrical distribution of their charge. Such bonds are weaker than p bonds, where the directional character allows considerable overlap. Both of these should be weaker than the sp$^3$ hybrid where the overlap is very great. Interesting examples of these rules are the molecules Li$_2$, F$_2$, and C$_2$ (as in C$_2$H$_6$) where the bond energies are 26, 35, and 80 kcal/mole, respectively.

The other Group IVb elements, silicon, germanium, tin, and lead form tetrahedral sp$^3$ hybrids in the same way. The above advantages of bonding with such orbitals accrue to these metals, and an extensive organic chemistry for each of them is found based on tetrahedral compounds of the type $R_4M$. In the heavier elements there can be the withdrawal of the s electrons as an inert pair and the use of only the p electrons to form metal alkyls of the type $R_2M$. The
compounds formed are unstable. The marked increase in stability of $R_4M$ over $R_2M$ emphasizes the benefits of hybridization.

Looking further, metals outside the fourth group may form sp hybrid orbitals, but necessarily of some type other than sp$^3$. The Group IIIb metals gallium, indium, and thallium, with their outermost electronic configuration of ns$^2$np$^1$ may promote one of the s electrons to the p level and form three trigonal sp$^2$ hybrid orbitals leading to volatile metallic alkyls of the type $R_3M$. In Group IIb, there is the promotion of one of the s electrons to the p level with the formation of two linear sp hybrid orbitals leading to volatile metallic alkyls of the type $R_2M$. Elements in Group Vb, with single electrons in each p orbital cannot improve matters by hybridization and are content with metallic alkyls of the type $R_3M$, where the s electrons probably remain as an inert pair. In the Group Vlb elements, the fourth p electron added goes into an orbital with one of the other p electrons; consequently matters cannot be improved by hybridization and metallic alkyls of the type $R_2M$ are formed, the s electrons and the paired p electrons forming two inert pairs.

If the metal-carbon bond is represented by M-C, we may designate relative polarity by indicating fractions of electronic charge in the following manner:

$$\delta^\oplus_{M-C} \delta^\ominus$$

The electronic cloud constituting the bond is not equidistant
between the nuclei, but is shifted towards the carbon atom because of its electronegativity.

A methyl group is rather positive relative to the hypothetical free carbon atom, for in a methyl group the carbon bears three hydrogen atoms which are considerably more electropositive than the carbon itself. In this way the electronegativity of the carbon is reduced and the metal-carbon bond will be more covalent with hydrocarbon group involved.

Suppose a methyl group is attached to a metal, and this bond is exposed to water. A single water molecule has a distribution of charge, both H atoms are positive with respect to the O atom. The H-O dipole will be attracted to the M-C dipole and orientated in the appropriate direction:

\[ \text{H-O} \rightarrow \text{M-C} \]

The approach of the dipole continues with a corresponding loss in potential energy, until repulsion by the electronic shells equalizes the attraction. We now have a four-centered active intermediate which may break apart into the original components or realign its bonds to form new substances. If the change in free energy favours the latter, the products will be:

\[ \text{C and M} \]
\[ \text{H} \quad \text{OH} \]

Hydrolysis of a metallic alkyl therefore produces a hydrocarbon and a metal hydroxide. The reaction is generally swift and violent for most metallic alkyls where the metal-
carbon bond is quite polar. When the metal-carbon bond is much less polar, as in \((\text{CH}_3)_4\text{Si}\) or \((\text{CH}_3)_2\text{Hg}\), the reaction is extremely slow and must be accelerated by the increase of temperature and pressure or by the use of catalysts.

**Properties of Metallic Alkyls**

1. General Trends in Physical Properties

The properties of a metallic alkyl depend on both the nature of the central atom and on the nature of the organic group(s) attached to that atom. Three trends of particular interest may be discussed using boiling points as a typical physical property:

a) Effect of the Organic Group(s): The differences in the boiling points with different organic derivatives are explained quite sufficiently on the basis of sizes, shapes, and polarities of the organic groups:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)_4\text{Si})</td>
<td>27</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5)_4\text{Si})</td>
<td>153</td>
</tr>
<tr>
<td>((\text{n-C}_3\text{H}_7)_4\text{Si})</td>
<td>212</td>
</tr>
<tr>
<td>((\text{C}_4\text{H}_9)_4\text{Si})</td>
<td>275</td>
</tr>
<tr>
<td>((\text{n-C}<em>5\text{H}</em>{11})_4\text{Si})</td>
<td>318</td>
</tr>
</tbody>
</table>

\((\text{CH}_3)_2\text{Hg}\) | 92 |
| \((\text{C}_2\text{H}_5)_2\text{Hg}\) | 127 |
| \((\text{C}_3\text{H}_7)_2\text{Hg}\) | 159 |
| \((\text{n-C}_3\text{H}_7)_2\text{Hg}\) | 189 |

This behaviour may be observed with the compounds of any element in Groups III through VII (excluding the transition elements in the a-subgroups) and the compounds of the Group IIb elements zinc, cadmium, and mercury. The solid polar compounds of the more strongly electropositive elements of Groups I and II are not volatile and cannot be compared in
this fashion.

The substitution of branched-chain hydrocarbon groups for straight chain, or normal hydrocarbon groups generally increases the volatility of the metallic alkyls:

\[
\begin{align*}
(n-C_5H_{11})_4Si & \text{ b.p. } 318^\circ C \\
(i-C_5H_{11})_4Si & \text{ b.p. } 76 \\
(n-C_3H_8)_2Hg & \text{ b.p. } 318^\circ C \\
(i-C_3H_8)_2Hg & \text{ b.p. } 87^\circ C
\end{align*}
\]

a) at 25 mm pressure

b) Transitions Within a Given Group: With but few exceptions, the different elements in a given group all form the same general type of organic derivative. In any homologous series, the weight and size of the parent element can be important in determining differences in physical properties; except for the heavier periods of the Group IIb metallic methyls, there is usually an increase in boiling point with molecular weight:

\[
\begin{align*}
\text{Group IIb} & & \text{Group IIIb} \\
(CH_3)_2Zn & \text{ b.p. } 142^\circ C & (CH_3)_3Ga & \text{ b.p. } 156^\circ C \\
(CH_3)_2Cd & 106 & (CH_3)_3In & 136 \\
(CH_3)_2Hg & 92 & (CH_3)_3Tl & 147
\end{align*}
\]

c) Transitions Across a Period: The physical properties across a period are determined, not only by the polarity of the metal-carbon bonds, but also by the molecular weight and symmetry of the compounds. In most cases, the
changes are gradual rather than abrupt. If the boiling point is considered a typical physical property, there is no set trend across a period:

Group: IIb IIIb IVb Vb VIb
alkyl: (CH₃)₂Cd (CH₃)₃In (CH₃)₄Sn (CH₃)₃Sb (C₃H₇)₂Te
b.p.: 106°C 136 78 81 82

2. General Trends in Chemical Properties

A few broad generalizations can similarly be made concerning the chemical behaviour of metallic alkyls under the following headings:

a) Thermal Stability: In any one group, it is generally observed that the compounds of the heavier elements are less stable towards thermal decomposition than those of the lighter elements (except in Group IIb). This trend is illustrated by the metallic alkyls of Group IIIb:

(CH₃)₃Ga \[ k = 10^{15.5} e^{-59,500/RT} \]
(CH₃)₃In \[ k = 10^{15.7} e^{-47,200/RT} \]
(CH₃)₃Tl \[ k = 10^{10.2} e^{-25,800/RT} \]

Also, it is observed that the thermal stability is generally higher in compounds of the more electronegative elements (except in Group IIb) in a given period. All rate constants given are corrected estimates for the high pressure limit:

(CH₃)₃Sb \[ k = 10^{15.2} e^{-57,200/RT} \]
(CH₃)₃Sn \[ k = 10^{14.5} e^{-55,000/RT} \]
(CH₃)₃In \[ k = 10^{15.7} e^{-47,200/RT} \]
(CH₃)₂Cd \[ k = 10^{12.5} e^{-48,000/RT} \]
This trend appears to hold for all periods except for the seventh.

The thermal stabilities of the organic compounds of a particular element depend largely on the nature of the attached groups. \((\text{CH}_3)_3\text{Tl}\) decomposes explosively above 90° C whereas \((\text{C}_6\text{H}_5)_3\text{Tl}\) melts at 170° C without decomposition.

b) Spontaneous Inflammability: Ignition on exposure to air is observed with a large number of metallic alkyls, particularly the lower alkyl derivatives of Group IIIb (Al, Ga, In, Tl), Group IIb (Be, Zn, Cd), the alkyls of the alkali metals and alkaline earth metals in Group Ia (Li, Na, K, Rb, Cs) and Group IIa (Mg, Ca, Sr, Ba), and with some of the compounds in Group Vb (P, As, Sb, Bi). Alkyl derivatives of many other metals are known to oxidize readily on exposure to air, but they may not ignite. The tendency to spontaneous ignition, which in reality is the consequence of a rapid exothermic reaction with atmospheric oxygen, possibly catalyzed by water vapour, is considerably reduced in higher alkyl and aryl derivatives.

c) Chemical Reactivity: The reactivity of metallic alkyls of the Groups Ia, IIa, and IIIa increases with increasing atomic weight of the parent \((\text{Cs-R} \succ \text{Rb-R} \succ \text{K-R} \text{etc})\). With the b-elements, the order of reactivity is reversed \((\text{Cu-R} \succ \text{Ag-R} \succ \text{Au-R})\). Within a given period, the reactivity decreases with increasing atomic weight \((\text{Na-R} \succ \text{Mg-R} \succ \text{Al-R})\).

In Groups V, VI, and VII the generalizations are just
the reverse of Group I, II, and III. In the transition
groups, reactivities decrease with increasing atomic weight
of the parent (Mn-R > Re-R), and the reactivities increase
with increasing atomic number in the non-transition b-groups
(Bi-R > Sb-R > As-R).

The organic derivatives of the Group IV elements are
intermediate, and there appears to be less difference be­
tween the compounds of the a- and b-groups of this group
than in other groups.

A further observation is that unsymmetrical compounds
are more reactive than the symmetrical derivatives of the
same metal (RMR' > RMR).

The Group IIIb Metals
The chemistries of gallium, indium, and thallium are
closely related. With atomic numbers of 31, 49, and 81,
respectively, gallium, indium, and thallium have outer
electronic configurations of the type ns²np¹ where n has
the values 4, 5, and 6, respectively. Increases in atomic
number and atomic weight are paralleled by increases in
density, atomic volume, and atomic and ionic sizes. The
metallic lattices have fairly weak bonding and are easily
ruptured to yield low melting points. On the other hand,
the boiling points are high with a slight decrease with
increasing atomic weight. Thus the elements of this group
are characterized by long liquid ranges, this property being
most pronounced with gallium (m.p. 30° C and b.p. 2070° C).
In this family the first ionization potentials are low, as the removal of one electron requires less energy than for the neighbouring elements. There is just one p electron in the nth quantum level, and since this electron is less penetrating than the previously added s electrons, it is better shielded from the positive nucleus by the electronic cloud around the element and thus easier to remove. However, the second and third ionization potentials are very high.

Inasmuch as the outer electronic arrangements in the atoms of gallium, indium, and thallium contain three more electrons than the pseudo inert gas structure ns$^2$np$^6$nd$^{10}$, a uniform +3 oxidation state is expected. This state is characteristic of all of these elements but potential data indicate that tendencies to enter this state decrease from gallium to thallium. The +3 state is largely covalent but tripositive ions are known in aqueous solution for all three of these elements.

The ns$^2$np$^1$ electronic arrangement also suggests the +1 oxidation state. This state is well known with thallium where oxidation potential data indicate that it is more stable in aqueous systems than the +3 state. The stability of the +1 state increases regularly with atomic weight in this family, the influence of the inert pair (the pair of s electrons in the nth quantum level) becoming increasingly more important for the heavier elements because of insufficient energy to cause unpairing.
Metallic MethyIs of Group IIIb

Relatively few organic compounds of gallium have been described, and those that have been were prepared from gallium metal and the appropriate mercury alkyl or from gallium trichloride and the appropriate Grignard reagent. They are highly reactive, violently hydrolyzed by water (the lower alkyls being spontaneously inflammable), but they are less reactive than their aluminum analogues. Trimethylgallium (m.p. -15° C) is a colourless liquid with a boiling point of 56° C. Trimethylgallium, unlike dimeric trimethylaluminum, is monomeric in the vapour phase.

The organic compounds of indium have not been studied extensively. Indium resembles gallium much more than thallium in its organic derivatives and reactivity because of their similar electronegativities (both have values of 1.6). Trimethylindium is a white volatile solid which melts at 89.5° C forming a colourless liquid which has a boiling point of 136° C. The vapour is monomeric. Trimethylindium can be readily transferred within a vacuum apparatus forming white needle-like crystals.

The organic compounds of thallium are similar in their general chemical character to their gallium and indium analogues. The trialkyls are prepared with the use of organolithium compounds, since the action of the less reactive Grignard reagents proceeds only as far as the introduction of two organic groups to give the structure R₂TlX. The failure of the reaction between thallium and organomercury
compounds, successful for the preparation of gallium and indium alkyls, is due to the low electronegativity of thallium compared to mercury. Trimethylthallium is a white volatile solid that melts at 38.5°C forming a pale yellow liquid which has a boiling point of 76°C at 85 mm (147°C extrapolated to 760 mm). Trimethylthallium should not be heated over 90°C for fear that it might detonate. The vapour is monomeric. Trimethylthallium can be transferred within a vacuum apparatus forming needle-like crystals. Trimethylthallium is stable if kept in the dark but darkens on exposure to light. Thallium has the only trimethyl in this group that reacts slowly with mercury at room temperature producing dimethylmercury and thallium amalgam.

**Mean Bond Energies by Calorimetric Methods**

The calorimetric methods for the determination of mean bond energies may be classified under two main classifications: solution calorimetry and bomb calorimetry (static and rotating).

The data obtained in solution calorimetry allows the heat of reaction, which is usually a halogenation or a hydrolysis, to be calculated. If the necessary auxiliary data are available, the heat of formation may then be calculated. The overall accuracy of the experimental results in solution calorimetry will depend upon the calorimetric and chemical aspects of the investigation. However, the limiting factor in attainable accuracy is more the chemical rather than the
calorimetric part of the determination $\Delta H$.

The heat of formation of trimethylgallium has been obtained from the reaction of trimethylgallium with iodine in benzene solution at 55°C $\Delta H_{f}$. With a molar ratio of trimethylgallium to iodine of 1:7, about 70% of the iodine theoretically required for complete halogenation was used. With a ratio of 1:20 the amount was 87%. Of the total heat of reaction, about 80% was evolved in the first 4 minutes, and after 45 minutes the heat continued to be evolved at a rate of 0.3% per minute. Because of the low solubility of iodine in benzene, higher concentrations could not be used; because of the low boiling point of benzene, higher temperatures could not be used to increase the solubility of the iodine. Because of these limits on the experimental conditions used, 100% reaction could not be achieved in a reasonable time. From these experiments, $\Delta H_{f}(CH_{3})_{3}Ga, liq$ was $-14.5 \pm 8$ kcal/mole. The rather large limits of error are a result of errors in auxiliary data and the need to extrapolate to 100% reaction.

