Studies of ethyl radical reactions and the pyrolysis of diethylzinc.

A. A. Koski
University of Windsor
STUDIES OF ETHYL RADICAL REACTIONS

AND THE PYROLYSIS OF DIETHYLZINC

BY

A. A. KOSKI

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ABSTRACT

The thermal decomposition of diethylzinc in a toluene carrier system has been studied over the temperature range of 360 to 500°C, and percent decompositions of 6.5 to 95%. The decomposition was found to occur by a two step mechanism, the second rapidly following the first,

\[ \text{Zn}(C_2H_5)_2 \rightarrow \text{ZnC}_2\text{H}_5 + \text{C}_2\text{H}_5^* \]

\[ \text{ZnC}_2\text{H}_5 \rightarrow \text{Zn} + \text{C}_2\text{H}_5^* \]

where \( \log k \text{(sec}^{-1}) = 14.2 - (48,500±2000)/2.3RT \). Thus the first bond dissociation energy was found to be 48.5 kcal./mole and by calculation the second bond dissociation was 21.2 kcal./mole.

Considerable rate enhancement was noted in many of the runs and this phenomenon was attributed to the catalytic effects of small quantities of surface oxides in the reaction vessel.

The overall progress of the reaction was followed by analysis of residual diethylzinc by two different methods, (i) decomposition gas analysis and (ii) by residual zinc analysis using atomic absorption. Reasonable agreement was obtained for the majority of runs in which complete analysis was available. The presence of methane and hydrogen in the gases resulting from the decomposition of residual alkyl were discussed in terms of purity of the starting material and the possibility of radical displacement reactions on the parent alkyl. Suggestions for further work and improvements in the apparatus were made.
ACKNOWLEDGEMENTS

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I am also grateful to Mr. B. Trudell for his help in running the gas analyses, and to Gesine Rodger for typing the manuscript.
To St. Jude
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\[ q_e \quad \text{Electronic partition function} \]
\[ Q_t \quad \text{Total partition function} \]
\[ R \quad \text{Gas constant} \]
\[ s \quad \text{Number of vibrational degrees of freedom} \]
\[ D \quad \text{Symmetry number} \]
\[ t_c \quad \text{Contact time} \]
\[ v \quad \text{Vibrational frequency (cm}^{-1}\text{)} \]
\[ x \quad \text{Percent decomposition} \]
\[ Z \quad \text{Collision number} \]
CHAPTER 1
INTRODUCTION

General Introductory Remarks

The bond dissociation energy $D [A \cdot B]$ of a molecule $A \cdot B$ is defined as the heat of reaction of process (I) at zero degrees absolute in the ideal gas state, the products being in their ground states.

$$A \cdot B \rightarrow A + B \quad (I)$$

If the activation energy of the reverse reaction is taken to be zero, then the bond energy becomes the activation energy of the reaction. If the reverse process were to have a finite activation energy, then a hump should appear on the potential energy curve. This effect is shown in figure 1, and results from the assumption that two atoms or radicals of appropriate spin would suffer repulsion before combining. Evidence from band spectrometric measurements seem to discount the existence of such an energy barrier to recombination, except in certain special cases which arise from radical stabilization through resonance, as in Ph$_3$C$. On the other hand, activation energies for the dissociation of some simple homonuclear diatomic molecules have been shown to be less than the bond dissociation energies as a result of a nonequilibrium distribution of reactant molecules over excited vibrational states.

When dealing with polyatomic molecules, one must distinguish between the terms 'bond dissociation energy' and 'mean bond energy'.
Figure 1: Potential Energy Curve for a Unimolecular Decomposition into two atoms or radicals.

\[ X = \text{Energy of Activation for Recombination, finite} \]

\[ Y = \text{Energy of Activation for Recombination, zero} \]
or 'bond strength'. Consider the stepwise decomposition of the triatomic molecule $A_2B$.

$$A_2B \rightarrow AB + A \quad (II)$$
$$AB \rightarrow A + B \quad (III)$$

The mean bond energy is the average energy of the bonds AB-A and A-B, while $D[AB-A]$ and $D[A-B]$ are specific bond dissociation energies. Mean bond energies are usually readily available from calorimetric work, while thermal equilibrium, electron impact, spectroscopic, photochemical and kinetic methods are used to determine specific bond dissociation energies. When one deals with more complex molecules, for instance the class known as metal alkyls, then the kinetic method appears to be the one of choice. The radicals produced are almost always too reactive for thermal equilibrium methods, electron impact methods are complicated by the large number of atoms in the parent molecule, the molecules are usually too complex for spectroscopic interpretation and photochemical methods are often frustrated by uncertainty in the mechanism of radiation absorption and decomposition.

Activation energies from the pyrolysis of metallic alkyls have been determined using both static and flow systems. Of these two methods, the flow technique appears superior in that it avoids the complexity of the reactions that tend to occur in static systems. If the process observed experimentally is a unimolecular decomposition,
the experimental energy of activation that is obtained should be a close approximation of the bond dissociation energy, provided of course that the recombination energy is relatively small and the reaction is being observed in the high pressure region.

In the present study, toluene was used as the carrier gas. It was preferable to others for the reasons that it did not interfere with the analysis of the condensable products from the pyrolysis, the apparatus required for the study was relatively simple, and the estimation of gaseous products was direct rather than by difference.

**Theories of Unimolecular Reaction Rates**

The basis of all modern theories of unimolecular reactions is Lindemann's assumption that when a collision occurs between two molecules, one of them will become sufficiently energized to enable it to become a product.

\[ R + R \rightleftharpoons R^* + R \]  \hspace{1cm} (1)

\[ R^* \rightarrow P \]  \hspace{1cm} (2)

If the rate of reaction (2) is much less than the reverse of (1), then a steady state concentration of \( R \) will occur and the rate of formation of \( R \) can then be set at zero:

\[ \frac{d[R^*]}{dt} = k_1 [R]^2 - k_{-1} [R] [R^*] - k_2 [R^*] = 0 \]  \hspace{1cm} (3)

This then yields the relation

\[ [R^*] = \frac{k_1 [R]^2}{k_{-1} [R] + k_2} \]  \hspace{1cm} (4)
The rate of formation of products then becomes
\[
\frac{d[P]}{dt} = k_2 [R] = \frac{k_1 k_2 [R]^2}{k_{-1} [R] + k_2}
\]  
(5)

At sufficiently high pressures, \( k_{-1}[R] \gg k_2 \). It follows that
\[
\frac{d[P]}{dt} = \frac{k_1 k_2 [R]}{k_{-1}} = k_\infty [R]
\]  
(6)

where \( k_\infty \) is defined as the first order high pressure rate constant.

At low pressures, \( k_{-1}[R] \ll k_2 \), then
\[
\frac{d[P]}{dt} = k_1 [R]^2
\]  
(7)

In this latter case, a steady state concentration of \( R^* \) cannot be maintained and any molecule becoming energized will be more likely to yield products since there are not sufficient numbers of molecules nearby for a deenergizing collision to take place. Thus, the rate of reaction becomes proportional to the rate of energization. This results in a change from first order to second order-kinetics as the pressure is lowered, a fact which has been observed experimentally in many cases.

From the first order rate coefficient, \( k \), defined as
\[
v = k [R]
\]  
(8)

and from equation (6) we obtain
\[
k = \frac{k_1 k_2 [R]}{k_{-1} [R] + k_2} = \frac{k_\infty}{1 + k_2/k_{-1} [R]}
\]  
(9)
so that \( k = k\nu /2 \) when \( k_{-1}[R]_{1/2} \to k_{2} \), \([R]_{1/2}\) being the concentration of \( R \) when \( k = k\nu /2 \). Thus it follows that

\[
[R]_{1/2} = \frac{k_{2}}{k_{-1}} = \frac{k\nu}{k_{1}k_{-1}} = \frac{k\nu}{k_{1}} \quad (10)
\]

The value of \( k \) is found by experiment and from simple collision theory we have

\[
k_{1}' = Z e^{-E* /RT}
\]

where \( E \) is the activation energy. Using this formula leads to the result that the first order rate constant should fall off at a much higher pressure than is observed experimentally.

Hinshelwood was the first to start treating unimolecular reactions on a statistical basis. He assumed that the energy of a complex molecule was distributed among a number of vibrational degrees of freedom, \( s \), giving

\[
k_{1} = \frac{Z_{-1}'}{(s-1)!} \left[ \frac{E}{RT} \right]^{s-1} \cdot e^{-E* /RT} \quad (11)
\]

The major difficulty here was that \( s \), the number of degrees of freedom had no direct relation to the number of degrees of freedom in the molecule, and had to be evaluated on a trial and error basis.

The theory of Hinshelwood did however bring out a new reaction sequence:

\[
R + R \rightleftharpoons R^* + R \quad (1)
\]

\[
R^* \longrightarrow R^\# \quad (12)
\]

\[
R^\# \longrightarrow P \quad (13)
\]
The major deviation from earlier theories was the introduction of a new term \( R^\# \) which described an activated complex with the proper vibrational changes necessary to become a product. Although \( R^\# \) had the proper energy, it had to undergo vibrational changes in order to become \( R^\# \). The fault with this theory was that it resulted in a very large value for the rate of formation of \( R^\# \). Thus it appeared that the theory once again required modification.

Rice-Ramsburger\(^9\) and Kassel\(^10\) assumed that the rate of formation of \( R^\# \) was proportional to the energy in \( R^\# \), thus

\[
k_{12} = f(\mathcal{E}^\star)
\]

where \( \mathcal{E}^\star \) is the energy of \( R^\# \). The RRK theory defined a molecule as a system of loosely coupled oscillators, equivalent to the normal vibrational modes, allowing a free flow of energy between the normal modes without destroying their separateness. The oscillators were regarded as having the same frequency of vibration. With these modifications a statistical treatment then gave

\[
k_1 = k^\# e^{-E^\star/RT} \sum_{i} x^{i-1} \frac{x^s-1 - x}{1+(k^\#/k_{-1})R ((x/x+b)s-1)}
\]

(14)

where

\[
\begin{align*}
x &= E - E^\star/RT \\
b &= E^\star/RT \\
s &= \text{the number of oscillators.}
\end{align*}
\]

The term \( s \) usually turned out to be one-half the number of normal modes so that the oscillators were not equivalent to the normal modes as assumed in the theory.
Once again the theory was modified. Marcus attempted to differentiate between contributing and non-contributing modes in the energized species and activated complex. He assumed non-contributing modes to be:

(i) The energies involved in most rotational and translational modes on the basis of conservation of angular momentum in going from the energized molecule to the activated complex.

(ii) The zero-point energies.

The active modes which contributed to the energy were defined as

(i) All vibrational modes since there appears to be a relatively free flow of energy between normal modes of vibration.

(ii) Certain specific rotations, particularly some free rotations. These could be determined from the particular model chosen for the activated complex.

The overall reaction process is shown in figure 2. Owing to collisions, some of the reactant molecules acquire an energy \( \mathcal{E} \), and thus become energized molecules. \((\mathcal{E} \gg \mathcal{E}_a, \text{ where } \mathcal{E}_a = E_a/N^a)\).

The energy \( \mathcal{E} \) is approximately equal to the active energy in the activated complex. (Active internal rotations, however, dictate that \( \mathcal{E}^* = \mathcal{E} + \frac{Q^R}{Q^R_{\text{fr}}} \).) The excess energy \( (\mathcal{E} - \mathcal{E}_a) \) in the energized molecule then redistributes itself via the active modes of vibration and rotation and the activated complex ensues. The excess energy of the activated complex is now \( \mathcal{E}^* = \mathcal{E}^* - \mathcal{E}_a \). This excess
Figure 2. Energy Diagram For RRKM Treatment.

\[ \varepsilon_{\text{t}} = \text{energy of translation along reaction coordinate} \]

\[ \varepsilon_{\text{n}} = \text{energy of active vibrations and rotations} \]
energy then distributes itself into the breaking bond and the products are formed. This process occurs as $E_0 = E_t + E_n$ when $E_t$, the energy of translation along the reaction coordinate increases from zero to its critical level; the energy being acquire from the energy of the active modes of rotation and vibration given by $E_n$.

In the Rice-Ramsperger-Kassel (RRK) and the revised Rice-Ramsperger-Kassel-Marcus (RRKM) theories, a free flow of energy between the normal modes of vibration is assumed. Slater's theory\textsuperscript{12} on the other hand, does not allow for a free flow of energy and assumes that a reaction ensues when a critical coordinate becomes sufficiently extended, as occurs when different normal modes of vibration come into phase. Application of Slater's theory results in a lower rate of energization than either the Hinshelwood, Rice-Ramsperger-Kassel or Rice-Ramsperger-Kassel-Marcus theories predict, and the rates are in fact even lower than experimentally obtained values. Although Slater's idea of a reaction occurring when a critical coordinate becomes sufficiently extended appears to be logical and appealing, his preclusion of free energy flow is somewhat questionable and has been the subject of considerable dispute.\textsuperscript{13}
Determination of Specific Bond Dissociation Energies

By the Kinetic Method

If no potential energy barrier for the recombination of two species exists, the unimolecular rate constant can be written as

\[ k = K \frac{kT}{h} \frac{Q^*_t}{Q_t} e^{-D/RT} \]

The total partition functions for the normal molecule and the activated complex, \( Q_t \) and \( Q^*_t \) respectively, each include contributions from translational \( (q_t) \), rotational \( (q_r) \) and vibrational \( (q_v) \) components. Thus, the total partition function for the normal molecule can be written as

\[ Q_t \propto q_t q_r q_v \]

and that for the activated complex as

\[ Q^*_t = q^*_t q^*_r q^*_v \]

The translational partition function is given by

\[ q_t = \left( \frac{2\pi m kT}{h^3} \right)^{3/2} \]

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

The rotational partition function is given by

\[ q_r = \frac{8\pi^2 (\pi^2 kT)^{3/2}}{6h^3} (ABC)^{1/2} \]

§ Provided that the elements are in their ground states, the electrical contribution, \( q_e \), is equal to unity and need not be considered. Similarly, a degeneracy of one is assumed.
where \( A, B, C \) are the principal moments of inertia and \( \sigma^* \) is the symmetry number.

If the molecule in question happens to be linear, then the preceding expression reduces to

\[
q_T = \frac{8 \pi^2 \kappa \frac{kT}{h^2}}{\sigma^* (A \ B \ C)}
\]

This will be nearly equal for both the activated complex and the normal molecule. Considering each mode of internal vibration as a linear harmonic oscillator, the rate constant can then be written as

\[
k = \frac{\kappa T}{h} \sigma^* (A \ B \ C) \frac{3n-6}{\pi} \frac{(1-e^{-hv/kT})}{(1 - e^{-hv/kT})} \ e^{-D/RT}
\]

Two limiting factors may now be imposed on this equation. If \( hv \ll kT \), which occurs if the bond in question is exceedingly weak or if the temperature is very high, then the expression \( (1-e^{-hv/kT}) \) is approximately equal to \( hv/kT \) and the equation reduces to

\[
k = \frac{\sigma^* (A \ B \ C)}{\pi \sigma^* (A \ B \ C)} \frac{3n-6}{\pi} \frac{(1)}{(1)} \ e^{-D/RT}
\]

Taking logarithms and differentiating yields

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

In this case, the Arrhenius activation energy is equal to the bond dissociation energy. In the case where \( hv > kT \), following the same procedure as before, the result becomes

\[
\frac{d \ln k}{dT} = \frac{D + RT}{RT^2}
\]
Thus, the experimental activation energy in any case can be equated to the bond dissociation energy within the limits of $\frac{1}{2}RT$, which at the usual temperatures employed in pyrolysis studies, say $1000^\circ K$ or lower, approaches 2 kcal. mole$^{-1}$ as a maximum, provided that the activation energy referred to is in the pressure independent region.
CHAPTER II

EXPERIMENTAL TECHNIQUE

Apparatus and Procedure

The toluene carrier flow system employed in the present study is represented schematically in figure 3. For the sake of clarity, the alkyl injection system has been omitted and is shown separately in figure 4.