For metallic alkyls, the mean metal-carbon bond energy is obtained by the following equations:

\[
\begin{align*}
M(o) + nC(graphite) + 3/2nH_{2}(g) & \longrightarrow (CH_{3})_{n}M(g) \\
M(g) & \longrightarrow M(o) \\
nCH_{3}(g) + nH(g) & \longrightarrow nCH_{4}(g) \\
nCH_{4}(g) & \longrightarrow nC(g) + 2nH_{2}(g) \\
1/2nH_{2}(g) & \longrightarrow nH(g) \\
nC(g) & \longrightarrow nC(graphite)
\end{align*}
\]
Adding, we obtain the result:

\[ M(g) + nCH_3(g) \rightarrow (CH_3)_nM(g) - \Delta H \]

where:

\[ -\Delta H = D_1 + D_2 + \ldots \ldots \ldots D_n = E \]

Thus \( D_1 + D_2 + \ldots \ldots \ldots D_n \) equal

\[ \Delta H_f^c(CH_3)_nM, g^c \] + \( \Delta H_f^cM, g^c \) - n\( \Delta H_f^cCH_3, g^c \)

In the case of trimethylgallium:

\[ \Delta H_f^c(CH_3)_3Ga, g^c = -6.7 \pm 8 \text{ kcal/mole} \]
\[ \Delta H_f^cGa, g^c = 65.6 \pm 0.5 \text{ kcal/mole} \]
\[ \Delta H_f^cCH_3, g^c = 32.6 \pm 1 \text{ kcal/mole} \]

Therefore \( D_1 + D_2 + D_3 = 170.1 \pm 11.5 \text{ kcal/mole} \)

or \( E = 56.7 \pm 4 \text{ kcal/mole} \).

The data obtained in bomb calorimetry by direct experimentation is the heat of combustion from which may be determined the heat of formation of the compound studied. When the combustion of an organometallic compound takes place in a conventional static-bomb calorimeter, oxides of the metal and in certain cases the metal itself are formed in addition to the usual products from the organic part of the molecule. The oxides are commonly found as a complex mixture and are often in such a finely divided state that their heat content differs from that of the bulk substances.

In the combustion of trimethylarsine the products are As, \( \text{As}_2\text{O}_3 \), \( \text{As}_2\text{O}_4 \), and \( \text{As}_2\text{O}_5 \) while in the combustion of trimethylgallium the products are Ga and \( \text{Ga}_2\text{O}_3 \), along with carbon dioxide and water.

In combustion calorimetry, the actual process that
occurs in the bomb must be related to the experimental heat of combustion. Thus we require the identity, the physical state, and the amounts of all products. Because of the ease of separation of the products of combustion in the experiments with either trimethylarsine or trimethylgallium, these requirements are met.

The heat of combustion of trimethylarsine is given by the following equation:

\[(\text{CH}_3)_3\text{As}(1) + 6\text{O}_2(\text{g}) \rightarrow \frac{1}{2}\text{As}_2\text{O}_3(\text{c}) + 3\text{O}_2(\text{g}) + 4\frac{1}{2}\text{H}_2\text{O}(1)\]

\[+ 664.6 \pm 1.2 \text{ kcal/mole} \]

The heat of formation of trimethylarsine can be obtained from the heat of combustion by the following equations:

\[\text{As}(\text{c}) + \frac{3}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{As}_2\text{O}_3(\text{c})\]
\[3\text{C(graphite)} + 3\text{O}_2 \rightarrow 3\text{CO}_2(\text{g})\]
\[4\frac{1}{2}\text{H}_2 + 2\frac{1}{2}\text{O}_2 \rightarrow 4\frac{1}{2}\text{H}_2\text{O}(1)\]
\[\frac{1}{2}\text{As}_2\text{O}_3(\text{c}) + 3\text{CO}_2 + 4\frac{1}{2}\text{H}_2\text{O}(1) \rightarrow (\text{CH}_3)_3\text{As}(1) + 6\text{O}_2\]

Therefore:

\[\Delta H_f^\circ(\text{CH}_3)_3\text{As}, 1\downarrow = 3.5 \pm 1.2 \text{ kcal/mole}\]

The mean bond energy for trimethylarsine is obtained by substituting the above value into the equations developed earlier in the discussion of solution calorimetry. Thus:

\[\text{As}(\text{g}) + 3\text{CH}_3(\text{g}) \rightarrow (\text{CH}_3)_3\text{As}(\text{g}) - \Delta H\]

or \(E = 51.5 \text{ kcal/mol}\)

Generally the requirements of identity, physical state, and amounts of all products can seldom be met in static-bomb methods for metallic alkyls if complex products are formed.
The rotating-bomb calorimeter provides a means for producing a final state of the bomb process that is easy to characterize both chemically and thermodynamically. A suitable solution is placed in the bomb so that the products of combustion can be dissolved. Rotation of the bomb immediately after the combustion reaction is finished assures the rapid solution of the solid products wherever they may be in the bomb. The final state consists of a gas phase and a liquid phase containing the metal in a single oxidation state, with both phases homogeneous and in equilibrium with one another.

The rotating-bomb method was used to determine the heat of formation of tetraethyllead \( \text{C}_4\text{H}_{10}\text{Pb} \). The products of combustion in addition to carbon dioxide and water were \( \text{Pb}, \text{PbO}, \text{PbO}_2, \text{PbCO}_3 \), and \( \text{Pb(NO}_3\text{)}_2 \). A solution of nitric acid (10%) and arsenious acid (0.1%) was used to convert all lead-containing products of combustion to the \( \text{Pb}^{++} \) ion.

**Bond Dissociation Energies by the Kinetic Method**

The direct kinetic determination of bond dissociation energies depends on the assumption that for the reaction

\[
R_1R_2 \rightarrow R_1 + R_2
\]

the activation energy of the reverse or recombination reaction is zero. Thus the activation of the forward reaction is equal to the energy of reaction, or the bond dissociation energy.

The assumption of zero activation energy for the recombination reaction has considerable experimental
justification in the case of atoms and small radicals. An energy of activation would imply that two radicals of appropriate spin approaching one another to form a molecule would suffer some repulsion before combining. Schematically this would be represented by a hump on the energy-interatomic distance curve, or 'potential energy curve', for the interaction of two radicals (Fig. 2, a). Much evidence on such potential energy curves where \( R_1 \) and \( R_2 \) are atoms has accumulated from band spectroscopic studies, and the results show that usually no such potential maximum as shown in Fig. 2, b occurs.

The rotating sector method has been applied to the determination of the rate constant of methyl radical recombination in the photo-decompositions of acetone (at 125° C and 175° C) and dimethylmercury (at 175° C and 220° C), using the small but accurately known rate of methane formation as a measure of the methyl radical steady-state concentration \(^{21}\). The resulting value of the recombination rate constant is \( 4.5 \times 10^{13} \) cc/mole-sec, with an activation energy of \( E = 0 \pm 700 \) cal/mole regardless of the radical source. A second determination of the rate constant of methyl radical recombination using the photo-decomposition of acetone (at 135° C and 165° C) by the rotating sector technique \(^{22}\) gives a value in agreement with the above work.

If there is no potential energy barrier for the recombination of two radicals, the transition state theory
Fig. 2: Potential energy curve for a unimolecular decomposition into two radicals. Curve \( \alpha \) represents a finite energy of activation for recombination. Curve \( \beta \) represents a zero energy of activation for recombination.
predicts that for a unimolecular reaction the rate constant is given by:

$$k = K \frac{k'T}{h} \frac{\phi'(T)}{\phi(T)} e^{-D/RT}$$

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 $v(T)$ contributions.

The translational partition function

$$\lambda(T) = \frac{(2\pi mk'T)^{3/2}}{h^3}$$

will be the same for the normal molecule and the activated complex.

The rotational partition function will be

$$r(T)/\sigma = 8\pi^2 Ak'T/\sigma h^2$$

for a linear molecule, and

$$r(T)/\sigma = 8\pi^2(2\pi k'T)^{3/2}(ABC)^{1/2}/\sigma h^3$$

for a non-linear molecule. The rotational partition function will be almost the same for the normal molecule and the activated complex, the rotational partition function for the activated complex being slightly larger.

If each mode of internal vibration behaves as a linear harmonic oscillator, the rate constant for a non-linear molecule undergoing unimolecular decomposition may be written:

$$k = K \frac{k'T}{h} \frac{\phi'(T)}{\phi(T)} \left[ \frac{A'B'C'}{ABC} \right]^t \frac{3n-6}{3n-7} \frac{\pi}{7} \frac{1 - e^{-hv/k'T}}{1 - e^{-hv/k'T}} e^{-D/RT}$$

If $hv \ll k'T$, then $(1 - e^{-hv/k'T}) \approx hv/k'T$, and we obtain:
Taking logarithms of both sides of this equation and differentiating with respect to temperature gives:

\[ \frac{d(\ln k)}{dT} = \frac{D}{RT^2} \]

The Arrhenius activation energy is therefore equal to the bond dissociation energy.

At the other extreme, if \( hv >> k'T \), \( (1 - e^{-hv/k'T}) \approx 1 \), such that:

\[ k = K \frac{g'[A'B'C']}{\sigma' \left[ \frac{A'B'C'}{ABC} \right]^k} \frac{k'T}{\hbar} e^{-D/RT} \]

Taking logarithms of both sides of this equation and differentiating with respect to temperature gives:

\[ \frac{d(\ln k)}{dT} = \frac{D + RT}{RT^2} \]

Therefore the limits \( D < E < D + RT \) may be placed upon the experimental activation energy. Thus if the experimental activation energy for a unimolecular decomposition can be accurately determined, it should be a reasonable approximation to the bond dissociation energy.

**Pressure Dependence of Bond Dissociation Energies**

One of the most satisfactory and realistic theories of unimolecular reactions is that of Slater. For his model, Slater takes a polyatomic molecule in which all oscillators are classical and harmonic. The molecular motions are described in terms of a series of internal coordinates,
and reaction is supposed to take place when a specified coordinate attains a critical value. If the reaction under consideration is the dissociation of a molecule into two radicals, the critical value of the specified coordinate is the critical length between the two atomic nuclei being separated in an activated molecule. If enough modes of vibration come into phase in the same instant, all of them together can achieve the critical value in the specified coordinate and lead to the rupture of the bond. The observed first order rate constant is the rate of decomposition of this activated molecule into products.

Slater defines the activation energy $E_a^{\infty}$ at high concentration to be:

$$E_a^{\infty} = RT \frac{d \ln k}{dT}$$

keeping either concentration or pressure constant, and this reduces to $E_o$ in the Arrhenius case where the activation energy was defined as the critical (minimum) energy for dissociation.

Slater has also postulated that if the unimolecular rate constant is measured in the pressure dependent region, the experimental activation energy $E$ is related to the experimental activation energy at infinite pressure $E_o$ ($E_a^{\infty}$) by the relation:

$$E = E_o - \frac{1}{2} n' RT g(\Theta)$$

where $n'$ is equal to the number of effective oscillators in the molecule and $g(\Theta)$ represents the fractional drop of $E$
from the high value \( E_0 \) to the low value \( E_0 - \frac{1}{4} n' RT \).
The function \( g(\theta) \) is related to the amplitude factor in the critical coordinate and goes from zero to unity.

In the previous section it was shown that the experimental activation energy \( E \) for a unimolecular dissociation lies within the limits \( D \leq E \leq D + RT \). The assumption that \( E = E_0 \) was inherent in the derivation of this result. Therefore, if the experimental activation energy has been determined in the pressure dependent region, the magnitude of \( E_0 - E \) must be determined to estimate the bond dissociation energy.

The calculation of \( k/k_\infty \) and hence of \( g(\theta) \) requires a complete vibrational analysis of the molecule in question. This is generally not available. The approximate value of \( k/k_\infty \) may be obtained from the slope of log \( k \) versus log \( P \) obtained experimentally. Values of \( k/k_\infty \) as a function of the pressure dependent parameter \( \Theta \) have been tabulated by Slater for values of \( n' \) from 1 to 13. Because no complete vibrational analysis is available for the molecule in question, it is necessary to arbitrarily choose a value of \( n' \), the number of effective oscillators in the molecule. For a non-linear molecule, there are \( 3n - 6 \) vibrational degrees of freedom \( (3n - 5 \) if linear). However, in a molecule with several heavy nuclei the contributions from the C-H bonds will usually be small except for the contributions from those bonds near the point of rupture. For purposes of further calculations, the number
of effective oscillators will be taken as \( \frac{1}{2}(3n - 6) \).

For dimethyl metals, \( n' \) may reasonably be assigned a value of about 10. The value of \( k/k_\infty \) obtained from the experimental data for these compounds at 13 mm is 0.40. This corresponds to a value for \( g(0) \) approximately equal to 0.35 \( \left( \text{23} \right) \). Hence at 700° K:

\[
E \approx E_0 - 2.5 \text{ kcal/mole}
\]
The effective number of oscillators in trimethyl metals may reasonably be assigned a value of 16. The value of \( k/k_\infty \) obtained from experimental data for these compounds at 13 mm is approximately 0.95 and this corresponds to \( g(0) \) approximately equal to 0.04. Hence at 700° K:

\[
E \approx E_0 - 0.4 \text{ kcal/mole}
\]

For methyl metals, \( n' \) may be assigned a value of 8. Since \( k/k_\infty \) is about 0.40, \( g(0) \) is 0.35. Hence at 700° K:

\[
E \approx E_0 - 2.0 \text{ kcal/mole}
\]

For the compounds studied, it is not unreasonable to assume \( h\nu/k'T \approx 1 \) at 700° K \((\nu \approx 10^{13}) \). Hence:

\[
E_0 \approx D + 0.82T = D + 0.7 \text{ kcal/mole}
\]

Therefore the errors obtained in assuming \( D = E \) will be 0.3 to 1.8 kcal/mole. In the following sections, the following corrections will be made to the experimental activation energies:

\[
\begin{align*}
D_1 &= E_1 + 0 \text{ kcal/mole} \\
D_2 &= E_2 + 1.8 \text{ kcal/mole} \\
D_3 &= E_3 + 1.3 \text{ kcal/mole}
\end{align*}
\]
The Toluene Carrier Gas Technique

The problem of determining bond dissociation energies by the kinetic method is reduced to that of finding the activation energy of the unimolecular dissociation process:

\[ R_1R_2 \rightarrow R_1 + R_2 \]

The investigation of the kinetics of the process may be complicated by various secondary reactions such as the recombination of \( R_1 \) and \( R_2 \) or abstraction from \( R_1R_2 \) by either \( R_1 \) or \( R_2 \). The first reaction leads to a loss of product, while the second might initiate a chain process. Consequently the kinetics of the whole process can be very complex and difficult to interpret.

A useful method which in some cases insures that complicating side reactions do not confuse the kinetics of the unimolecular dissociation reactions is the toluene carrier technique \( ^{24, 25} \). Toluene reacts readily with various radicals or atoms according to the equation:

\[ R + C_6H_5-CH_3 \rightarrow C_6H_5-CH_2 + RH \]

The radicals react preferentially with the toluene which is present in a very large excess, each radical being therefore completely surrounded by toluene. The formation of the stable molecule RH prevents the back reaction and possible side reactions. The benzyl radicals do not react in the hot zone under the experimental conditions used, and eventually dimerize outside the reaction zone. To prevent the formation and decomposition of dibenzyl in the reaction zone, short contact times (approximately 1 to 2 seconds) and high
flow rates (flow rate of toluene should be at least 100 times greater than the flow rate of the compound to be decomposed) are used. The rate of initial dissociation may be measured by the formation of products of the type RH, C₆H₅-CH₂-R, or by the measurement of dibenzyl itself.

Under 700° C, the decomposition of toluene is negligible, being less than 0.01% \( \leq 26 \), and approaches 1% decomposition at 800° C. The thermal decomposition may be represented by the following mechanism:

\[
\begin{align*}
C₆H₅-CH₃ & \longrightarrow C₆H₅-CH₂ \\
H + C₆H₅-CH₃ & \longrightarrow C₆H₅-CH₂ + H₂ \\
\text{and} \quad H + C₆H₅-CH₃ & \longrightarrow C₆H₆ + CH₃ \\
CH₃ + C₆H₅-CH₃ & \longrightarrow C₆H₅-CH₂ + CH₄
\end{align*}
\]

followed by the dimerization of the benzyl radicals. The quantity of dibenzyl recovered is one mole of dibenzyl per mole of gas (H₂ and CH₄ in the ratio 60:40) produced. More recent investigations indicate H₂ and CH₄ are produced in the ratio of 67:33 \( \leq 27 \) and the first order rate constant for the thermal decomposition of toluene is given by:

\[
\log_{10} k \ (\text{sec}^{-1}) = 14.8 - (85,000/2.303RT)
\]

It is important to make clear the limitations of the toluene carrier technique. This method cannot be used for the determination of bond dissociation energies greater than that for the carbon-hydrogen bond in toluene unless a different product is formed. Even if such a product is formed, the large quantities of H₂ and CH₄ produced often create physical problems unless they can be continuously pumped
away without losing the desired product. The most favourable case is that in which the dissociation energy of the bond to be broken is at least 10 kcal/mole lower than $D_{C_6H_5CH_2-H}$. 

Secondly, the radical or atom produced in the initial dissociation should react easily with toluene to produce the stable molecule $RH$. It is also possible to use this technique even if the initial radical decomposes producing a new radical that reacts with toluene. On the other hand, it might appear that the toluene carrier technique could be used to determine the dissociation energies of very weak bonds. This is not the case. For a very low bond dissociation energy, the temperature required might be so low that the abstraction reaction would be too slow to remove the radical $R$, since this reaction requires some activation energy $\geq 28$. However, even at these low temperatures where the methyl radicals released dimerize to a large extent, the toluene still performs its essential function of reducing any attack of the released radicals on the parent substance.

**Kinetics of Unimolecular Decompositions**

In the unimolecular thermal decomposition of a metallic alkyl, the activated complex consists of a single activated reactant molecule which follows first order kinetics. The mechanism of decomposition may be represented by:

$$A \rightarrow B + R$$
Let the initial concentration of A be \( a \) moles per cc. At any time \( t \):

\[
- \frac{d[A]}{dt} = k_1 [A]
\]

Separating the variables and integrating, we obtain:

\[
\ln \left( \frac{[A]}{a} \right) = -k_1 t
\]

or

\[
[A] = a e^{-k_1 t}
\]

The most common form of this equation and the one that will be used in this work is:

\[
k_1 = \frac{2.303 \log \frac{a}{a-x}}{t_c}
\]

where \( x \) is the amount of A that has decomposed.

If we have a series of consecutive reactions:

\[
\begin{align*}
A & \xrightarrow{k_1} B + R_1 \\
B & \xrightarrow{k_2} C + R_2
\end{align*}
\]

the total concentration remains constant:

\[
a = [A] + [B] + [C]
\]

The net rate of formation of B is the rate of its formation from A minus the decomposition of B to give C:

\[
\frac{d[B]}{dt} = k_1 [A] - k_2 [B]
\]

\[
= k_1 a e^{-k_1 t} - k_2 [B]
\]

Integrating, we obtain:

\[
[B] = a \frac{k_1}{k_2-k_1} (e^{-k_1 t} - e^{-k_2 t})
\]

The concentration of C is obtained by:

\[
[C] = a - ([A] + [B])
\]

\[
\therefore [C] = a - \left[ a e^{-k_1 t} + a \frac{k_1}{k_2-k_1} (e^{-k_1 t} - e^{-k_2 t}) \right]
\]
In the step-wise decomposition of a metallic trimethyl, we have:

\[ M(CH_3)_3 \xrightarrow{k_1} M(CH_3)_2 + CH_3 \]
\[ M(CH_3)_2 \xrightarrow{k_2} M(CH_3) + CH_3 \]

The total methyl radicals released equals \( M(CH_3)_2 + 2M(CH_3) \)

The total methyl radicals equals \([B] + 2[C]\)

Substituting for \([B]\) and \([C]\) from above, we obtain the consecutive order equation:

\[
\text{total methyl radicals} = a \left[ 2 + \frac{k_1}{k_2-k_1} (e^{-k_1t} + e^{-k_2t}) - 2 \frac{k_2}{k_2-k_1} e^{-k_1t} \right]
\]

**Kinetics of Methyl Extraction**

In the thermal decomposition of metallic methyls, methyl radicals are released into the toluene carrier flow system, and their reaction with toluene, i.e. the abstraction reaction, is given by:

\[ CH_3 + C_6H_5-CH_3 \rightarrow C_6H_5-CH_2 + CH_4 \]

The rate of formation of methane is given by:

\[
\frac{d[CH_4]}{dt} = k_a [CH_3] [C_6H_5-CH_3]
\]

Methyl radicals are also removed from the system by the combination of two methyl radicals:

\[ CH_3 + CH_3 \rightarrow CH_3-CH_3 \]

The rate of formation of ethane is given by:

\[
\frac{d[C_2H_6]}{dt} = k_r [CH_3]^2
\]

From the rates of formation of methane and ethane, we obtain the following equation:
The rate of formation of methane or ethane during a run is found by:
\[
\frac{d[\text{CH}_4 \text{ or } \text{C}_2\text{H}_6]}{dt} = \frac{\text{total } \text{CH}_4 \text{ or } \text{C}_2\text{H}_6 \text{ obtained}}{\text{reaction volume } \times \text{time}}
\]
The result is in moles/cc/sec. The concentration of toluene in moles/cc is obtained by:
\[
[\text{C}_6\text{H}_5-\text{CH}_3] = \frac{PV}{RT} = \frac{P_{mm}}{760} \times \frac{1}{82.05 T_{\theta K}}
\]
The most usable form of \( \frac{k_a}{k_r} \) is given by:
\[
\frac{k_a}{k_r} = \frac{(\text{total methane})}{(\text{total ethane})} \times \frac{1}{(\text{rx vol } \times \text{time})}^{\frac{1}{2}} \times \frac{62360T}{P}
\]
which has the units (cc/mole-sec)^\(\frac{1}{2}\).

The value of \( k_r \) has been obtained from rotating sector experiments \(^21, 22^7\), and consequently a value for \( k_a \) can be calculated from experimental results. However it is more convenient to assume that the methyl radical combination reaction has zero activation energy.

The normal form of the Arrhenius equation is given by:
\[
k = A e^{-E/RT}
\]
Alternately, we may write:
\[
\log k = \log A - E/2.303RT
\]
Differentiating with respect to \( T \), we obtain:
\[
\frac{d}{dT} (\log k) = \frac{E}{2.303RT^2}
\]
or
\[
\frac{d}{d(1/T)} (\log k) = \frac{E}{2.303R}
\]
From an Arrhenius plot of \( \log k \) against the reciprocal of
the absolute temperature, the activation energy can be obtained:

\[ E = -2.303R \times \text{slope} \]

For the abstraction and combination reactions of methyl radicals, we have \( k_a = A_a e^{-E_a/RT} \) and \( k_r = A_r e^{-E_r/RT} \) so that we may write:

\[ \frac{k_a}{k_r^+} = \frac{A_a e^{-E_a/RT}}{A_r^+ e^{-E_r/RT}} \]

Rewriting:

\[ \frac{d(\log k_a/k_r^+)}{d(1/T)} = \frac{E_a - \frac{E_r}{2}}{2.303R} \approx \frac{E_a}{2.303R} \]

since the methyl radical combination reaction has zero activation energy. Thus, from the Arrhenius plot of \( k_a/k_r^+ \), the activation energy for the abstraction reaction is given by:

\[ E_a = -2.303R \times \text{slope} \]
CHAPTER III

EXPERIMENTAL

Preparation of Materials

1. Toluene
   a) Toluene was prepared by the diazotization of o-toluidine followed by deamination with sodium hypophosphite. The organic layer was dried over anhydrous calcium chloride and then fractionally distilled using a 1-meter glass bead packed column. The fraction boiling 109 - 110° C (uncorrected) was dried by refluxing over sodium ribbon under vacuum and then degassed by bulb-to-bulb distillation.

   Toluene prepared in this manner was found to be more suitable than the sulphur free reagent grade toluene previously used which required 30% prepyrolysis in order to obtain reproducible rate constants in the pyrolysis of toluene itself [27].

   b) Toluene from sulphonic acid (Eastman Organic number X 325) has been found to be as suitable as that described above. It was dried by refluxing over sodium under vacuum and then degassed by bulb-to-bulb distillation.

2. Trimethylgallium

   Trimethylgallium was prepared by refluxing pure gallium metal with dimethylmercury in an atmosphere of dry nitrogen
The overall reaction is given by:

\[ 3 \text{Hg(CH}_3\text{)}_2 + 2 \text{Ga} \rightarrow 2 \text{Ga(CH}_3\text{)}_3 + 3 \text{Hg} \]

A trace of mercuric chloride was added as catalyst with the formation of methyl mercuric chloride as the intermediate. The reactants and the catalyst were initially placed in a quickfit flask equipped with a take-off head. After 24 hrs the temperature in the take-off head dropped from 92° C (b.p. of dimethylmercury) to become steady at 56° C (b.p. of trimethylgallium. Small fractions were taken at 56° C over the next 24 hrs until only a residue of about 1 cc was left in the flask.

The conversion was virtually complete and no purification of the product was necessary. The fraction boiling at 53.6° C at 714 mm was frozen down with liquid air and transferred to a degassing system. The sample was degassed by bulb-to-bulb distillation in vacuum and stored under its own vapour pressure at -190° C. The melting point was found to be -16.5° C and the vapour pressure was 65 mm at 0° C, both values in agreement with literature values \[14\].

3. **Trimethylindium**

Trimethylindium was prepared by refluxing pure indium metal with dimethylmercury in an atmosphere of dry nitrogen \[30\]. The overall reaction is given by:

\[ 3 \text{Hg(CH}_3\text{)}_2 + 2 \text{In} \rightarrow 2 \text{In(CH}_3\text{)}_3 + 3 \text{Hg} \]

A trace of mercuric chloride was added as catalyst with the formation of methyl mercuric chloride as the intermediate.
After 8 days, the reaction flask was cooled to 0°C (vapour pressure of trimethylindium: 0.2 mm) and the unreacted dimethylmercury (vapour pressure: 17 mm) was distilled off. The crude trimethylindium was then distilled into a degassing system and purified by repeated degassings at 0°C. The final product had a melting point of 89.5°C and a vapour pressure of 37 mm at 60°C, both values consistent with literature values. The trimethylindium was stored under its own vapour pressure at -190°C.

4. **Trimethylthallium**

Trimethylthallium was prepared by adding dropwise an ether solution of methyllithium to a suspension of dry powdered thallous iodide in anhydrous ether containing methyl iodide. The methyllithium was prepared by adding methyl iodide dropwise to a suspension of finely cut lithium metal in ether. The thallous iodide suspension was stirred at room temperature under a dry nitrogen atmosphere. As each drop of methyllithium hit the suspension, a black dot (finely divided, highly reactive thallium) formed momentarily and then disappeared. As the addition of methyllithium progressed, the suspension became darker. After standing for 36 hours the mixture cleared. The overall reaction is given by:

\[ 2 \text{CH}_3\text{Li} + \text{CH}_3\text{I} + \text{TlI} \longrightarrow \text{Tl}((\text{CH}_3)_3) + 2 \text{LiI} \]

The reaction mixture was heated in a water bath at 75°C to distill the ether. Maintaining the water bath at
this temperature, the residue was then vacuum distilled into a trap at -30° C. The crude metallic alkyl was transferred to a degassing system where the remaining ether was removed by repeated bulb-to-bulb distillations with the cold trap at 0° C. The final product had a melting point of 38.5° C and was consistent with the literature value \(32\). Trimethyl-thallium in the pure form was always handled and stored in the dark as it was sensitive to light. Vapour pressures were measured from -25° C (1.0 mm) to 60° C (17.5 mm). The vapour pressure data of Gilman and Jones \(31\) from 54° C to 74° C gave vapour pressures that were higher than those obtained here (45 mm at 60° C compared to 17.5 mm), and this was probably due to decomposition at higher temperatures and exposure to light.

**Apparatus**

The toluene carrier flow system used in this work is shown in Fig. 3. The description of this system may be discussed under the following sections:

1. **Vacuum System**

The source of high vacuum was a two-stage mercury diffusion pump (Precision Glass Company, Toronto, Ontario) backed by a two-stage oil-sealed Rotary Vane Pump DUO 5 (Balzers, Principality of Liechtenstein). To prevent oil or mercury from entering the system, a liquid air trap was interposed before the main body of the system. All ground glass joints and heated taps in the system were lubricated

The degree of vacuum in the system was read on a McLeod Gauge constructed to measure pressures as low as $10^{-6}$ mm of mercury. A vacuum of $10^{-4}$ mm or better was considered to be a workable vacuum.

2. **Carrier Gas Storage and Control**

The carrier gas used throughout this work was toluene, purified as previously described, and stored in a vessel ($R_1$) of about 150 cc. The vessel was attached to the main system by means of a $\#1^{1/4}$ ground glass standard taper joint so that it could be weighed before and after each run. Carrier control was maintained by a constant temperature bath. Cooling effects due to vaporization were counteracted by use of an immersion heater in the bath. The toluene pressure (the pressure in the reaction zone) was read on a di-octyl phthalate-mercury differential manometer ($M_1$). The sensing side of the manometer consisted of 25 mm OD tubing; the responding side consisted of $1^{1/4}$ mm OD tubing with 2.1 mm ID capillary. This combination gave a monometer so constructed that a 1 mm pressure on the sensing side gave a 9.06 mm rise in the capillary.