The main vacuum source for the system was a two stage mercury diffusion pump backed initially by a Balzers Duo 5 two stage oil sealed rotary vane fore pump, and later by a Sargent-Welch "Duo-Seal" model R-1400 high vacuum pump. Dow Corning High Vacuum Silicon stopcock grease was used to lubricate all ground glass joints except for those situated between the furnace exit port and the mercury diffusion pump, where Apiezon N grease was used instead. All heated and unheated taps were lubricated with Apiezon T and Apiezon N grease, respectively. In many cases, Ace Glass greaseless Viton-O-Ring taps (0-3 mm) were used which required no lubrication.

The alkyl reaction vessel consisted of a specially designed quartz cylinder which was joined into the pyrex glassware of the system by means of graded quartz-to-pyrex seals. The reaction vessel was heated by means of an electric furnace constructed from a
Figure 3: Schematic Diagram of the Toluene Carrier Flow System.
Figure 4: Alkyl Injection System
quartz cylinder three inches in diameter and twenty-four inches long with a wall thickness of one quarter inch. Chromel-A resistance ribbon, 2 mm wide and 0.2 mm thick, with a resistance of 0.603 ohm per foot was used to wind the furnace. Sauerisen Cement, Number 31 served to hold the windings in place.

The heating element was tapped at seven points to enable the temperature profile to be adjusted by means of shunt resistances. In order to flatten out the temperature profile, an inconel liner 2.5 inches in diameter, 12 inches long and 0.25 inch thick was centrally located inside the quartz cylinder.

The furnace was centered in a box (12x12x24 inches) of 0.25 inch asbestos with a 0.75 inch iron frame. Three inch diameter holes were drilled in the ends of the box to accommodate the furnace and the remaining space filled with powdered alumina (size 50 mesh) for insulation. The furnace element was connected through a type W20HM Variac Autotransformer to a 220 volt a.c. power source, yielding a maximum operating temperature of about 1200°C for the furnace.

The furnace temperature was controlled initially by a Sunvic Resistance Thermometer Controller type RT. 2. and in the latter stages by a CNS Instruments Limited Proportional Temperature Controller type SR 2. Reaction vessel temperatures were monitored by means of a Chromel-P-Alumel thermocouple inserted axially in a well within the vessel. The output was measured using a Leeds and Northrup
Millivolt Potentiometer type 8691 and the appropriate temperature obtained from standard tables. By proper adjustment of the shunt resistances a flat temperature profile (+2°C) could be maintained within the furnace with a sharp decrease occurring at the ends. The shunt tap locations and a typical temperature profile are illustrated in figure 5. A 10 ohm platinum resistance thermometer mounted along the inside wall of the inconel furnace liner served as a sensing device for the particular temperature controller used.

Each of the reaction vessels employed was made of fused quartz tubing which widened in two separate steps to a diameter of approximately 40 mm in the centre of the reaction zone and then constricted again at the end of the furnace. An axial well of 10 mm O.D. running the length of the reaction vessel housed the thermocouple and also served to minimize channeling. The vessels were 40 mm O.D. and 6.5 to 8 inches long sealed to 20 mm ends and having a reaction zone volume of 139 and 156 cc's respectively.

In order to prevent premature condensation of the metal alkyl, the tubing and all taps leading from the alkyl injection system to the furnace were wound with Chromel "A" asbestos heating wire connected to a variac. Asbestos and fiberglass plugs were inserted in the ends of the furnace in order to insulate the system from stray air currents within the laboratory. Each reaction vessel used in the study was thoroughly cleaned with several rinses of boiling fuming nitric acid.
Figure 5: Top: Schematic of Furnace Block showing tap locations
Bottom: A typical temperature profile
before insertion in the furnace, and then baked out overnight under
vacuum at 650°C.

The flow rate of the reactants through the furnace was con-
trolled by two means, firstly by the size of the opening in a high
vacuum valve (FC) located between the exit port of the furnace and the
trap T1, and secondly by raising or lowering the temperature of the
thermostatted baths surrounding the toluene and the metal alkyl. The
baths also served to minimize any pressure changes due to surface
cooling during the course of a run.

Both the metal alkyl and the toluene were stored in removable
vessels which could be weighed prior to and following a run to deter-
mine the amount of each used. The pressure in the system could be
checked periodically by means of a dioctyl phthalate and mercury
differential manometer with a magnification factor of 8.86 times that
of mercury.

Preparation of the alkyl consisted of distilling an amount
slightly larger than that to be used for the run over into the alkyl re-
servoir P1 which was then thermostated with a water bath to maintain
the desired pressure. After the run was over, the alkyl remaining
was distilled back into the weighed vessel and the amount used deter-
mined by difference. Both the toluene and alkyl were vigorously de-
gassed before the weighing procedure at the start of the run.

Once the temperature of the furnace had stabilized and a
vacuum of $10^{-4}$ mm or better was obtained, a run was initiated. The
initial manometer pressure was noted and then the toluene vessel tap was opened. Once toluene had flowed through the system for several minutes to stabilize the flow conditions, tap S1 was opened and the alkylation flow initiated. After the alkylation had flowed through the system for the desired length of time, the tap S1 was closed and the toluene allowed to flow for several additional minutes in order to purge the reaction vessel. Alkylation pressure, total pressure and furnace temperature were continuously monitored during the course of the run. At all times the alkylation pressure exceeded that of the toluene in order to prevent back diffusion of toluene vapour.

The gaseous products formed during the pyrolysis were continuously collected in the gas buret (GB) by means of a manually operated Toepler (TP) pump.

Unreacted toluene and alkylation and any condensible products were removed by traps T1 and T2 which were maintained at -7.8°C using a dry ice-acetone slurry. Usually trap T1 was sufficient to remove all the condensables, however, T2 was used as an added precaution.

After the run was over the trapping system was isolated from the furnace and the toepler continued for several minutes to collect any remaining gases. Once a good vacuum was again achieved, taps t1, t2, and FC were closed to isolate the condensible products and the pressure, volume and temperature of the collected gases noted. Several samples of the gases were taken in specially constructed break-
seal tubes for later analysis by gas chromatography.

After the gas samples had been collected, tap t1 was opened and trap T2 allowed to warm up so as to distill all condensed liquid products over to T1. Once this had been accomplished, tap t1 was again closed and trap T2 recooled to -78°C. Trap T1 was then allowed to warm up to room temperature. The sidearm on trap T1 was filled with deionized distilled water and a small amount of this introduced into trap T1 via the tap t2. Great care was taken to prevent the entry of air into the system. Once the water had been added, the mixture was agitated by means of a magnetic stirrer and a stirring bar which had been placed in trap T1 prior to the start of the run.

Once the evolution of gases had ceased, tap t1 was opened briefly to introduce the decomposition gases into trap T2. With tap t1 closed, and after allowing time for any liquids which may have been carried over to condense, tap t3 was opened and the gases toepled over into the previously evacuated gas buret (GB). This process was repeated several times until all the decomposition gases had been collected and all the condensable liquids were in trap T2. With taps FC, t1 and t3 closed, trap T1 was removed and the zinc hydroxide dissolved in nitric acid and set aside for analysis by atomic absorption. Samples of the decomposition gases were taken in the same manner as those for the product gases, and stored for later analysis by gas chromatography.
Trap T2 was then allowed to warm up to room temperature to separate the water and organic layers. Having accomplished this, trap T2 was then cooled to -12°C with a salt-ice mixture, removed, and the condensed liquid products analyzed immediately by gas chromatography.

Analysis of gaseous products was carried out on a Perkin Elmer model 154 gas chromatograph equipped with a 0.25 inch, 6 foot silica gel column maintained at 80°C and having a helium flow rate of 20 cc per minute. The gas injection system is represented in figure 6.

The special break-seal vial containing the gas sample (G) was fitted with a suitable ground glass joint and a steel bar placed in contact with the break seal. The vial was then fitted on the injection system and the tap g1 opened to evacuate the region. After a good vacuum had been achieved, tap g1 was closed and the steel bar lifted by means of a magnet. Removing the magnet caused the bar to fall and resulted in the breaking of the seal. Taps g2 and g3 were opened briefly to evacuate the "U" tube and then closed. By manipulating tap g1, a suitably sized sample was transferred to the gas buret and the pressure measured with a cathetometer. Tap g3 was then opened and the gas sample forced into the "U" tube by raising the level of the mercury. Tap g3 was then turned to allow the helium flow to enter the "U" tube simultaneously as tap g4 was turned to connect the "U" tube to the column of the gas chromatograph. Pure gases were stored in the gas storage vessels (G.S.V.) and used for calibration purposes.
Figure 6: Gas Product Analysis Injection System
Calibration curves were plotted prior to each set of analysis using the same injection technique. Peak height comparisons were used to determine the concentration of any particular gas in the product and decomposition gas mixtures. Later, when the presence of hydrogen became apparent, nitrogen was substituted as the carrier gas. Results from the two sets of carrier gases compared favourably.

The liquid products from each run were analyzed on a Perkin Elmer model 800 gas chromatograph equipped with a flame ionization detector. A 0.02 inch I.D. 150 foot open tubular column coated with poly(propylene glycol) (Perkin Elmer Column R) was used. The column and injection port temperatures were set at 75°C and 135°C respectively. Nitrogen was used as the carrier gas.

Standards were prepared containing the components found in the condensible liquid samples, namely benzene, ethylbenzene and propylbenzene, in concentrations comparable to those obtained during a run. The preparation consisted essentially of injecting a known volume of each of the components into a known weight of toluene. Densities of the various materials were obtained from a handbook and the molar concentrations calculated. The standards were stored in a glass stoppered 25 ml volumetric flask.

To check for dissolved butane in the condensible products, a butane standard was prepared in the following manner. A known amount of toluene, comparable to that used during a run was allowed
to run through the system to trap T1 where it was collected using a dry ice-acetone bath. This bath was then removed and replaced with one of liquid nitrogen. The alkyl finger was removed and then replaced with a bulb containing a known volume and pressure of butane. After evacuating the system, the butane was allowed to flow in the same manner as the alkyl normally would. Having completed the transfer, the liquid nitrogen bath was removed and replaced with the dry ice-acetone slurry. A portion of the trapped butane would then dissolve in the toluene, while the rest would flow through the system and be collected and measured in the gas buret. The amount of butane recovered was subtracted from the amount contained initially in the vessel, and consequently the amount dissolved in the toluene was known. The dry ice-acetone bath was then removed and replaced with the salt-ice slurry normally used. After the trap and contents had reached -12°C, the trap and bath were removed and the toluene solution was analyzed immediately on the Perkin Elmer 800. A precooled syringe was used for all injections. After reproducible peak heights were obtained, the sample was allowed to warm up to room temperature and a known volume of benzene was added to the toluene. Several injections were then made. Since the concentrations of the benzene and butane were known, peak height correlations could be made between the two sets of standards and the condensable products. Calibrations were done prior to each liquid analysis. As an added precaution, the toluene
was checked after each run for traces of accumulated contaminants, mainly benzene and ethylbenzene, and the appropriate corrections made. Corrections were necessary only in several runs where the first and last fractions of a particular batch of toluene were used.

The analysis of the residual zinc hydroxide was accomplished as follows. A small quantity of nitric acid was added to convert the zinc hydroxide to zinc nitrate.

\[ \text{Zn(OH)}_2 + x. s. \text{HNO}_3 \rightarrow \text{Zn(NO)}_3_2 + 2\text{H}_2\text{O} \]

The trap was then carefully washed several times to remove all traces of zinc. The washings were concentrated in a beaker and then heated to ensure complete dissolution. The solution was subsequently transferred to a 1000 ml volumetric flask and diluted to the line with deionized distilled water. A 5 ml sample was then taken and rediluted to 100 ml in a volumetric flask in order to bring the zinc concentration into the appropriate range for analysis via atomic absorption.

Standards for the metal analysis were prepared by dissolving a known weight of A.C.S. grade zinc (mossy) in nitric acid. The solution was then heated to drive off the excess acid and the appropriate dilutions made to give standards in the range of 0-6 ppm zinc. These were stored in 100 ml stoppered volumetric flasks. Standards were run before and after the residual zinc analysis for added accuracy in order to eliminate errors which might result from instrumental drift during the course of the analysis. The instrument used was a Pye
Unicam SP 90 Atomic Absorption-Flame Emission Spectrophotometer equipped with a hollow zinc cathode lamp.

**Preparation of Materials**

(i) **Toluene**

The toluene employed was toluene from sulfonic acid, number X325 as supplied by Eastman Organic Chemicals. It was dried by refluxing under vacuum at least 24 hours over freshly pressed sodium ribbon and then degassed by bulb to bulb distillation.

(ii) **Diethylzinc**

The diethylzinc was obtained from Alfa Inorganics, stock number 85101. It was used as supplied, except for a vigorous degassing. Analysis of residue remaining after decomposition by water yielded 99+% \( \text{ZnEt}_2 \), measured as \( \text{Zn}^{++} \) using atomic absorption. Later analysis of the decomposition gases showed up to 4% of a methyl containing impurity, probably dimethylzinc. This impurity would undoubtedly be greatly reduced during a few degassings owing to a much higher vapour pressure than diethylzinc. Any small quantity remaining would presumably remain inert during passage through the furnace and be subsequently collected in the condensable liquids trap.
CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental data on the pyrolysis of diethylzinc under various conditions are presented in Table 1.

Proposed Mechanism

The pyrolytic decomposition of diethylzinc in toluene vapour occurs by successive rupture of both zinc-carbon bonds, the second step rapidly following the first:

\[ \text{ZnEt}_2 \rightarrow \text{ZnEt} + \text{Et} \]  

\[ \text{ZnEt} \rightarrow \text{Zn} + \text{Et} \]

(1)  

(2)

The ethyl radicals produced in the decomposition will then abstract hydrogen atoms from either the ring or side chain of toluene to yield ethane, recombine to produce butane, disproportionate to give ethylene and ethene, or decompose. The major ethyl radical reactions are shown below:

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

\[ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10} \]  

\[ \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \]  

(3)  

(4)  

(5)

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

(6)

A combination reaction between benzyl radicals formed in equation (3) and ethyl radicals was also found to occur as evidenced by the production of significant amounts of propylbenzene:

\[ \text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_6\text{H}_5\text{C}_3\text{H}_7 \]

(7)
TABLE I
THE PYROLYSIS OF DIETHYLZINC
EXPERIMENTAL PARAMETERS AND PRODUCT ANALYSIS

<table>
<thead>
<tr>
<th>Run#</th>
<th>Temp. (°K)</th>
<th>Pressure (mm.)</th>
<th>Time* (min.)</th>
<th>Toluene (moles x 10⁻¹)</th>
<th>Alkyl (moles x 10⁻³)</th>
<th>Toluene/Alkyl (molar ratio)</th>
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<tbody>
<tr>
<td>Zn 91</td>
<td>674.2</td>
<td>23.4</td>
<td>35/45</td>
<td>1.689</td>
<td>2.2658</td>
<td>75/1</td>
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<td>Zn 90</td>
<td>694.2</td>
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<td>40/50</td>
<td>1.796</td>
<td>3.3428</td>
<td>54/1</td>
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<td>Zn 96</td>
<td>700.2</td>
<td>14.5</td>
<td>20/30</td>
<td>0.800</td>
<td>1.0802</td>
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<td>Zn 81</td>
<td>703.2</td>
<td>12.7</td>
<td>20/30</td>
<td>0.731</td>
<td>1.2948</td>
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<tr>
<td>Zn 89</td>
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<td>24.1</td>
<td>35/50</td>
<td>1.862</td>
<td>2.3565</td>
<td>79/1</td>
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<td>0.870</td>
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<td>73/1</td>
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*Alkyl flow time/Total run time
### TABLE I
(continued)