3. **Metallic Alkyl Storage and Control**

Each metallic alkyl was introduced into the system by
degassing under vacuum into $R_2'$. About 3 grams were distilled into a small vessel ($R_2$) attached to the system by a #14 joint so that it could be weighed before and after each run. The injection system shown in Fig. 4 was used for trimethylgallium and that shown in Fig. 5 was used for trimethylindium and trimethylthallium.

4. Furnace

a) Construction: The furnace consisted of a quartz cylinder, 3 inches in diameter and 24 inches long, wound on the outside with Chromel-A Resistance Ribbon (Hoskins Manufacturing Company, Detroit, Michigan). The ribbon was about 2 mm wide and about 0.2 mm thick, giving a resistance of 0.603 ohms per foot. The windings were cemented into place by Sauereisen Cement, Number 31 (E.H. Sargent and Company, Detroit, Michigan).

To obtain an even temperature profile in the centre 8 inches of the furnace, the windings were arranged as shown in Fig. 6. The total resistance of the furnace was 60 ohms. The heating elements were tapped at 7 points so that the heating could be adjusted by shunt resistances. An inconel liner, 2.5 inches in diameter, 12 inches long, and 0.25 inches thick, was placed in the centre of the furnace to smoothen the temperature profile in the centre of the furnace and give a sharp temperature fall-off at each end. A typical temperature profile is shown in Fig. 7.

The wound quartz tube was centered in a box (24" X 12"
Fig. 4: Injection system for a volatile metal alkyl, as used in the experiments with trimethylgallium.
Fig. 5: Pick-up system for metal alkyls of low volatility, as used in the experiments with trimethylindium and trimethylthallium.
centre line of furnace

distance from centre line in inches
turns per inch

tap tap tap tap

Fig. 6: Placement of heating windings in furnace construction.

Distance from exit end (inches)

thermocouple placement
platinum resistance thermometer placement

Fig. 7: A typical temperature profile.
X 12") with a frame of three-quarter inch angle iron and sides of asbestos board one-quarter inch thick. Similar ends, but with 3-inch holes to accomodate the quartz tube, were fitted. All seams were filled with asbestos cement (E.H. Sargent and Company, Detroit, Michigan). The box was filled with powdered alumina C-1 (particle size 50 mesh, low density - approximately 1.8 grams per cc, gift of the Aluminum Company of Canada, Toronto, Ontario) for insulation. The maximum operating temperature was 1000° C.

b) Temperature Control: The centre 8 inches of the furnace, the area where the reaction zone of the reaction vessel was situated, was constant in temperature to within ±1° C. Accurate and reproducible temperature control was achieved by the use of a Sunvic Platinum Resistance Thermometer Controller, Type RT2 (Sunvic Controls Limited, London, England).

The temperature was read in the axial thermocouple well of the reaction vessel using a Chromel-P-Alumel thermocouple (28 gauge wire, Hoskins Manufacturing Company, Detroit, Michigan) in conjunction with a millivolt potentiometer (model 8691, Leeds and Northrup, Philadelphia, Pennsylvania).

5. Reaction Vessels

A reaction vessel consisted of a quartz tube, 40 mm OD and 8 inches long, sealed to 20 mm OD ends. An axial thermocouple well constructed of 10 mm OD tubing ran the length of the reaction vessel. Graded quartz-to-pyrex seals were
situated a few centimeters beyond each end of the furnace. The average reaction volume was 195 cc.

For temperatures below 460° C, similar vessels were constructed of pyrex.

To test for surface effects, a quartz vessel was packed with fine quartz tubing, 3 mm OD and a wall thickness of 0.8 mm, increasing the surface-to-volume ratio by a factor of 12 and reducing the volume to 145 cc. The packing completely filled the cross-section of the reaction zone.

The flow through the reaction zone was regulated by a control capillary (CC, Fig. 3), 1 mm ID and 40 mm long, sealed in at the outlet of the reaction vessel.

6. Product Separation, Collection, and Analysis

Beyond the control capillary at the outlet of the reaction vessel, a high capacity trap (T₁) maintained at -80° C with an acetone-dry-ice sludge removed unreacted alkyl, toluene, ethylbenzene, dibenzyl, and similar products. A mercury diffusion pump transferred the remaining products to a second trap (T₂) maintained at -100° C with an acetone-toluene sludge to remove hydrocarbons higher than C₄'s. The remaining gaseous mixture was transferred past a non-return valve to a gas burette (calibrated volumes: 0.44, 4.34, 45.36, and 142.9 cc) with the aid of a Toepler Pump. A small McLeod Gauge (M₃) indicated complete transfer of the products to the gas burette.

After each run, a sample was taken for chromatographic
analysis. A portion of this sample was accurately measured in a gas burette adjacent to a gas chromatograph (Model 154, Perkin-Elmer Corporation, Norwalk, Connecticut). Using a 2-metre silica gel column (Perkin-Elmer Column J) at 80 °C, with a helium flow rate of approximately 20 cc per minute, internal standards were run with each set of analyses so that peak heights could be used. The contents of T₁ were analyzed using a temperature of 75 °C in a Model 800 Gas Chromatograph (Perkin-Elmer Corporation, Norwalk, Connecticut), equipped with a 150 foot Golay Column (Perkin-Elmer Column R), 0.02 inches ID coated with poly(propylene glycol).

Hydrogen was analyzed by allowing an original sample from the gas burette to be in contact with tiny pellets of copper oxide for 15 minutes in a furnace maintained at 275 °C.

**Experimental Technique**

After the furnace reached the desired temperature and the vacuum was 10⁻⁴ mm or better, a run could be carried out in the following manner.

The weighed toluene storage vessel R₁ (Fig. 3) contained degassed ready-to-use toluene. A fixed temperature bath was placed around the vessel to obtain the desired pressure (example: a bath of 14 °C gave an operating pressure of 13 mm).

The weighed metallic alkyl storage vessel R₂ contained degassed ready-to-use alkyl. In the study of trimethyl-
gallium, a small sample (0.2 to 0.3 grams) was distilled from \( R_2 \) into the alkyl finger \( F_1 \) (Fig. 4). A fixed temperature bath was placed around the finger to obtain the desired pressure (example: \(-20^\circ C\) gave a pressure of 20 mm). The alkyl pressure was such that at all times the minimum acceptable pressure difference was 5 mm to insure against pressure surges that might cause toluene to enter the alkyl injection system. This pressure difference also determined the concentration of the alkyl passing to the reaction zone; higher pressure differences gave larger concentrations of alkyl and decreased the toluene-to-alkyl ratio. To start a run, the flow of toluene was commenced and the pressure measured by the differential manometer. After a 3 to 5 minute flow of toluene to stabilize flow conditions, the trimethylgallium vapour was injected into the toluene stream through a fine capillary sealed to the base of a stopcock \( S_1 \) (Fig. 4) at the top of the alkyl reservoir. The flow of alkyl continued from 20 to 120 minutes (depending on the reaction conditions) and was followed by another 3 to 5 minute flow of toluene alone to remove all products from the reaction zone while conditions were still stabilized. The alkyl remaining in \( F_1 \) was redistilled into \( R_2 \). The amounts of trimethylgallium and toluene used were determined from the weight losses of \( R_2 \) and \( R_1 \) respectively.

In the studies of trimethylindium and trimethylthallium, approximately 0.1 to 0.2 grams of alkyl were distilled from \( R_2 \) into the U-tube projection \( P \) (Fig. 5). The entire sample
in the U-tube was used in the run. After a 3 to 5 minute flow of toluene by-passing the U-tube, stopcocks $S_3$ and $S_4$ were opened to allow the toluene to sweep the alkyl vapour to the reaction vessel. The alkyl concentration and the toluene-to-alkyl ratio were controlled by the proper manipulation of stopcocks $S_3$, $S_4$, and $S_5$ in conjunction with the temperature of the projection. The alkyl run was ended when the last crystal of alkyl was observed to sublime into the toluene stream. A 3 to 5 minute flow of toluene alone removed all products from the reaction zone while conditions were still stabilized. The amounts of trimethylindium or trimethylthallium and toluene used in a run were determined from the weight losses of $R_2$ and $R_1$, respectively. In the runs with trimethylthallium, the entire system was kept in the dark to neutralize the light sensitivity of the compound.

All tubing on the inlet side of the reaction vessel was maintained at about $40^\circ$ C to prevent condensation of either the carrier or the alkyl. The injection system was heated as required. The tubing from the outlet of the reaction vessel to trap $T_1$ was heated to about $60^\circ$ C.

Trap $T_1$ cooled to $-80^\circ$ C with an acetone-dry-ice sludge removed unreacted alkyl, toluene, ethylbenzene, dibenzyl, and similar products. The remaining products were transferred by a diffusion pump to a trap cooled to $-100^\circ$ C with an acetone-toluene sludge to remove traces of toluene and hydrocarbons higher than C$_4$'s. The remaining gaseous mixture was then transferred past a non-return valve to a gas.
burette with the aid of a Toepler Pump. After the gaseous mixture was measured, a sample was taken for chromatographic analysis.

In several of the runs, the contents of the acetone-dry-ice trap were analyzed for the metal content. After adding 50 ml of concentrated hydrochloric acid, the mixture was twice evaporated to near dryness. The solution was diluted with distilled water to a volume of 50 ml. Analysis for gallium was carried out by titration with 0.01 M potassium ferrocyanide using 3,3'-dimethyl naphthadine in the presence of a trace of potassium ferricyanide (freshly prepared) as indicator $\text{K}_{347}$. Analysis for indium or thallium was carried out by buffering the weekly acidic solution with hexamethylene tetramine and titrating with 0.02 M EDTA using xylenol orange as indicator $\text{K}_{357}$. In several of the runs, the contents of the reaction zone were similarly analyzed for its metallic content.

The first order rate constants were calculated from the equation:

$$k = \frac{2.303 \log \frac{1}{1-f}}{t_c} \text{ (sec}^{-1}\text{)}$$

where: $f = \text{fraction of the metallic alkyl decomposed}$

$t_c = \text{contact time, and is given by:}$

$$t_c = \frac{(rx \text{ volume})(P_{mn})(273)}{(r_f)(T_{ok})(760)(22416)} \text{ sec}$$

where: $r_f = \text{rate of flow of gas through the reaction zone (moles/sec)}$. 
CHAPTER IV

EXPERIMENTAL RESULTS

The Pyrolysis of Trimethylgallium

The pyrolysis of trimethylgallium has been carried out in the toluene carrier flow system from 686° K to 983° K using total pressures from 6.1 mm to 31.1 mm. The progress of the reaction was followed by measuring the amounts of methane, ethane, and ethylene formed.

The complete experimental results are given in Tables 1, 2, and 3. Analysis of the data indicates that the thermal decomposition of trimethylgallium does not occur by the simple release of three methyl radicals. It was found that even at 1075° K no more than two-thirds of the theoretical quantity of methyl radicals could be accounted for. This was similar to the decomposition of trimethylantimony [6] where the formation of (SbCH₃)ₙ was indicated. To test for the formation of a similar gallium polymer, a black deposit scraped from the reaction zone was analyzed. The results of this analysis indicated: 80% gallium (I) oxide, 8% methylgallium polymer, and 12% carbon. The carbon is probably due to decomposition of the carrier in the high temperature runs. Since limited quantities of air were admitted to the reaction zone between certain runs to test for surface effects, gallium (I) oxide could easily have been formed by the
TABLE 1

The Pyrolysis of Dimethylgallium

<table>
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<tr>
<th>Temp (K)</th>
<th>t (sec)</th>
<th>P (mm)</th>
<th>Length of run (mm)</th>
<th>GaMe₃ (mM)</th>
<th>CH₄ (mM)</th>
<th>C₂H₆ (mM)</th>
<th>C₂H₄ (mM)</th>
<th>k₂/sec⁻¹</th>
<th>kₐ/Kₗ</th>
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<td>13.0</td>
<td>50.0</td>
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<td>13.0</td>
<td>50.0</td>
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<td>70.0</td>
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<td>0.0662</td>
<td>0.0181</td>
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<td>1.032</td>
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<td>40.0</td>
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<td>0.0158</td>
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</table>

a units are $\left[\frac{cc}{mole-sec}\right]^\dagger$
TABLE 2

The Pyrolysis of Trimethylgallium

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>$t_c$ (sec)</th>
<th>$P$ (mm)</th>
<th>Length of run (min)</th>
<th>GaMe$_3$ (mM)</th>
<th>CH$_4$ (mM)</th>
<th>C$_2$H$_6$ (mM)</th>
<th>C$_2$H$_4$ (mM)</th>
<th>$k_1$ (sec$^{-1}$)</th>
<th>$\frac{k_a}{k_r}$</th>
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<tbody>
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<td>0.0040</td>
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<td>0.0068</td>
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<td>0.0014</td>
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<td>0.0005</td>
<td>0.0003</td>
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*a units are $\frac{cc}{mole\cdot sec}^{\frac{1}{2}}$
### TABLE 3

The Pyrolysis of Dimethylgallium and Trimethylgallium  
(Packed Vessel Runs)

<table>
<thead>
<tr>
<th>Temp $(O_K)$</th>
<th>$t_c$ (sec)</th>
<th>$P$ (mm)</th>
<th>Length of run (min)</th>
<th>GaMe$_3$ (mM)</th>
<th>CH$_4$ (mM)</th>
<th>C$_2$H$_6$ (mM)</th>
<th>C$_2$H$_4$ (mM)</th>
<th>$k_2$ (sec$^{-1}$)</th>
<th>$\frac{k_a}{k_r^{1/2}}$</th>
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<table>
<thead>
<tr>
<th>Temp $(O_K)$</th>
<th>$t_c$ (sec)</th>
<th>$P$ (mm)</th>
<th>Length of run (min)</th>
<th>GaMe$_3$ (mM)</th>
<th>CH$_4$ (mM)</th>
<th>C$_2$H$_6$ (mM)</th>
<th>C$_2$H$_4$ (mM)</th>
<th>$k_1$</th>
<th>$\frac{k_a}{k_r^{1/2}}$</th>
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<td>0.0052</td>
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<td>0.00010</td>
<td>0.00000</td>
<td>0.0216</td>
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</tbody>
</table>

*a units are $\left[\frac{cc}{mole \cdot sec}\right]^{1/2}$*
reaction of oxygen with the methylgallium polymer. Subsequently, analyses were carried out on the contents of the acetone-dry-ice trap and on the deposit in the furnace following each of a series of experiments. Under conditions such that less than one-third of the theoretical yield of methyl radicals was observed, the gallium was found to be quantitatively in the acetone-dry-ice trap. At temperatures above which two-thirds decomposition occurred, the gallium was found quantitatively in the reaction vessel, as a thin, apparently non-metallic film. It therefore seems plausible that methylgallium does not decompose, but deposits in the reaction vessel as \((\text{GaCH}_3)_n\).

The following mechanism was proposed:

\[
\begin{align*}
\text{Ga(CH}_3)_3 & \quad \longrightarrow \quad \text{Ga(CH}_3)_2 + \text{CH}_3 & (1) \\
\text{Ga(CH}_3)_2 & \quad \longrightarrow \quad \text{Ga(CH}_3) + \text{CH}_3 & (2) \\
n \text{Ga(CH}_3) & \quad \longrightarrow \quad (\text{GaCH}_3)_n & (3) \\
\text{CH}_3 + \text{C}_6\text{H}_5\text{-CH}_3 & \quad \longrightarrow \quad \text{C}_6\text{H}_5\text{-CH}_2 + \text{CH}_4 & (a) \\
2 \text{CH}_3 & \quad \longrightarrow \quad \text{CH}_3\text{-CH}_3 & (r) \\
2 \text{C}_6\text{H}_5\text{-CH}_2 & \quad \longrightarrow \quad (\text{C}_6\text{H}_5\text{-CH}_2)_2 & (4)
\end{align*}
\]

The ethylene and the hydrogen observed in small amounts result from the reactions:

\[
\begin{align*}
\text{CH}_3 + \text{C}_2\text{H}_6 & \quad \longrightarrow \quad \text{C}_2\text{H}_5 + \text{CH}_4 & (5) \\
\text{C}_2\text{H}_5 & \quad \longrightarrow \quad \text{C}_2\text{H}_4 + \text{H} & (6) \\
\text{H} + \text{C}_6\text{H}_5\text{-CH}_3 & \quad \longrightarrow \quad \text{C}_6\text{H}_5\text{-CH}_2 + \text{H}_2 & (7)
\end{align*}
\]

In the runs with low toluene-to-alkyl ratios, propane, ethylbenzene, and xylenes observed in small amounts result from the reactions:
\[
\begin{aligned}
\text{CH}_3 + \text{C}_2\text{H}_5 & \longrightarrow \text{C}_2\text{H}_5-\text{CH}_3 \\
\text{C}_6\text{H}_5-\text{CH}_2 + \text{CH}_3 & \longrightarrow \text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_3 \\
\text{CH}_3-\text{C}_6\text{H}_4 + \text{CH}_3 & \longrightarrow \text{CH}_3-\text{C}_6\text{H}_4-\text{CH}_3
\end{aligned}
\]
(8)
(9)
(10)

Reaction (10) occurred to a very small extent because reaction (a) proceeded mainly as written but with a small percentage of abstraction from the ring.

The values of \(\frac{k_a}{k_r}^\frac{1}{2}\) given in Tables 1, 2, and 3 have been calculated using the equation:

\[
\frac{k_a}{k_r}^\frac{1}{2} = \frac{[\text{moles CH}_4]}{[\text{moles C}_2\text{H}_6 + \text{C}_2\text{H}_4]^\frac{1}{2}} \times \frac{1}{V^\frac{1}{2}} \times \frac{1}{t^\frac{1}{2}} \times \frac{1}{[\text{toluene}]}
\]

If in the decomposition of a compound of the type \(\text{M(\text{CH}_3)}^n\) we have:

\[
\text{M(\text{CH}_3)}^n \longrightarrow \text{M(\text{CH}_3)}^{n-y} + y \text{CH}_3
\]

(11)

occurring over a temperature range \(T_1\) to \(T_2\) while:

\[
\text{M(\text{CH}_3)}^{n-y} \longrightarrow \text{M(\text{CH}_3)}^{n-y-z} + z \text{CH}_3
\]

(12)

occurs appreciably only above \(T_2\), we will have a number of factors which will influence the value of \(\frac{k_a}{k_r}^\frac{1}{2}\). First, in a flow reaction, the temperature increases as the reaction zone is approached; therefore when the temperature in the reaction zone (\(T_3\)) is above \(T_2\), reaction (11) will occur partly in the tube leading to the reaction zone and will be complete in some small fraction of the zone. This has a dual effect on \(\frac{k_a}{k_r}^\frac{1}{2}\):

1) reaction (11) is occurring at an average temperature above \(T_2\) but below \(T_3\),

II) the volume over which reaction (11) occurs is no longer the total volume of the reaction zone.
The net effect is to hold the apparent observed value of $k_a/k_r$ approximately constant as the temperature increases. Actually, the net effect might be a slight decrease except for the fact that reaction (12) is occurring over the entire reaction zone at $T_3$. Experimentally, for dimethylzinc:

$$\text{Zn(CH}_3\text{)}_2 \longrightarrow \text{Zn(CH}_3\text{)} + \text{CH}_3 \quad (13)$$

$$\text{Zn(CH}_3\text{)} \longrightarrow \text{Zn} + \text{CH}_3 \quad (14)$$

the ratio shows a slight decrease above $T_2$.

The Arrhenius plot of $k_a/k_r$ for the present work is shown in Fig. 8. In this case the characteristic break in the curve occurred at 33% theoretical yield of methyl radicals and the ratio continued to rise only slightly. Thus it was apparent from the analysis of the data that the second methyl radical was not immediately released after the first.

According to the mechanism, the number of moles of methane plus twice the number of moles of ethane and ethylene formed during a run (correction being made for any carrier decomposition at higher temperatures) should be equal to the total moles of methyl radicals released. Below 820° K the methyl radicals released were essentially due to the first bond rupture. Thus the fraction of trimethylgallium decomposed was given by:

$$\frac{\text{moles of methyl radicals released}}{\text{moles of alkyl used}}$$

Above 840° K, the methyl radicals released were essentially due to the successive ruptures of the first two bonds. Thus
Fig. 8: Arrhenius plots of rate constants for the decomposition of trimethylgallium and dimethylgallium and the reaction of methyl radicals with toluene. O rate constant; $\theta k_a/k_r$. Subscripts denote the number of runs averaged to obtain the given point.
the fraction of dimethylgallium decomposed was given by:

\[
\frac{\text{moles of methyl radicals released}}{\text{moles of alkyl used}} - \frac{\text{moles of alkyl used}}{\text{moles of alkyl used}}
\]

Between 820° K and 840° K, the methyl radicals from the thermal decomposition of dimethylgallium became appreciable. The rate constant for the thermal decomposition of trimethylgallium was thus calculated from the usual equation for consecutive unimolecular reactions by the method of successive approximations:

\[
\left[ \frac{\text{total methyl radicals}}{\text{used}} \right] = \left[ \text{Ga(CH}_3\text{)}_3 \right] \left[ 2 + \frac{k_2}{k_2-k_1} (e^{-k_1t} - e^{-k_2t}) \right] - 2 \frac{k_2}{k_2-k_1} e^{-k_1t}
\]

The value of \( k_2 \) used in the above equation was obtained from the Arrhenius plot for the decomposition of dimethylgallium (Fig. 8) extrapolated to the temperature range between 820° K and 840° K. Since any methyl radicals due to the decomposition of dimethylgallium tended to raise the value of \( k_1 \), lower values of \( k_1 \) were used in the above equation. Only one or two approximations were required to obtain substantial agreement between (methyl radicals released)_{calc.} and (methyl radicals released)_{obs.} The percentage decomposition of dimethylgallium was of the order of 4% at 820° K and 7% at 840° K.

The mechanism further assumed that the methyl radicals were not removed by any reactions other than the abstraction and recombination reactions. Extensive work with dimethylmercury by Gowenlock, Polanyi, and Warhurst has shown
that the percentage decomposition based on total methyl radicals released in the form of methane, ethane, and ethylene was in good agreement with that calculated from the weight of mercury produced. The loss of methyl radicals by reactions (8), (9), and (10) was therefore negligible under ordinary conditions. The following evidence indicated the validity of this assumption. Values of $k_1$ at 817° K using toluene-to-alkyl molar ratios between 60 and 120 showed little variation. Similarly values of $k_2$ at 916° K with the same ratios showed little variation. However, as shown in Fig. 9, the value of $k_1$ (Table 4) fell sharply when the toluene-to-alkyl molar ratio was decreased below 60. Values for $k_2$ were similarly affected. Additional gas chromatographic analyses have shown that the apparent decrease was due in part at least to the formation of propane, propylene, ethylbenzene, and xylenes. Analysis for butanes could not be made at that time, but these were probably formed.

The Arrhenius plots shown in Fig. 8 were plotted using runs with toluene-to-alkyl molar ratios greater than 60. The simple linear nature of these plots supports the method of calculation used. The curves may be represented by:

$$\log_{10} k_1 \text{ (sec}^{-1}) = 15.54 - \frac{59,500}{2.303RT}$$
$$\log_{10} k_2 \text{ (sec}^{-1}) = 7.94 - \frac{35,410}{2.303RT}$$

at 13.0 mm pressure. No other plausible explanation of the results could be found.

The values of $k_1$ and $k_2$ were both extremely sensitive to the nature of the surface in the reaction zone.
TABLE 4

Variation of k with C\textit{tol}/C\textit{alk}

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>tc (sec)</th>
<th>P (mm)</th>
<th>Length of run (min)</th>
<th>GaMe$_3$ (mM)</th>
<th>CH$_4$ (mM)</th>
<th>C$_2$H$_6$ (mM)</th>
<th>C$_2$H$_4$ (mM)</th>
<th>k (sec$^{-1}$)</th>
<th>C\textit{tol}/C\textit{alk}</th>
</tr>
</thead>
<tbody>
<tr>
<td>817</td>
<td>1.468</td>
<td>13.0</td>
<td>24.0 15.0</td>
<td>1.290</td>
<td>0.388</td>
<td>0.0181</td>
<td>0.0090</td>
<td>0.283</td>
<td>23.7</td>
</tr>
<tr>
<td>817</td>
<td>1.481</td>
<td>13.0</td>
<td>31.0 15.0</td>
<td>1.018</td>
<td>0.495</td>
<td>0.0209</td>
<td>0.0083</td>
<td>0.525</td>
<td>39.9</td>
</tr>
<tr>
<td>817</td>
<td>1.462</td>
<td>13.0</td>
<td>36.0 25.0</td>
<td>1.090</td>
<td>0.410</td>
<td>0.0209</td>
<td>0.0083</td>
<td>0.388</td>
<td>46.7</td>
</tr>
<tr>
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<td>1.390</td>
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<td>0.0068</td>
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<td>61.0</td>
</tr>
<tr>
<td>817</td>
<td>1.450</td>
<td>13.0</td>
<td>69.0 60.0</td>
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<td>0.482</td>
<td>0.0156</td>
<td>0.0104</td>
<td>0.524</td>
<td>124.0</td>
</tr>
</tbody>
</table>

801a 2.050 13.0 30.0 18.0 2.020 0.494 0.0711 0.0230 0.200 7.6

801a 1.536 13.0 25.0 15.0 0.969 0.169 0.0119 0.0051 0.203 22.8

801a __________ Packed Vessel Arrhenius Curve __________ 0.500 96

a runs in a packed vessel

b molar ratio
Fig. 9: Variation of rate constants with the molar ratio of toluene-to-alkyl. O unpacked vessel runs at 817° K; θ packed vessel runs at 801° K.
Admission of limited quantities of air to the conditioned vessel between runs resulted in approximately a 100% increase in $k_1$ and a 200% increase in $k_2$ even after pumping over a period of 48 hours. Approximately 3 to 4 runs were required to bring the values of the rate constants back to those normally observed in the conditioned vessels.

Using a conditioned packed vessel with a surface-to-volume ratio 12 times that of the unpacked vessel gave values of $k_1$ 2.0 times and values of $k_2$ 1.4 times those observed in the unpacked conditioned vessel. The percentage of heterogeneous reaction was calculated in the following manner. A value of $k_1$ for the unpacked vessel was chosen at about the mid-point on the Arrhenius curve and the corresponding value of $k_1$ in the packed vessel (0.10 and 0.20 respectively). The 0.10 increase in $k_1$ (unpacked vessel) was due to an increase of 11 in the surface-to-volume ratio. Thus the increase per unit surface-to-volume ratio was $0.10/11 = 0.009$. The percentage increase in $k_1$ was $0.009/0.10 \times 100\% = 9\%$, and this was due to the heterogeneous contribution. It was concluded therefore that in the conditioned unpacked vessel the first bond rupture was predominantly a homogeneous process with a 9% heterogeneous contribution. In the same manner, the second bond rupture was a predominantly homogeneous process with a 4% heterogeneous contribution.

Both $k_1$ and $k_2$ depended on the total pressure in the system, although the dependence of $k_1$ was very slight.
(Fig. 10), and was similar to the pressure dependence of trimethylbismuth [6]. The pressure dependence of $k_2$ was similar to that observed for dimethylmercury and dimethylcadmium [4] and dimethylzinc [1] (Table 5 and Fig. 11). The reactions were investigated under conditions such that the rate of energy transfer was not sufficient to maintain the high pressure rate constant. Therefore based solely on unimolecular pressure effects, the value of $A_2$ was expected to be of the order of $10^{11}$ to $10^{13}$ sec$^{-1}$. However, the observed value ($A_2 = 8.71 \times 10^7$ sec$^{-1}$) was much lower than expected. This was presumably due to a change in multiplicity from the triplet to the singlet state as the second methyl radical was released from the trimethylgallium molecule.

The pressure dependence of $k_a/k_{r^t}$ is shown in Fig. 12. The fall-off with increasing pressure was similar to that previously observed with the data obtained in similar studies with other metal alkyls studied [1, 4, 6], and was attributed to the third body requirements of the methyl radical recombination reaction. The ratio $k_a/k_{r^t}$ decreased at higher pressures due to the greater number of collisions to remove the energy of the excited ethane formed and therefore a lesser extent of redissociation occurred.
Fig. 10: Variation of rate constants with pressure for trimethylgallium (817° K) and dimethylgallium (914° K). Subscripts denote the number of runs averaged to obtain the given point.
### TABLE 5

Pressure Dependence of the Metal Dimethyls

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log P</th>
<th>Log k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylmercury (816° K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log P: 1.01</td>
<td>1.21</td>
<td>1.41</td>
</tr>
<tr>
<td>Log k: T.56</td>
<td>T.68</td>
<td>T.80</td>
</tr>
<tr>
<td>Dimethylcadmium (825° K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log P: 0.74</td>
<td>0.80</td>
<td>1.19</td>
</tr>
<tr>
<td>Log k: T.58</td>
<td>T.52</td>
<td>T.80</td>
</tr>
<tr>
<td>Dimethylzinc (870° K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log P: 0.86</td>
<td>1.10</td>
<td>1.21</td>
</tr>
<tr>
<td>Dimethylgallium (914° K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log P: 0.79</td>
<td>0.96</td>
<td>1.22</td>
</tr>
<tr>
<td>Log k: T.28</td>
<td>T.30</td>
<td>T.45</td>
</tr>
</tbody>
</table>
Fig. 11: Variation of rate constants of various dimethyl metals with pressure. ○ dimethylcadmium ($825^\circ$ K); O dimethylmercury ($816^\circ$ K); ● dimethylgallium ($914^\circ$ K); ● dimethylzinc ($870^\circ$ K).
Fig. 12: Variation of $k_a/k_r^{1/4}$ with pressure. Upper curve - 817° K (first bond region); lower curve - 914° K (second bond region). Subscripts denote the number of runs averaged to obtain the given point.
The Pyrolysis of Trimethylindium

The pyrolysis of trimethylindium was studied in the toluene carrier flow system from 550° K to 781° K using total pressures from 6.0 mm to 33.5 mm. The progress of the reaction was followed by measuring the amount of methane, ethane, ethylene, propane, and ethylbenzene formed, and in a number of cases by direct indium analysis.