<table>
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<tr>
<th>Run#</th>
<th>$H_2^p$ (moles x 10$^{-4}$)</th>
<th>$CH_4^p$ (moles x 10$^{-4}$)</th>
<th>$C_2H_4^p$ (moles x 10$^{-4}$)</th>
<th>$C_2H_6^p$ (moles x 10$^{-4}$)</th>
<th>$C_4H_{10}^p$ (moles x 10$^{-4}$)</th>
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<td>0.076</td>
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<td>0.026</td>
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*p=Product gas
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<tr>
<th>Run#</th>
<th>C₄H₁₀* (moles x 10⁻⁴)</th>
<th>n-propyl benzene¹ (moles x 10⁻⁴)</th>
<th>benzene¹ (moles x 10⁻⁴)</th>
<th>ethyl benzene¹ (moles x 10⁻⁴)</th>
<th>C₄H₁₀⁺ (moles x 10⁻⁴)</th>
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*¹=liquid (condensable) product  N.A. = not available, t=total
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<tr>
<th>Run#</th>
<th>$d^\text{H}_2$ (moles x 10$^{-4}$)</th>
<th>$\text{CH}_4$ (moles x 10$^{-4}$)</th>
<th>$\text{C}_2\text{H}_4^d$ (moles x 10$^{-4}$)</th>
<th>$\text{C}_2\text{H}_6^d$ (moles x 10$^{-4}$)</th>
<th>$\text{C}<em>4\text{H}</em>{10}^d$ (moles x 10$^{-4}$)</th>
<th>Recovered Zinc (moles x 10$^{-3}$)</th>
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*d*= Decomposition gas, tr. = trace
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<thead>
<tr>
<th>Run#</th>
<th>$H_2^\dagger$ (moles x 10^{-4})</th>
<th>$CH_4^\dagger$ (moles x 10^{-4})</th>
<th>$C_2H_4^\dagger$ (moles x 10^{-4})</th>
<th>$C_2H_6^\dagger$ (moles x 10^{-4})</th>
<th>$10^3/T$ (°K -1)</th>
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<td>Run#</td>
<td>Temp (°K)</td>
<td>Pressure (mm.)</td>
<td>Time (min.)</td>
<td>Toluene (moles x 10^-1)</td>
<td>Alkyl (moles x 10^-3)</td>
<td>Toluene/Alkyl (molar ratio)</td>
</tr>
<tr>
<td>------</td>
<td>-----------</td>
<td>----------------</td>
<td>-------------</td>
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### Table I
(Continued)

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<td>$CH_4^d$ (moles x 10^{-4})</td>
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<td>CH$_4^t$ (moles x 10^{-4})</td>
<td>C$_2$H$_4^t$ (moles x 10^{-4})</td>
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<td>$10^3/T^\circ$ ($^\circ\text{K}^{-1}$)</td>
</tr>
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Numerous reactions involving methyl and hydrogen radicals are also proposed:

$$\begin{align*}
\text{H}^\cdot + \text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{CH}_3^\cdot + \text{C}_6\text{H}_6 \quad (8) \\
& \rightarrow \text{H}_2 + \text{C}_6\text{H}_5\text{CH}_2^\cdot \quad (9) \\
\text{CH}_3^\cdot + \text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{CH}_4 + \text{C}_6\text{H}_5\text{CH}_2^\cdot \quad (10) \\
\text{CH}_3^\cdot + \text{C}_2\text{H}_5 & \rightarrow \text{C}_3\text{H}_8 \quad (11) \\
\text{CH}_3^\cdot + \text{C}_2\text{H}_5\text{ZnC}_2\text{H}_5 & \rightarrow \text{CH}_3\text{ZnC}_2\text{H}_5 + \text{C}_2\text{H}_5^\cdot \quad (12) \\
\text{H}^\cdot + \text{C}_2\text{H}_5\text{ZnC}_2\text{H}_5 & \rightarrow \text{H}\text{ZnC}_2\text{H}_5 + \text{C}_2\text{H}_5^\cdot \quad (13)
\end{align*}$$

Reactions represented by equations (12) and (13) are proposed on the basis of evidence that significant amounts of methane and hydrogen were produced when residual alkyl was decomposed with water at the end of the run. The decomposition of small amounts of diethylzinc by water has been the subject of several investigations, and the only volatile product reported formed was ethane. An earlier study, utilizing considerably more drastic conditions for the decomposition, in which relatively large samples of the alkyl were decomposed with water or acid, did yield hydrogen and ethylene in small quantities. To test the possibility that the same situation might obtain in the present study, a sample of diethylzinc obtained directly from the storage vessel was decomposed under the same conditions as the residual alkyl normally would have been. No traces of ethylene or hydrogen were detected in the decomposition gases, however, methane was detected in quantities corresponding to a 4%
impurity in the original diethylzinc. Although this at first appeared to explain the methane in the decomposition gases, it was felt that equation (12) should be considered on the basis of (i) rate constants which were calculated for the displacement process. (Since mass balance for zinc obtained between undecomposed alkyl and the decomposition residue, it seems that the impurity in question is mainly ZnMe₂, which should be inert under the reaction conditions.), and (ii) equation (13) being the only logical explanation for the production of hydrogen from the residual alkyl. (The temperature of the condensation traps (-78°C) and the pressure in the system appears to preclude the possibility that hydrogen and methane were trapped by solution in toluene although this is true for butane and may apply for traces of ethane and ethylene.) If one accepts the displacement process represented by equation (13) to be valid, then it would seem reasonable to expect reaction (12) to also occur when one considers that the Zn-H and Zn-C mean bond strengths are comparable. Adding support to the proposed methyl displacement reaction is the fact that ZnMe₂ is considerably more volatile than ZnEt₂ and would thus be expected to distill off rather quickly under the pressures and alkyl bath temperatures used during the run, if in fact it even survived the degassing procedure. Thus, although the ZnMe₂ impurity may represent a significant source of methane in the decomposition gases from a few runs, (those done with a new batch of alkyl), it seems...
worthwhile to consider the displacement reaction.*

The production of hydrogen and methane from the reaction between water and \( \text{HZnC}_2\text{H}_5 \) and \( \text{CH}_3\text{ZnC}_2\text{H}_5 \) might then be expected to proceed in a manner analogous to that proposed by Ishimori et al. \(^{14}\) for \( \text{ZnEt}_2 \). The following mechanisms appear likely:

\[
\begin{align*}
\text{HZnC}_2\text{H}_5 + \text{H}_2\text{O} & \rightarrow \text{C}_2\text{H}_5\text{ZnOH} + \text{H}_2 \\
n\text{C}_2\text{H}_5\text{ZnOH} & \rightarrow (\text{C}_2\text{H}_5\text{ZnOH})_n \rightarrow \text{C}_2\text{H}_5(\text{ZnO})_n\text{H} + n\cdot \text{I} (\text{C}_2\text{H}_6) \\
\text{C}_2\text{H}_5(\text{ZnO})_n\text{H} + \text{C}_2\text{H}_5\text{ZnH} & \rightarrow \text{C}_2\text{H}_5(\text{ZnO})_n\text{ZnC}_2\text{H}_5 + \text{H}_2 \\
\text{C}_2\text{H}_5(\text{ZnO})_n\text{H} + \text{H}_2\text{O} & \rightarrow \text{HO}(\text{ZnO})_n\text{H} + \text{C}_2\text{H}_6 \\
\text{CH}_3\text{ZnC}_2\text{H}_5 + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{ZnOH} + \text{C}_2\text{H}_6 \\
n\text{CH}_3\text{ZnOH} & \rightarrow (\text{CH}_3\text{ZnOH})_n \rightarrow \text{CH}_3(\text{ZnO})_n\text{H} + n\cdot \text{I} (\text{CH}_4) \\
\text{CH}_3(\text{ZnO})_n\text{H} + \text{C}_2\text{H}_5\text{ZnCH}_3 & \rightarrow \text{CH}_3(\text{ZnO})_n\text{ZnCH}_3 + \text{C}_2\text{H}_6 \\
\text{CH}_3(\text{ZnO})_n\text{H} + \text{H}_2\text{O} & \rightarrow \text{HO}(\text{ZnO})_n\text{H} + \text{CH}_4
\end{align*}
\]

The reaction sequence shown by equation 11, the combination reaction between \( \text{CH}_3^* \) and \( \cdot \text{C}_2\text{H}_5 \) appears to be negligible in that only minute traces of propane were found. The presence of hydrogen in the product gases gives evidence for reaction (9).