The complete experimental results are given in Tables 6, 7, and 8. They may be discussed in terms of the following mechanism:

\[
\begin{align*}
\text{In(CH}_3\text{)}_3 & \rightarrow \text{In(CH}_3\text{)}_2 + \text{CH}_3 \quad (1) \\
\text{In(CH}_3\text{)}_2 & \rightarrow \text{In(CH}_3\text{)} + \text{CH}_3 \quad (2) \\
\text{In(CH}_3\text{)} & \rightarrow \text{In} + \text{CH}_3 \quad (3) \\
n \text{InCH}_3 & \rightarrow (\text{InCH}_3)_n \quad (4) \\
\text{CH}_3 + \text{C}_6\text{H}_5-\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5-\text{CH}_2 + \text{CH}_4 \quad (a) \\
2 \text{CH}_3 & \rightarrow \text{CH}_3-\text{CH}_3 \quad (r) \\
2 \text{C}_6\text{H}_5-\text{CH}_2 & \rightarrow (\text{C}_6\text{H}_5-\text{CH}_2)_2 \quad (5)
\end{align*}
\]

The abstraction reaction (a) is a composite reaction proceeding mainly as written but with a small percentage of abstraction from the ring. The ethylene and the hydrogen observed in small amounts result from the reactions:

\[
\begin{align*}
\text{CH}_3 + \text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_5 \quad (6) \\
\text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4 + \text{H} \quad (7) \\
\text{H} + \text{C}_6\text{H}_5-\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5-\text{CH}_2 + \text{H}_2 \quad (8)
\end{align*}
\]

In the runs with low toluene-to-alkyl ratios, propane, ethylbenzene, and xylenes observed in small amounts result from the reactions:
### Table 6

**The Pyrolysis of Methylindium**

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>t_c (sec)</th>
<th>P (mm)</th>
<th>InMe₃ (mM)</th>
<th>CH₄ (mM)</th>
<th>C₂H₆ (mM)</th>
<th>C₂H₄ (mM)</th>
<th>C₃H₈ (mM)</th>
<th>Ψ-C₂H₅ (mM)</th>
<th>k₃ (sec⁻¹)</th>
<th>k₃ / k_r²</th>
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<tr>
<td>781</td>
<td>1.702</td>
<td>13.0</td>
<td>0.670</td>
<td>0.704</td>
<td>0.430</td>
<td>0.0307</td>
<td>0.0228</td>
<td>0.196</td>
<td>1.02</td>
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<tr>
<td>779</td>
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<td>13.0</td>
<td>0.644</td>
<td>0.687</td>
<td>0.417</td>
<td>0.0404</td>
<td>0.0336</td>
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<td>773</td>
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<td>0.0286</td>
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<td>0.0201</td>
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<td>0.0095</td>
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<td>0.160</td>
<td>0.251</td>
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<td>0.0110</td>
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<td>0.0110</td>
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a units are \[
\left[\text{cc/mole-sec}\right]^\frac{1}{2}
\]
<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>tc (sec)</th>
<th>P (mm)</th>
<th>InMe₃ (mM)</th>
<th>CH₄ (mM)</th>
<th>C₂H₆ (mM)</th>
<th>C₂H₄ (mM)</th>
<th>C₃H₈ (mM)</th>
<th>ß-C₂H₅ (mM)</th>
<th>k₁ (sec⁻¹)</th>
<th>k₂/a</th>
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<td>0.0050</td>
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<td>0.0007</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0013</td>
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a units are \( \frac{\text{cc}}{\text{mole-sec}} \)
TABLE 8

The Pyrolysis of Methylindium and Trimethylindium
(Packed Vessel Runs)

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>( t_c ) (sec)</th>
<th>P (mm)</th>
<th>InMe3 (mM)</th>
<th>CH(_4) (mM)</th>
<th>C(_2)H(_6) (mM)</th>
<th>C(_2)H(_4) (mM)</th>
<th>C(_3)H(_8) (mM)</th>
<th>( \theta)-C(_2)H(_5) (mM)</th>
<th>( k_3 ) (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>764</td>
<td>1.602</td>
<td>13.0</td>
<td>0.797</td>
<td>0.936</td>
<td>0.402</td>
<td>0.0105</td>
<td>0.0035</td>
<td>0.351</td>
<td>0.980</td>
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<tr>
<td>753</td>
<td>1.668</td>
<td>13.0</td>
<td>1.070</td>
<td>1.005</td>
<td>0.712</td>
<td>0.0375</td>
<td>0.0400</td>
<td>0.448</td>
<td>1.080</td>
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<tr>
<td>728</td>
<td>1.715</td>
<td>13.0</td>
<td>1.038</td>
<td>1.068</td>
<td>0.565</td>
<td>0.0056</td>
<td>0.0050</td>
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<tr>
<td>619</td>
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<td>13.0</td>
<td>1.306</td>
<td>0.345</td>
<td>0.440</td>
<td>0.0021</td>
<td>0.0085</td>
<td>0.213</td>
<td>0.351</td>
</tr>
<tr>
<td>612</td>
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<td>13.0</td>
<td>1.008</td>
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<td>0.302</td>
<td>0.0018</td>
<td>0.0018</td>
<td>0.182</td>
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<tr>
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<td>1.106</td>
<td>0.164</td>
<td>0.0659</td>
<td>0.0009</td>
<td>0.0023</td>
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<td>0.0720</td>
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<td>0.00026</td>
<td>0.00087</td>
<td>0.0148</td>
<td>0.0190</td>
</tr>
<tr>
<td>554</td>
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<td>1.230</td>
<td>0.0228</td>
<td>0.0029</td>
<td>0.00015</td>
<td>0.00013</td>
<td>0.0014</td>
<td>0.0047</td>
</tr>
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</table>
\[
\begin{align*}
\text{CH}_3 & + \text{C}_2\text{H}_5 \longrightarrow \text{C}_2\text{H}_5\text{-CH}_3 \\
\text{CH}_3 & + \text{C}_6\text{H}_5\text{-CH}_2 \longrightarrow \text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_3 \\
\text{CH}_3 & + \text{CH}_3\text{-C}_6\text{H}_4 \longrightarrow \text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_3
\end{align*}
\]

The Arrhenius plot of \( \frac{k_a}{k_r^+} \) is shown in Fig. 13. The characteristic break at 67% theoretical yield of methyl radicals released indicated that below 670° K reaction (2) followed rapidly after reaction (1), but reaction (3) did not occur to any appreciable extent. Rate constants below this temperature (\( k_1 \)) have therefore been calculated assuming that two methyl radicals were released for each trimethylindium molecule undergoing decomposition. Above 680° K, all of the trimethylindium was converted to methylinidium plus two methyl radicals in a very small fraction of the contact time. Rate constants in this region (\( k_3 \)) have therefore been calculated assuming that the fraction of the third bond ruptured was given by:

\[
\frac{(\text{moles of methyl radicals}) - (2 \text{ moles of trimethylindium})}{(\text{moles of trimethylindium})}
\]

Although the break in the Arrhenius curve of \( \frac{k_a}{k_r^+} \) was indicative of the process outlined, independent tests have been made to verify the mechanism:

a) In 18 of the runs, the contents of the acetone-dry-ice trap located at the outlet of the furnace were analyzed for indium. If reaction (3) is responsible for the removal of methylinidium, then above 670° K all of the indium should be deposited in the reaction zone. Table 9 shows that over the entire third bond region only traces of indium reach the acetone-dry-ice trap. Below this temperature the quantity
Fig. 13: Arrhenius plots for the decomposition of methylindium and trimethylindium and the reaction of methyl radicals with toluene. 0 rate constant based on gas analysis; O rate constant based on metal analysis; $k_a/k_r^*$. Subscripts denote the number of runs averaged to obtain the given point.
TABLE 9

Runs with Indium Analyses

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Percent Decomposition</th>
<th>Trap Analysis</th>
<th>kg (sec(^{-1}))</th>
<th>km (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas (%)</td>
<td>Metal (%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Third Bond Region:**

753 83.3 1.5 729a 98.3 1.5 726 57.9 3.9 720 72.8 0.9 697 63.1 2.5 684 45.3 1.2

**First Bond Region:**

644a 91.7 73.5 26.5 0.945 0.510 637a 64.8 46.5 53.2 0.533 0.320 633a 77.8 51.8 48.1 0.606 0.298 624a 50.3 36.9 63.7 0.292 0.183 623a 57.2 40.7 59.0 0.338 0.209 620a 19.7 13.3 85.7 0.219 0.138 613 40.0 58.0 613 12.0 87.8 612 11.0 90.1 610 15.0 81.0 594 16.3 83.0 556 1.2 98.0

*runs in an unconditioned vessel*
of indium found in the trap was in agreement with the proposed mechanism.

b) In 7 of these 18 runs a clean pyrex vessel was used. In each of these 7 runs the indium content of the reaction zone was analyzed. The values of $k_1$ calculated assuming moles of indium in the reaction zone equals moles of trimethylindium decomposed are shown in Fig. 13. The agreement with $k_1$ values in a seasoned vessel calculated assuming two methyl radicals released for each trimethylindium decomposed was excellent.

c) The rate constants for the reaction in a clean vessel based on gas analysis lie above the Arrhenius curve. The difference in the extent of reaction compared to the metal analyses was a result of reaction on the unconditioned surface. The most probable surface reactions consistent with the experimental results were the surface decomposition of methylindium to give indium metal plus a methyl radical and the surface decomposition of trimethylindium. The first of these reactions lead to a decrease in the quantity of methylindium deposited in the reaction zone. Hence in an experiment in an unconditioned vessel in which 1.0 mM of methylindium would have been deposited in the reaction zone in a conditioned vessel, addition of bromine vapour to the hot reaction zone (637° K) while still under vacuum produced only 0.34 mM of hydrogen bromide and a quantity of polymethylene quantitatively in agreement with the reaction:

$$2n \text{Br}_2 + (\text{InCH}_3)_n \longrightarrow n \text{InBr}_3 + n \text{HBr} + (\text{CH}_2)_n$$
The 0.66 mM of methylindium apparently lost by the surface reaction was in good agreement with the additional methyl radicals detected in the gas analysis (0.58 mM).

d) In a run in the unconditioned vessel in the third bond region, the vessel was removed from the furnace under vacuum to visually inspect the methylindium polymer. It appeared as a white non-metallic solid coating the entire surface of the reaction zone. To determine the indium content, concentrated hydrochloric acid was admitted to the reaction zone and reaction with the methylindium polymer was observed. After the indium chloride solution was removed, a thin white coating appeared to remain on the surface. Addition of 20% hydrofluoric acid almost immediately caused the coating to peel from the surface. This coating again was polymethylene, and was probably formed by the reaction:

$$3n \text{HCl} + (\text{InCH}_3)_n \rightarrow n \text{InCl}_3 + 2n \text{H}_2 + (\text{CH}_2)_n$$

Starting with a clean vessel, both $k_1$ and $k_3$ decreased over several runs to a fixed minimum value in what was subsequently called a conditioned vessel. If air was admitted to the reaction vessel between runs, an additional 2 to 3 runs were required to recondition the surface of the reaction zone. The percentage of heterogeneous reaction was estimated by carrying out a series of runs in a packed vessel with a surface-to-volume ratio 12 times that of the unpacked vessel. Because of the large surface area, complete conditioning was not obtained, but after a series of
runs $k_1$ was reduced to about 2.2 times its value in the unpacked vessel and $k_3$ was reduced to about 1.3 times its value in the unpacked vessel. Therefore, in the unpacked vessel used in this work, the reaction was at least 90% homogeneous in the first bond region and at least 97% homogeneous in the third bond region.

Both $k_1$ and $k_3$ depended on the total pressure in the system, although the pressure dependence of $k_1$ was very slight (Fig. 14). The slight pressure dependence of $k_1$ was similar to that observed for the thermal decomposition of trimethylgallium $^3$ or trimethylbismuth $^6$. As shown in Fig. 15, the pressure dependence of the thermal decomposition of methylindium was somewhat less than that of methylzinc $^1$. This was presumably due to the large temperature difference at which these decompositions occurred.

The pressure dependence of $k_a/k_r^+$ is shown in Fig. 16. The fall-off with increasing pressure was similar to that previously observed $^1, 4, 6, 37$, and was attributed to the third body requirements of the methyl radical recombination reaction. The ratio $k_a/k_r^+$ decreased at higher pressures due to the greater number of collisions that deactivated the excited ethane formed and therefore a lesser extent of redissociation occurred.

As shown in Fig. 17, the value of $k_1$ fell sharply when the toluene-to-alkyl molar ratio was decreased below 150 (Table 10). Values for $k_3$ were similarly affected. The Arrhenius curves shown in Fig. 13 were therefore plotted
Fig. 14: Variation of rate constants with pressure for trimethylindium (610° K) and methyldinindium (744° K). Subscripts denote the number of runs averaged to obtain the given points.
Fig. 15: Variation of Rate Constant with Pressure for the Metal Methlys.  ○ Methylindium at 7440 K; ● Methylsinc at 10560 K. Subscripts denote the number of runs averaged to obtain the given point.
Fig. 16: Variation of $k_a/k_r^2$ with pressure. Upper curve - 610° K (first bond region); lower curve - 744° K (second bond region). Subscripts denote the number of runs averaged to obtain the given point.
Fig. 17: Variation of rate constants with molar ratio of toluene-to-alkyl. O runs at 613° K; ◆ runs at 629° K.
using only rate constants obtained in runs where the toluene-to-alkyl ratio was greater than 150. The simple linear nature of these plots supports the method of calculation used. The curves may be represented by:

$$\log_{10} k_1 \text{ (sec}^{-1}) = 15.72 - \left(\frac{47,200}{2.303RT}\right)$$

$$\log_{10} k_3 \text{ (sec}^{-1}) = 10.91 - \left(\frac{38,700}{2.303RT}\right)$$

**TABLE 10**

Variation of k with C_{tol}/C_{alk}
at 13.0 mm

<table>
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<tr>
<th>Temp (°K)</th>
<th>t (sec)</th>
<th>InMe₃ (mM)</th>
<th>CH₄ (mM)</th>
<th>C₂H₆ (mM)</th>
<th>C₂H₄ (mM)</th>
<th>k₁ (sec⁻¹)</th>
<th>C_{tol}/C_{alk}</th>
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<tr>
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<td>0.076</td>
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<td>0.665</td>
<td>0.187</td>
<td>0.1110</td>
<td>0.0020</td>
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<td>0.1050</td>
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<td>0.138</td>
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a molar ratio
The Pyrolysis of Trimethylthallium

The pyrolysis of trimethylthallium was studied in the toluene carrier flow system from 458°K and 591°K using total pressures from 5.6 mm to 33.0 mm. The progress of the reaction was followed by measuring the amount of methane, ethane, ethylene, propane, and ethylbenzene formed, and in a number of cases by direct thallium analysis.

The complete experimental results are given in Tables 11, 12, 13, and 14. They may be discussed in terms of the following mechanism:

\[ \text{Tl}(\text{CH}_3)_3 \rightarrow \text{Tl}(\text{CH}_3)_2 + \text{CH}_3 \] (1)

\[ \text{Tl}(\text{CH}_3)_2 \rightarrow \text{Tl}(\text{CH}_3) + \text{CH}_3 \] (2)

\[ \text{Tl}(\text{CH}_3) \rightarrow \text{Tl} + \text{CH}_3 \] (3)

\[ \text{CH}_3 + \text{C}_6\text{H}_5\text{-CH}_3 \rightarrow \text{C}_6\text{H}_5\text{-CH}_2 + \text{CH}_4 \] (a)

\[ 2 \text{CH}_3 \rightarrow \text{CH}_3\text{-CH}_3 \] (r)

\[ 2 \text{C}_6\text{H}_5\text{-CH}_3 \rightarrow (\text{C}_6\text{H}_5\text{-CH}_2)_2 \] (4)

The abstraction reaction (a) was a composite reaction proceeding mainly as written but with a small percentage of abstraction from the ring. The ethylene and the hydrogen observed in very small amounts (usually less than 0.05%) result from the reactions:

\[ \text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4 \] (5)

\[ \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H} \] (6)

\[ \text{H} + \text{C}_6\text{H}_5\text{-CH}_3 \rightarrow \text{C}_6\text{H}_5\text{-CH}_2 + \text{H}_2 \] (7)

In runs with low toluene-to-alkyl ratios, propane, ethylbenzene, and xylenes observed in small amounts result from the reactions:
TABLE II

The Pyrolysis of Trimethylthallium
(in a unpacked unconditioned vessel)

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>( t_c ) (sec)</th>
<th>( P ) (mm)</th>
<th>( \text{TiMe}_3 ) (mM)</th>
<th>( \text{CH}_4 ) (mM)</th>
<th>( \text{C}_2\text{H}_6 ) (mM)</th>
<th>( \text{C}_2\text{H}_4 ) (mM)</th>
<th>( \text{C}_3\text{H}_8 ) (mM)</th>
<th>( \text{C}<em>6\text{H}</em>{15} ) (mM)</th>
<th>( k ) (sec(^{-1}))</th>
<th>( \frac{k_a a}{k_T} )</th>
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<tr>
<td>543</td>
<td>0.969</td>
<td>13.0</td>
<td>0.630</td>
<td>0.060</td>
<td>0.765</td>
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<td>0.040</td>
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<td>0.075</td>
<td>1.192</td>
<td>0.000</td>
<td>0.000</td>
<td>0.034</td>
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<td>1.069</td>
<td>0.070</td>
<td>1.121</td>
<td>0.000</td>
<td>0.000</td>
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* units are \( \frac{\text{cc}}{\text{mole} \cdot \text{sec}} \) \(^\dagger\)
### TABLE 12

The Pyrolysis of Trimethylthallium
(in a packed unconditioned vessel)

<table>
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<tr>
<th>Temp (°K)</th>
<th>t&lt;sub&gt;c&lt;/sub&gt; (sec)</th>
<th>P (mm)</th>
<th>TlMe&lt;sub&gt;3&lt;/sub&gt; (mM)</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt; (mM)</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (mM)</th>
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<th>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt; (mM)</th>
<th>o-C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; (mM)</th>
<th>k (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>( \frac{k_a}{k_r} )^a</th>
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*Units are \[ \frac{cc}{[mole \cdot sec]} \]"
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<th>$t_c$ (sec)</th>
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<th>CH$_4$ (mM)</th>
<th>C$_2$H$_6$ (mM)</th>
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<th>$k$ (sec$^{-1}$)</th>
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a units are \[ \frac{\text{cc}}{\text{mole-sec}} \] \(^t\)
### TABLE 14

The Pyrolysis of Trimethylthallium
(in a packed conditioned vessel)

<table>
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<th>Temp (°K)</th>
<th>t&lt;sub&gt;c&lt;/sub&gt; (sec)</th>
<th>P (mm)</th>
<th>TlMe&lt;sub&gt;3&lt;/sub&gt; (mM)</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt; (mM)</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; (mM)</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; (mM)</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt; (mM)</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; (mM)</th>
<th>k (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>k&lt;sub&gt;a&lt;/sub&gt;/k&lt;sub&gt;r&lt;/sub&gt;&lt;sup&gt;½&lt;/sup&gt;</th>
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a units are \( \left[ \frac{cc}{mole\cdot sec} \right]^{\frac{1}{2}} \)

b run 95 (vessel only partially conditioned)
c run 96 (vessel almost completely conditioned)
d run 97 (first run in fully conditioned vessel)
\[
\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5-\text{CH}_3 \quad (8)
\]
\[
\text{CH}_3 + \text{C}_6\text{H}_5-\text{CH}_2 \rightarrow \text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_3 \quad (9)
\]
\[
\text{CH}_3 + \text{CH}_3-\text{C}_6\text{H}_4 \rightarrow \text{CH}_3-\text{C}_6\text{H}_4-\text{CH}_3 \quad (10)
\]

The Arrhenius plot of \( k_a/k_r \frac{1}{2} \) shown in Fig. 18 shows no characteristic break at 33\% or 67\% theoretical yield of methyl radicals indicating that at all temperatures reactions (2) and (3) follow rapidly after reaction (1). Thus the rate constants were calculated assuming that three methyl radicals were released for each trimethylthallium molecule undergoing decomposition.

Although the continuity of the Arrhenius curve of \( k_a/k_r \frac{1}{2} \) was indicative of the process outlined, independent tests have been made to verify the mechanism:

a) In most runs (see Table 15), the contents of the acetone-dry-ice trap located at the outlet of the furnace were analyzed for thallium. Over the entire temperature range of decomposition, the thallium found in this trap was equal to the quantity of undecomposed trimethylthallium expected if each alkyl molecule that decomposed liberated three methyl radicals.

b) In 10 runs, the contents of the reaction vessel were analyzed for thallium. In all cases the quantity of thallium deposited in the reaction zone was in agreement with the postulated release of three methyl radicals. To insure that the deposit was actually thallium, 0.082 grams of the deposit was scraped from the reaction zone while in an inert atmosphere and analyzed for thallium. 19.0 mls of
Fig. 18: Arrhenius plot for the reaction of methyl radicals with toluene. • runs in the unpacked unconditioned vessel; ○ runs in the packed unconditioned vessel; ⋄ runs in the unpacked conditioned vessel; ⋆ runs in the packed conditioned vessel.
TABLE 15

Runs with Thallium Analyses

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>Gas Percent Decomposition (%)</th>
<th>Metal Percent Decomposition (%)</th>
<th>Trap Analysis (%)</th>
<th>Trap kg</th>
<th>Trap km</th>
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<td>593</td>
<td>95.2</td>
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<tr>
<td>560</td>
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<td>38.7</td>
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<tr>
<td>473</td>
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<td>1.8</td>
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<td>0.016</td>
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<tr>
<td>470</td>
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<td>0.019</td>
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<tr>
<td>466</td>
<td>16.4</td>
<td></td>
<td>0.212</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

I runs in the unpacked unconditioned vessel
II runs in the packed unconditioned vessel
III runs in the unpacked conditioned vessel
0.02 M EDTA were required giving a thallium analysis of 99.8%. No evidence was found for the formation of polymer of the type \((\text{TlCH}_3)_n\), as found in the pyrolysis of trimethylgallium or trimethylindium.

Starting with a clean vessel (I), the rate constants did not decrease over several runs to a fixed minimum value as in the case of trimethylgallium or trimethylindium. On the other hand, the rate constants remained at a constant value; near 95% decomposition in successive runs, the rate constants were 2.24, 2.28, and 2.1\(4 \text{ sec}^{-1}\). One of these runs would have deposited enough thallium to change the surface, however no effect due to coating the surface with thallium was observed. In another series of runs, small amounts of air accidentally introduced into the reaction zone between runs produced no observable effect on the rate constants. The experimental data under these conditions (unconditioned and unpacked vessel) is given in Table 11 and constitutes curve I in Fig. 19.

The percentage of heterogeneous reaction was estimated by carrying out a series of runs in a packed vessel (II) with a surface-to-volume ratio 12 times that of the unpacked vessel I, and the results are given in Table 12 and constitutes curve II of Fig. 19. The rate constants obtained using vessel II were a factor 3.7 greater than those obtained in vessel I. The overall reaction in vessel I was therefore apparently about 25% heterogeneous.

In an attempt to reduce the amount of surface reaction,
Fig. 19: Arrhenius plots for the decomposition of trimethylthallium. O runs in unpacked unconditioned vessel (curve I); O runs in packed unconditioned vessel (curve II); O runs in unpacked conditioned vessel (curve III) (θ based on metal analysis); O runs in packed conditioned vessel (curve IV). Subscripts denote the number of runs averaged to obtain the given point.
the unpacked vessel was initially treated with hot 50% hydrofluoric acid for 10 minutes. This treatment was repeated for at least 2 minutes between each run. The experimental results are given in Table 13 and constitute curve III of Fig. 19. The rate constants in vessel III could never be reduced below this curve even by longer treatments with hot 50% hydrofluoric acid. Therefore throughout this work vessels treated as described above are termed conditioned vessels.

To estimate the percentage of heterogeneous reaction in vessel III, a packed pyrex vessel (IV) with a surface-to-volume ratio 9 times that of vessel III was treated with hot 50% hydrofluoric acid for 10 minutes. This gave a rate constant high by a factor of 13. Further conditioning with the hot acid reduced the rate constants to approximately a factor of 4 times those obtained in vessel III. These results are tabulated in Table 14 and constitute curve IV in Fig. 19. These results indicated that the reaction in vessel III was approximately 14% heterogeneous.

Comparison of curves I and III indicated that the reaction in vessel I was about 79% heterogeneous. This result was obtained by the following calculation:

if the rate constant k in vessel III was 0.100 units and 14% of this was due to the heterogeneous component, the homogeneous component was 0.086. The k in vessel I was 0.400 and its heterogeneous component 0.400 - 0.086 = 0.314. Thus the percentage of heterogeneous reaction in vessel I is
The above calculated large percentage heterogeneous reaction is consistent with the greater than 45% heterogeneous reaction that would be indicated by comparison of curve I with the initial runs in the partially conditioned packed vessel (vessel IV before it was fully conditioned). The low estimate of percent heterogeneous reaction in vessel I obtained by comparison of runs in vessels I and II was probably due to the fact that vessel II had been washed with hydrofluoric acid before being stored at the conclusion of previous work.

The pressure dependence of $k_a/k_r$ is shown in Fig. 20. The fall-off with increasing pressure was similar to that previously observed with values obtained in similar studies with trimethylgallium, trimethylindium, and other metallic alkyls studied $^{1, 4, 6}$ and was attributed to the third body requirements of the methyl radical recombination reaction. However, at the low temperatures at which trimethylthallium released methyl radicals into the toluene stream, the fall-off was less than at higher temperatures. Less thermal energy was available for the methyl radicals and thus there was less energy in the ethane formed and the tendency for the methyl radicals to fly apart after recombination was reduced. The ratio $k_a/k_r$ was higher at lower pressures due to the fact that there were less collisions to remove the energy of the excited ethane formed and therefore a greater extent of redissociation occurred.
Fig. 20: Variation of $\frac{k_a}{k_f}$ with pressure at 528° K.  
0 represent individual runs;  • point taken from Fig. 18.

Fig. 21: Variation of rate constant with pressure for trimethylthallium at 528° K.
The rate constant $k$ depended on the total pressure in the system, although the pressure dependence was very slight (Fig. 21). This slight pressure dependence was very similar to that observed for the thermal decomposition of trimethyl-gallium of trimethylindium.

The overall reaction in the unpacked conditioned vessel may be represented by the equation:

$$\log_{10} k \text{ (sec}^{-1}) = 10.2 - \left(\frac{25,800}{2.303RT}\right)$$

However, at low temperatures the heterogeneous component consisted of 16% while at higher temperatures the heterogeneous component was only 13%. The homogeneous reaction in the unpacked conditioned vessel may be represented by:

$$\log_{10} k \text{ (sec}^{-1}) = 10.4 - \left(\frac{26,400}{2.303RT}\right)$$
CHAPTER V

DISCUSSION

Reaction of Methyl Radicals with Toluene

The values of $k_a/k_r^+$ have been calculated using the equations:

$$\frac{k_a}{k_r^+} = \frac{\text{moles CH}_4}{[\text{moles C}_2\text{H}_6 + \text{C}_2\text{H}_4]^t} \times \frac{62360}{(\text{rx vol} \times \text{time})^t} \times \frac{\text{T}}{\text{P}}$$

$$\frac{k_a}{k_r^+} = \frac{\text{moles CH}_4}{[\text{moles C}_2\text{H}_6 + \text{C}_2\text{H}_4]^t} \times \frac{62360}{(\text{rx vol} \times \text{time})^t} \times \frac{\text{T}}{\text{P}}$$

If in the thermal decomposition of poly-methyl metallic alkyls of the type M(CH$_3$)$_n$, we have:

$$M(\text{CH}_3)_n \rightarrow M(\text{CH}_3)_{n-y} + y \text{CH}_3 \quad (1)$$

occurring over a temperature range $T_1$ to $T_2$ while:

$$M(\text{CH}_3)_{n-y} \rightarrow M(\text{CH}_3)_{n-y-z} + z \text{CH}_3 \quad (2)$$

occurs appreciably only above $T_2$, we will have a number of factors which will influence the value of $k_a/k_r^+$. First, in a flow reactor the temperature increases as the reaction zone is approached; when the temperature in the reaction zone ($T_3$) is above $T_2$, reaction (1) will occur partly in the tube leading to the reaction zone and will be complete in some small fraction of the reaction zone. This has a dual effect on $k_a/k_r^+$:

1) reaction (1) is occurring at an average temperature above $T_2$ but below $T_3$,

2) the volume over which reaction (1) occurs is no longer the total volume of the reaction zone.

The net effect is to hold the apparent observed value of $k_a/k_r^+$.
\( \frac{ka}{k_F} \) constant as the temperature increases.