The first order rate constants for the study were calculated from the first order rate expression given by

\[
k = 2.303 \log \frac{100}{100-x}
\]

* A similar displacement reaction has been found to occur between \( \text{CH}_3^* \) and \( \text{B(Et)}_3^* \), although other examples in the literature are somewhat scarce.
where $x$ denotes the percent decomposition and $t_c$ is the contact time or the average time that a molecule spends in the reaction zone in the furnace. This was calculated from the expression

$$t_c = \frac{V}{22,416} \times \frac{P}{760} \times \frac{x}{T} \times \frac{273}{F}$$

where $V$ is the reaction zone volume in cubic centimeters, $P$ is the average total pressure in millimeters of mercury, $T$ is the absolute temperature in the reaction zone and $F$ is the flow rate through the furnace in moles sec$^{-1}$.

The percent decomposition, $x$, was evaluated by two separate methods, (i) by analysis of zinc residue using atomic absorption techniques and (ii) by decomposition gas analysis via gas chromatography. The first method was direct and the percent decomposition is given by

$$x = \frac{(\text{moles ZnEt}_2 \text{ used} - \text{moles Zn}^{++} \text{ recovered}) 100}{\text{moles ZnEt}_2 \text{ used}}$$

The second method was based on the analysis of decomposition gases and is derived from

$$x = \frac{100 [\text{moles ZnEt}_2 \text{ used} - \frac{1}{2}(\text{moles C}_2\text{H}_5^d + \text{moles CH}_4^d + \text{moles H}_2^d)]}{\text{moles ZnEt}_2 \text{ used}}$$

($d =$ decomposition gas, 'used' = amount originally started with)

For the runs in which both methods were used for determination of the percent decomposition, agreement was generally favourable. The numerical values from the two different techniques for a series of runs are shown in table II along with other pertinent data.
TABLE II
THE PYROLYSIS OF DIETHYLZINC
EXPERIMENTAL RESULTS

<table>
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<tr>
<th>Run#</th>
<th>*Alk. Rec. (mole x 10⁻³)</th>
<th>% Decomp.</th>
<th>% Decomp.</th>
<th>km (sec⁻¹)</th>
<th>kg (sec⁻¹)</th>
<th>log km</th>
<th>log kg</th>
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*Alk. Rec. = \([CH₄^d + H₂^d + C₂H₆^d]/2\); g = gas analysis, m = metal analysis (A.A.)
<table>
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<tr>
<th>Run#</th>
<th>Alk. Rec. (moles x 10⁻³)</th>
<th>% Decomp.</th>
<th>% Decomp. g</th>
<th>km (sec⁻¹)</th>
<th>kg (sec⁻¹)</th>
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Hydrogen Abstraction by Ethyl Radicals

The rate expressions for reactions (3) and (4) may be written as

\[
\frac{d(C_2H_6^* - C_2H_4^* \cdot)}{dt} = k_a(C_2H_5\cdot)(C_6H_5CH_3)
\]

and

\[
\frac{d(C_2H_10)}{dt} = k_r(C_2H_5\cdot)^2
\]

respectively.

(Note: \(C_2H_4^* = C_2H_4\) from disproportionation only.)

Thus,

\[
k_a \frac{k_{r1/2}}{k_r} = \frac{d(C_2H_6^* - C_2H_4^* \cdot)/dt}{\left[ d(C_2H_10)/dt \right]^{1/2} [C_6H_5CH_3]}
\]

where

\[
\frac{d(C_2H_6^* - C_2H_4^* \cdot)}{dt} = \frac{\text{mole's } C_2H_6 - \text{mole's } C_2H_4}{n \times t}
\]

If one assumes the ideal gas law to hold true for toluene vapour under the conditions employed in the present study, then the concentration of toluene can be obtained from

\[
C_6H_5CH_3 = \frac{n}{V} = \frac{P}{RT} = \frac{P (\text{mm})}{82.06 \times T^\circ A}
\]

The disproportionation/combination ratio for ethyl radicals was approximated as 0.11 on the basis of previous studies so that

\[
\text{moles } C_2H_4^* = 0.11(\text{moles } C_4H_{10})
\]

and

\[
C_2H_6^a = C_2H_6^p - 0.11(C_4H_{10}^t)
\]

(a: abstraction, p: product gas, t: total gas)

Thus,

\[
k_a = \left[ C_2H_6^p - 0.11(C_4H_{10}^t) \right] 760 \times 82 \times T^\circ A
\]

\[
\frac{k_a}{k_r^{1/2}} = \left[ C_4H_{10}^t \right]^{1/2} (V \times t)^{1/2} \times P \ (\text{mm})
\]
These results are tabulated in Table IIa. The validity of the preceding formula is based on the assumption that the decomposition occurs at a constant and uniform rate. By maintaining the pressure of the metal alkyl constant throughout the duration of the run, one obtains ethyl radicals at a constant rate; however, they are not produced uniformly throughout the furnace except perhaps at very low decompositions. During a typical run, ethyl radicals will be at a high concentration at the start of the reaction zone, favouring the recombination reaction and at a low concentration at the end of the reaction zone, favouring the abstraction reaction. Although this appears to present a major problem, these factors are believed to be somewhat self-compensating.

**Displacement Reactions**

As mentioned previously, the release of methane and hydrogen from the decomposition of residual alkyl was taken as an indication of the formation of $\text{CH}_3\text{ZnC}_2\text{H}_5$ and $\text{HZnC}_2\text{H}_5$ during the course of the pyrolysis. The rate constants for the displacement reaction of the methyl radicals have been evaluated and are presented in Table III.

The methyl radical concentrations can be evaluated from the expression

$$\frac{d(\text{CH}_4)}{dt} = k_a (\text{CH}_3) (\text{C}_6\text{H}_5\text{CH}_3)$$

where

$$\frac{d(\text{CH}_4)}{dt} = \frac{\text{moles CH}_3^\circ}{V \times t}$$
<table>
<thead>
<tr>
<th>Run#</th>
<th>$[\text{C}_2\text{H}_5^·]$ (m.cc$^{-1} \times 10^{-11}$)</th>
<th>[Toluene] (m.cc$^{-1} \times 10^{-7}$)</th>
<th>$\text{C}_2\text{H}_6^a$ (mole$^{-1} \times 10^{-4}$)</th>
<th>$k_a/k_r 1/2$</th>
<th>$\log k_a/k_r 1/2$</th>
<th>$k_a^a$ (cc.mole$^{-1} \text{sec}^{-1/2}$) x 10$^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 91</td>
<td>0.65</td>
<td>5.56</td>
<td>1.32</td>
<td>55.9</td>
<td>1.75</td>
<td>11.2</td>
</tr>
<tr>
<td>Zn 90</td>
<td>1.79</td>
<td>5.27</td>
<td>2.22</td>
<td>30.6</td>
<td>1.49</td>
<td>6.3</td>
</tr>
<tr>
<td>Zn 96</td>
<td>0.75</td>
<td>3.32</td>
<td>0.61</td>
<td>65.9</td>
<td>1.82</td>
<td>13.1</td>
</tr>
<tr>
<td>Zn 89</td>
<td>1.85</td>
<td>5.42</td>
<td>3.05</td>
<td>46.3</td>
<td>1.67</td>
<td>9.3</td>
</tr>
<tr>
<td>Zn 88</td>
<td>1.37</td>
<td>4.30</td>
<td>2.75</td>
<td>62.5</td>
<td>1.80</td>
<td>12.5</td>
</tr>
<tr>
<td>Zn 86</td>
<td>1.94</td>
<td>3.34</td>
<td>2.03</td>
<td>83.7</td>
<td>1.92</td>
<td>16.7</td>
</tr>
<tr>
<td>Zn 87</td>
<td>1.65</td>
<td>3.82</td>
<td>2.52</td>
<td>53.6</td>
<td>1.73</td>
<td>10.7</td>
</tr>
<tr>
<td>Zn 98</td>
<td>1.35</td>
<td>3.30</td>
<td>0.95</td>
<td>57.0</td>
<td>1.76</td>
<td>11.4</td>
</tr>
<tr>
<td>Zn 78</td>
<td>1.84</td>
<td>3.35</td>
<td>1.45</td>
<td>63.0</td>
<td>1.80</td>
<td>12.6</td>
</tr>
<tr>
<td>Zn 100</td>
<td>1.40</td>
<td>3.18</td>
<td>1.02</td>
<td>60.8</td>
<td>1.78</td>
<td>12.2</td>
</tr>
<tr>
<td>Zn 101</td>
<td>1.67</td>
<td>3.44</td>
<td>1.29</td>
<td>60.3</td>
<td>1.78</td>
<td>12.0</td>
</tr>
<tr>
<td>Zn 102</td>
<td>1.61</td>
<td>3.30</td>
<td>1.59</td>
<td>80.0</td>
<td>1.90</td>
<td>16.0</td>
</tr>
</tbody>
</table>

Runs are listed in order of increasing temperature, $a=\text{abstraction}$, $r=\text{recombination}$.