In the thermal decomposition of dimethylzinc, it was proposed that the break in the Arrhenius plot of \( \frac{ka}{k_F} \) indicated consecutive decompositions of the metal-methyl bonds at measurable rates. The theoretical discussion above predicted there should be a break for any poly-methyl metallic alkyl that underwent consecutive reactions as indicated. Further experimental evidence which confirmed this prediction was given by the thermal decompositions of trimethylgallium, trimethylindium, and trimethylthallium. The metallic deposits in the reaction vessel and in the acetone-dry-ice trap located at the outlet of the furnace were in complete agreement with the mechanisms as predicted by the Arrhenius plots of \( \frac{ka}{k_F} \).

The Arrhenius plot of \( \frac{ka}{k_F} \) from 200°C to 660°C is shown in Fig. 22. At lower temperatures, the experimental activation energy for abstraction was approximately 8 kcal/mole (assuming zero activation energy for the recombination of methyl radicals), but increased to approximately 13 kcal/mole at higher temperatures. Low-temperature photolyses have given values of 7.0 kcal/mole \( \sim 38 \) and 8.3 kcal/mole \( \sim 39 \). At higher temperatures, the increase in \( \frac{ka}{k_F} \) above the values expected on the basis of the photochemical and low temperature pyrolysis results may be attributed to the redissociation of the thermally excited ethane formed. At higher temperatures the methyl radicals have a higher average thermal energy and therefore at constant pressure
Fig. 22: Arrhenius Plot for the Reaction of Methyl Radicals with Toluene. • Dimethylzinc; ◁ Dimethylmercury and Dime-thylmercury; ● Trimethylgallium; ◇ Trimethylindium; ○ Trimethylthallium.
the extent of redissociation will increase as the temperature is increased. Thus the amount of ethane formed was smaller than it should have been and large values of $k_a/k_f$ were obtained.

The Toluene Carrier Technique

The thermal decomposition of trimethylantimony has been studied by the toluene carrier technique $^{6,7}$, but the decomposition was not simple. Even at the highest temperatures, the yields of methane and ethane fell far below the amount that would be expected if all of the alkyl decomposed. The first order rate constant based on either gas or metal analysis decreased with increasing concentration of the trimethylantimony. This decrease was probably due to some sort of back reaction as the toluene-to-alkyl ratios employed (40 to 50) probably did not afford complete removal of the radicals on formation, and the increased difference of rate constants based on gas and metal analyses was probably due to incomplete analysis or the formation of a polymer of the type $(\text{SbCH}_3)_n$.

Much less complexity was obtained in the thermal decompositions of trimethylgallium, trimethylindium, and trimethylthallium, as higher toluene-to-alkyl ratios were employed. It was found that at low toluene-to-alkyl ratios the rate constants decreased, and from the plot of rate constant versus the toluene-to-alkyl ratio, a minimum acceptable toluene-to-alkyl ratio was obtained.
A series of runs were carried out using dimethylmercury as the radical source. At toluene-to-alkyl molar ratios of 7.6 and 9.5, the analysis of methane, ethane, ethylene, propane, and proylene yielded only 67% and 77% of the theoretical amount of methyl radicals expected, respectively. Analysis for ethylbenzene, meta-, ortho-, and para-xylene yielded the remaining methyl radicals expected. With trimethylgallium and trimethylindium a similar apparent loss of products was observed; in these cases only 20% to 40% of the lost products was found in the liquid analyses. The remaining loss was presumably due to some back reaction.

The Pyrolysis of Trimethylgallium

No previous studies on the bond dissociation energies of trimethylgallium have been reported. The mean bond energy has been obtained by the reaction of trimethylgallium with iodine in benzene solution $\Delta H_{13}^\circ$, and by the combustion of trimethylgallium with oxygen in a static-bomb calorimeter $\Delta H_{14}^\circ$. The mean gallium-methyl bond energies from these studies were 56.7 kcal/mole and 57.7 kcal/mole, respectively. However Long, using $\Delta H_{CH_3-H}^\circ = 102.5$ kcal/mole, has recommended a value of 57.5 kcal/mole $\Delta H_{15}^\circ$.

In this work, the experimental evidence indicated that the Arrhenius equations for the pyrolysis of trimethylgallium and dimethylgallium were:

\[
\begin{align*}
\log_{10} k_1 \text{ (sec}^{-1}) &= 15.54 - \left(\frac{59,500}{2.303RT}\right) \\
\log_{10} k_2 \text{ (sec}^{-1}) &= 7.94 - \left(\frac{35,410}{2.303RT}\right)
\end{align*}
\]
respectively.

From theoretical considerations, it has been shown that the experimental activation energy at the high pressure limit may be approximately related to the bond dissociation energy. Thus we may write:

\[ D_{\text{CH}_3\text{Ga-CH}_3} = 59.5 \text{ kcal/mole} \]

as the rate constant for the pyrolysis of trimethylgallium was independent of pressure. The pyrolysis of dimethylgallium was carried out in the pressure dependent region. Assuming 10 effective oscillators, \( D_2 = E_2 + 2.5 \text{ kcal/mole} \), and we obtain:

\[ D_{\text{CH}_3\text{Ga-CH}_3} = 37.2 \text{ kcal/mole} \]

Since the sum of the three gallium-methyl bond strengths is \( 172.5 \text{ kcal/mole} \), by difference we obtain:

\[ D_{\text{Ga-CH}_3} = 75.8 \text{ kcal/mole} \]

Even as high as \( 1075^\circ \text{ K} \), the methylgallium did not decompose; rather a polymer of the type \( (\text{GaCH}_3)_n \) was formed. Assuming \( A = 10^{11} \) (which is reasonable because for methylindium \( A = 10^{10.91} \)), the Arrhenius equation would be of the form:

\[ \log_{10} k_3 (\text{sec}^{-1}) = 11 - (75.800/2.303RT) \]

Measurable decomposition of methylgallium will occur when \( k_3 \) is of the order 0.1 units. Solving for \( T \), we obtain a value of approximately \( 1350^\circ \text{ K} \). If we assume \( A \) is of the order of \( 10^9 \), we obtain a value for \( T \) of approximately \( 1650^\circ \text{ K} \). In either case, the experimental conditions that would be required are beyond those afforded by the toluene
carrier technique.

The Pyrolysis of Trimethylindium

No previous studies on the bond dissociation energies of trimethylindium have been reported and only a tentative experimental value of the mean bond energy is available equal to 38.2 kcal/mole \( \sim 17 \)\(^\circ\). This value is in agreement with the estimated value \( 41 \pm 3 \) kcal/mole obtained from the available data of the neighbouring metallic methyls.

In this work, the experimental evidence indicated that the Arrhenius equations for the thermal decomposition of trimethylindium and methylindium were:

\[
\log_{10} k_1 \text{ (sec}^{-1}) = 15.72 - \left( \frac{47,200}{2.303RT} \right) \\
\log_{10} k_3 \text{ (sec}^{-1}) = 10.91 - \left( \frac{38,700}{2.303RT} \right)
\]

respectively.

From theoretical considerations, it has been shown that the experimental activation energy at the high pressure limit may be approximately related to the bond dissociation energy. The rate constant for the pyrolysis of trimethylindium was independent of pressure so we may write:

\[
D(\text{CH}_3)_2\text{In-CH}_3 = 47.2 \text{ kcal/mole}
\]

The pyrolysis of methylindium was carried out in the pressure dependent region. Assuming 8 effective oscillators, 

\[
D_3 = E_3 + 1.3 \text{ kcal/mole, and we obtain:}
\]

\[
D(\text{In-CH}_3) = 40.0 \text{ kcal/mole}
\]

Since the sum of the three indium-methyl bond strengths is 114.6 kcal/mole, by difference we obtain:
\[ \text{D}^\text{\textsuperscript{\textit{CH}}\text{\textsubscript{3}In-CH\textsubscript{3}}\text{\textsuperscript{\textit{\)}} = 27.4 \text{ kcal/mole.}} \]

**The Pyrolysis of Trimethylthallium**

No previous studies on the bond dissociation energies or mean bond energy of trimethylthallium have been reported. From the known total metal-methyl bond strengths of the neighbouring elements, a value of 65±5 kcal/mole was estimated for trimethylthallium.

In this work, the experimental evidence indicated that the Arrhenius equation for the pyrolysis of trimethylthallium was:

\[ \log_{10} k \ (\text{sec}^{-1}) = 10.4 - \left(26,400/2.303RT\right) \]

From theoretical considerations, it has been shown that the experimental activation energy at the high pressure limit may be approximately related to the bond dissociation energy. The rate constant for the pyrolysis of trimethylthallium was independent of pressure so we may write:

\[ \text{D}^\text{\textsuperscript{\textit{(CH}}\text{\textsubscript{3})\text{2Tl-CH\textsubscript{3}}}\text{\textsuperscript{\textit{\)}} = 26.4 \text{ kcal/mole}} \]

Unfortunately, nothing could be said about the remaining two bonds except that D\textsubscript{2} plus D\textsubscript{3} are approximately equal to 39 ± 5 kcal/mole where D\textsubscript{3} would be expected to be stronger than D\textsubscript{2} because of the tendency of thallium to bond chemically in the monovalent state.

The thermal decomposition of trimethylthallium was very surface dependent (greater than 79% heterogeneous reaction in an unpacked unconditioned vessel). Trimethylgallium and trimethylindium decompositions would condition the reaction
vessel. The rate constant was reduced to a fixed value after 3 to 5 runs. On the other hand, the thermal decomposition of trimethylthallium would not condition the vessel between runs when starting with a unconditioned vessel. However, starting with a conditioned vessel, successive runs producing an increasing deposit of thallium metal on the surface raised the rate constant to the level of the unconditioned vessel. Consequently, conditioning with hot 50% hydrofluoric acid was required between runs to obtain reproducible results in the conditioned vessel. Moreover, if the amount of trimethylthallium used in a run was 0.5 to 2.0 mM, no variation in the rate constant was observed signifying that the maximum amount of alkyl used in a run did not deposit enough thallium to significantly increase the rate. Therefore the rate constants observed in the individual runs were a true indication of the decomposition in the conditioned vessel.

Suggestions for Further Work

The available bond dissociation energies (at the high pressure limit) and mean bond energies of covalent metal-methyl bonds are given in Table 16. Values for the methyl derivatives of some of the non-metals of Groups IV to VII are included for comparison.

All of the mean bond energies in Table 16 have been calculated from the appropriate heat of formation at 25°C, the heat of atomization of the parent element, and
### TABLE 16

Metal-Methyl Bond Strengths

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<tr>
<th></th>
<th>total energy</th>
<th>$E^b$</th>
<th>$D_1^b$</th>
<th>$D_2^b$</th>
<th>$D_3^b$</th>
<th>ref.</th>
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<td><strong>Group IIb:</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$(\text{CH}_3)_2\text{Zn}$</td>
<td>82.9</td>
<td>41.5</td>
<td>49.0</td>
<td>33.9</td>
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<td>119</td>
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<tr>
<td>$(\text{CH}_3)_2\text{Cd}$</td>
<td>66.2</td>
<td>33.1</td>
<td>48.8</td>
<td>17.4</td>
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<td>140</td>
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<td>$(\text{CH}_3)_2\text{Hg}$</td>
<td>58.9</td>
<td>29.5</td>
<td>53.7</td>
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<tr>
<td><strong>Group IIIb:</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$(\text{CH}_3)_3\text{Al}$</td>
<td>185.8</td>
<td>61.9</td>
<td>78</td>
<td>-</td>
<td>-</td>
<td>114</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Ga}$</td>
<td>172.5</td>
<td>57.5</td>
<td>59.5</td>
<td>37.2</td>
<td>75.8</td>
<td></td>
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<tr>
<td>$(\text{CH}_3)_3\text{In}$</td>
<td>114.6</td>
<td>38.2</td>
<td>47.2</td>
<td>40.0</td>
<td>27.4</td>
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<tr>
<td>$(\text{CH}_3)_3\text{Tl}$</td>
<td>65±5°</td>
<td>22</td>
<td>26.4</td>
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<td>-</td>
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<tr>
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<tr>
<td>$(\text{CH}_3)_4\text{Si}$</td>
<td>284.5</td>
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<tr>
<td>$(\text{CH}_3)_4\text{Ge}$</td>
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<td>-</td>
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<td>$(\text{CH}_3)_4\text{Sn}$</td>
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<td>52.1</td>
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<td>$(\text{CH}_3)_4\text{Pb}$</td>
<td>139.6</td>
<td>34.9</td>
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<tr>
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</tr>
<tr>
<td>$(\text{CH}_3)_3\text{P}$</td>
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<td>65.3</td>
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</tr>
<tr>
<td>$(\text{CH}_3)_3\text{As}$</td>
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<td>51.5</td>
<td>54.6</td>
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<td>-</td>
<td>110</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Sb}$</td>
<td>149.1</td>
<td>49.7</td>
<td>57.0</td>
<td>-</td>
<td>-</td>
<td>116</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{Bi}$</td>
<td>101.2</td>
<td>33.7</td>
<td>44.0</td>
<td>-</td>
<td>-</td>
<td>116</td>
</tr>
<tr>
<td><strong>Group VIb:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{S}$</td>
<td>140.6</td>
<td>70.3</td>
<td>73.6</td>
<td>57.0</td>
<td></td>
<td>147</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{Se}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{Te}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><strong>Group VIIb:</strong></td>
<td>$(\text{CH}_3)\text{Cl}$</td>
<td>82.1</td>
<td>82.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(\text{CH}_3)\text{Br}$</td>
<td>68.9</td>
<td>68.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(\text{CH}_3)\text{I}$</td>
<td>54.4</td>
<td>54.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- $a$: total energy of the metal-methyl bonds in kcal/mole
- $b$: kcal/mole
- $c$: estimated value
\[ \Delta^{\text{CH}_3-\text{H}} = 102.5 \text{ kcal/mole}. \]

The value of \( D_1 \) for dimethylzinc is obtained by correcting the 16 mm value of 47.2 \( \Delta^{1} \) by adding 1.8 kcal/mole. \( D_2 \) is obtained by adding 1.3 kcal/mole to the 16 mm kinetic value or by difference from thermochemical data; this latter value is probably the more correct value.

As \( D_1 \) for trimethylaluminum is about 78 kcal/mole, the toluene carrier would also decompose appreciably. The use of benzene as the carrier would be better because benzene decomposition gives mainly ethylene and no methane. The mean bond energy of trimethylthallium needs investigation.

The mean bond energy of tetramethylgermanium needs investigation. The tetramethyIs of Group IVb should be studied by the toluene carrier technique (except tetramethylsilicon - benzene as carrier might be better), and if difficulties arise the dichlorodimethyls may give good estimates (maximum values) of the first bond energies.

Although trimethylantimony has been studied by the toluene carrier technique, it should be redone at much higher toluene-to-alkyl ratios. Trimethylphosphorous and trimethylarsenic should also be studied in this manner.

The mean bond energies of dimethylselenium and dimethyltellurium need investigation. The dimethyIs of sulphur, selenium, and tellurium should be studied by the toluene carrier technique.
REFERENCES


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Born:

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