$^a$ Based on $k_{rec} = 10^{12.6}$ from JACS 94, 6886 (1972).
<table>
<thead>
<tr>
<th>Run#</th>
<th>[CH$_3$.] $\text{cc}^{-1} \times 10^{-13}$</th>
<th>[ZnEt$_2$.] Avg. $\text{cc}^{-1} \times 10^{-8}$</th>
<th>$\frac{d[CH_3ZnC_2H_5]}{dt} \text{cc}^{-1} \times 10^{-10}$</th>
<th>$k_{\text{disp}} \text{cmole}^{-1} \text{sec}^{-1} \times 10^{-11}$</th>
<th>log $k_{\text{disp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 91</td>
<td>1.12</td>
<td>0.846</td>
<td>4.55</td>
<td>4.80</td>
<td>11.681</td>
</tr>
<tr>
<td>Zn 90</td>
<td>1.34</td>
<td>1.076</td>
<td>5.95</td>
<td>4.12</td>
<td>11.615</td>
</tr>
<tr>
<td>Zn 96</td>
<td>1.73</td>
<td>0.575</td>
<td>1.01</td>
<td>1.01</td>
<td>11.004</td>
</tr>
<tr>
<td>Zn 89</td>
<td>1.06</td>
<td>0.732</td>
<td>0.52</td>
<td>0.67</td>
<td>10.826</td>
</tr>
<tr>
<td>Zn 88</td>
<td>0.87</td>
<td>0.390</td>
<td>0.59</td>
<td>1.73</td>
<td>11.238</td>
</tr>
<tr>
<td>Zn 86</td>
<td>5.50</td>
<td>0.600</td>
<td>4.65</td>
<td>1.41</td>
<td>11.149</td>
</tr>
<tr>
<td>Zn 87</td>
<td>1.31</td>
<td>0.457</td>
<td>2.32</td>
<td>3.88</td>
<td>11.589</td>
</tr>
<tr>
<td>Zn 98</td>
<td>1.01</td>
<td>0.604</td>
<td>6.41</td>
<td>1.05</td>
<td>11.021</td>
</tr>
<tr>
<td>Zn 78</td>
<td>4.21</td>
<td>0.765</td>
<td>6.86</td>
<td>2.13</td>
<td>11.328</td>
</tr>
<tr>
<td>Zn 100</td>
<td>4.23</td>
<td>0.860</td>
<td>16.23</td>
<td>4.46</td>
<td>11.649</td>
</tr>
<tr>
<td>Zn 101</td>
<td>2.57</td>
<td>0.678</td>
<td>5.34</td>
<td>3.06</td>
<td>11.486</td>
</tr>
<tr>
<td>Zn 102</td>
<td>1.97</td>
<td>0.472</td>
<td>3.63</td>
<td>3.87</td>
<td>10.588</td>
</tr>
</tbody>
</table>

Avg. = average, disp. = displacement
and the toluene concentration is given by
\[
(C_6H_5CH_3) = \frac{P \text{ mm}}{760} \frac{82.06 \times T^o A}{mm}
\]

Values of \(k_m\), the abstraction rate constant for the reaction
\[
CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2
\]
were obtained from work done previously in this laboratory by J. Kominar.\(^20\) The rate of formation of CH\(_3\)ZnC\(_2\)H\(_5\) is given by
\[
\frac{d(CH_3ZnC_2H_5)}{dt} = \frac{\text{moles CH}_4^d}{V \times t}
\]

and the rate constant for the displacement reaction by
\[
k = \frac{d(CH_3ZnC_2H_5) / dt}{(CH_3^+) (C_2H_5ZnC_2H_5)}
\]

where the concentration of the parent alkyl is evaluated from
\[
[ZnEt_2] = \frac{t_c [\text{moles ZnEt}_2 \text{ used} + \text{moles (Zn}^{++} \text{ rec. -CH}_4^d \text{ - H}_2^d)]^{1/2}}{V \times t}
\]

Lack of available data on the analogous abstraction reaction between hydrogen radicals and toluene precludes the possibility of calculating similar rate constants for the process
\[
H^+ + C_2H_5ZnC_2H_5 \rightarrow HZnC_2H_5 + C_2H_5
\]

**Catalytic Effects and Arrhenius Plot**

The rate of the thermal decomposition of diethylzinc appears to be markedly influenced by the presence of small amounts of oxidation products in the reaction zone. A similar rate enhancement was previously encountered in a study on the related compound dimethylzinc.\(^21\)
In the present work, evidence of the formation of oxides such as ZnO, ZnEt₂O, and ZnEt₂O₂ was indicated by the appearance of a white deposit at the entrance to the reaction zone. Unlike the zinc metal deposit which sublimed readily, this material was relatively immobile under the pressure and temperature conditions of the furnace. Attempts to dissolve the material in organic solvents such as petroleum ether or toluene proved futile and appeared to indicate that the material was inorganic in nature.

The appearance of the aforementioned material in the entrance to the reaction zone of the furnace coincided with a large increase in the rate constants observed for any particular temperature and necessitated the removal of the reaction vessel and its subsequent cleaning as previously described. Attempts at removing the oxides by reduction with hydrogen at elevated furnace temperatures proved fruitless, possibly because the area of most oxidation could not be effectively heated. Attempts at preventing the formation of this oxide by regreasing the taps and changing the viton 'O' rings met with very little success and the amount of oxidated products gradually increased with time regardless of what corrective measures were undertaken. No noticeable leaks were detected in either the reaction vessel or the main vacuum system. It remains possible that the source of the oxidation process was a trace amount of water remaining in the toluene.

* For a discussion of the decomposition of ZnEt₂ by O₂, see J. Chem. Soc., 688-95 (1946)
after drying with sodium metal although this was not proven conclusively. Specific positional leakage of some taps may also have been a possibility.

The Arrhenius plot for the thermal decomposition of diethylzinc is shown in figure 7. The points chosen for the line of best fit represent those runs in which little or no catalytic effects were noticed. A series of points in which catalytic effects were pronounced are also plotted on the same graph and show the flattening of the Arrhenius plot which is characteristic of catalytic reactions. The majority of runs in which no oxide deposit was visible appeared to fall along a limiting line which was chosen as the line of best fit. The slope and intercept of this line was then used for the determination of the rate equation for the decomposition reaction and the zinc-carbon bond energies.

**Surface Effects**

During the latter stages of this work, a series of runs were done using a packed vessel containing quartz rods. The volume of this vessel was approximately 96 cc's as compared to the unpacked vessels which had volumes of 139 and 156 cc's respectively. Attempts to obtain meaningful results from this study were frustrated by the formation of the oxide layer as previously mentioned. Although the rate constants were considerably higher for these runs, one cannot state conclusively whether this increase was due to a simple increase
Figure 7: Arrhenius plot for the decomposition of diethylzinc showing typical scatter.

- Based on gas analysis
- Based on metal analysis
- A series of runs illustrating the effect of oxide catalysis
in the surface area or due to the oxide. The latter cause appears the most likely.

Effect of the Variables of Contact Time, Pressure and Alkyl Concentration on the Rate Constant.

In order to ascertain the order of the reaction, it is necessary to study the effects of contact time, total pressure and initial reactant concentrations on the rate constant. If the thermal decomposition of diethylzinc is first order, varying these parameters should have no effect on \( k \). In the present study, the problem remained to select runs in which the differences in \( k \) (if any) could be directly attributed to changes in one of the variable reaction parameters, as opposed to (indeterminable) changes in quantities of surface oxide.

Thus, comparisons are meaningful only between runs in which the quantities of surface oxide were similar, for instance successive runs, or deemed absent. Since determination of oxide amounts could only be effectively accomplished by a visual means, considerable errors are expected to ensue. A further problem arises from the observation that the catalytic effects decrease somewhat with time on a series of runs done with supposedly comparable oxide quantities. It appears that the zinc metal residue tends to cover the oxide film as it distills from the reaction zone, effectively eliminating a portion of the active sites and thereby reducing the rate constant observed at that temperature. As
time progresses, and no further metal is deposited, the zinc gradually moves further out of the hot zone, uncovering the oxide once again so that in the next run the rate will have increased substantially again. Thus, a few 'conditioning' runs in which comparatively large quantities of the alkyl were introduced into the furnace at a high temperature in order to "plate out" the active sites were only marginally successful. Table IV shows the effect of oxide buildup on the rate constant in a series of consecutive runs as compared to random runs in which the quantities of visible surface oxide were greatly reduced or absent.

CONCENTRATION AND CONTACT TIME EFFECTS

Table V(a) lists a number of runs carried out in the temperature range 739-756°C at comparable pressures and serves well to illustrate the difficulty in extracting information from pressure, concentration and contact time studies when catalytic effects are pronounced. As an example, if runs Zn 49 (oxide catalysed) and Zn 17 (oxide free) were compared on their own merits, it would appear that the reaction is far from first order, as a slight increase in contact time and the alkyl to toluene ratio increased the rate constant threefold. However, runs Zn 63 and Zn 64 are perhaps the best supporting evidence of a first order reaction; increasing the alkyl concentration fivefold and the contact time threefold had only a doubling effect on the rate constant. Although ideally no effect should be noticed at all, this appears as reasonable as can be expected as even these runs were probably somewhat oxide catalysed.

PRESSURE EFFECTS

Table V(b) shows that increasing the pressure significantly from
<table>
<thead>
<tr>
<th>Run#</th>
<th>tc (sec.)</th>
<th>AVG. PRES. (mm.)</th>
<th>CONC. Ratio Tol./Alk.</th>
<th>km (sec.)</th>
<th>T °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 42</td>
<td>2.01</td>
<td>15.8</td>
<td>57/1</td>
<td>0.52</td>
<td>675.7</td>
</tr>
<tr>
<td>Zn 43</td>
<td>1.47</td>
<td>8.0</td>
<td>30/1</td>
<td>0.67</td>
<td>675.2</td>
</tr>
<tr>
<td>Zn 44</td>
<td>3.32</td>
<td>16.3</td>
<td>42.5/1</td>
<td>0.48</td>
<td>673.2</td>
</tr>
<tr>
<td>Zn (29)</td>
<td>1.35</td>
<td>13.8</td>
<td>60/1</td>
<td>0.15</td>
<td>674.7</td>
</tr>
<tr>
<td>Zn (91)</td>
<td>1.39</td>
<td>19.0</td>
<td>75/1</td>
<td>0.15</td>
<td>674.2</td>
</tr>
<tr>
<td>Zn 45</td>
<td>1.30</td>
<td>13.4</td>
<td>43/1</td>
<td>0.75</td>
<td>691.2</td>
</tr>
<tr>
<td>Zn (90)</td>
<td>1.41</td>
<td>23.4</td>
<td>54/1</td>
<td>0.17</td>
<td>694.2</td>
</tr>
<tr>
<td>Zn 46</td>
<td>1.39</td>
<td>8.1</td>
<td>18/1</td>
<td>0.74</td>
<td>704.2</td>
</tr>
<tr>
<td>Zn (79)</td>
<td>1.26</td>
<td>14.9</td>
<td>57/1</td>
<td>0.17</td>
<td>702.7</td>
</tr>
<tr>
<td>Zn (35)</td>
<td>1.10</td>
<td>14.3</td>
<td>62/1</td>
<td>0.20</td>
<td>705.2</td>
</tr>
<tr>
<td>Zn 47</td>
<td>0.87</td>
<td>12.7</td>
<td>54/1</td>
<td>1.13</td>
<td>717.2</td>
</tr>
<tr>
<td>Zn (24)</td>
<td>1.27</td>
<td>13.7</td>
<td>66/1</td>
<td>0.21</td>
<td>715.0</td>
</tr>
<tr>
<td>Zn 48</td>
<td>0.96</td>
<td>9.3</td>
<td>40.5/1</td>
<td>1.24</td>
<td>731.2</td>
</tr>
<tr>
<td>Zn 49</td>
<td>1.16</td>
<td>13.8</td>
<td>60/1</td>
<td>2.57</td>
<td>743.7</td>
</tr>
<tr>
<td>Zn 50</td>
<td>0.98</td>
<td>15.8</td>
<td>86/1</td>
<td>5.78</td>
<td>731.2</td>
</tr>
<tr>
<td>Zn 51</td>
<td>0.77</td>
<td>12.9</td>
<td>81/1</td>
<td>4.50</td>
<td>707.7</td>
</tr>
</tbody>
</table>

* A sequence of runs illustrating increasing catalytic effects as compared to runs in which catalytic effects were much reduced or absent ( ).
### TABLE V(a)  
CONCENTRATION RATIO-CONTACT TIME EFFECTS

<table>
<thead>
<tr>
<th>Run#</th>
<th>TEMP. (°K)</th>
<th>$t_c$ (sec.)</th>
<th>PRESSURE (mm.)</th>
<th>TOLUENE/ALKYL (molar ratio)</th>
<th>$K$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 103</td>
<td>756.2</td>
<td>1.37</td>
<td>15.1</td>
<td>84/1</td>
<td>1.00</td>
</tr>
<tr>
<td>Zn 63</td>
<td>751.2</td>
<td>2.78</td>
<td>13.1</td>
<td>11/1</td>
<td>1.29</td>
</tr>
<tr>
<td>Zn 39</td>
<td>746.7</td>
<td>0.97</td>
<td>12.9</td>
<td>54/1</td>
<td>1.10</td>
</tr>
<tr>
<td>Zn 22</td>
<td>747.2</td>
<td>1.18</td>
<td>13.4</td>
<td>59/1</td>
<td>0.95</td>
</tr>
<tr>
<td>Zn 64</td>
<td>750.7</td>
<td>0.90</td>
<td>13.5</td>
<td>58/1</td>
<td>0.66</td>
</tr>
<tr>
<td>Zn 102</td>
<td>746.2</td>
<td>1.20</td>
<td>15.4</td>
<td>73/1</td>
<td>0.62</td>
</tr>
<tr>
<td>Zn 49</td>
<td>743.7</td>
<td>1.16</td>
<td>13.8</td>
<td>60/1</td>
<td>2.57</td>
</tr>
<tr>
<td>Zn 17</td>
<td>739.2</td>
<td>1.08</td>
<td>13.0</td>
<td>89/1</td>
<td>0.74</td>
</tr>
</tbody>
</table>

### TABLE V(b)  
PRESSURE EFFECTS

<table>
<thead>
<tr>
<th>Run#</th>
<th>TEMP. (°K)</th>
<th>$t_c$ (sec.)</th>
<th>PRESSURE (mm.)</th>
<th>TOLUENE/ALKYL (molar ratio)</th>
<th>$K$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 92</td>
<td>760.7</td>
<td>1.24</td>
<td>22.4</td>
<td>86/1</td>
<td>1.57</td>
</tr>
<tr>
<td>Zn 93*</td>
<td>762.2*</td>
<td>1.31*</td>
<td>23.3</td>
<td>69/1*</td>
<td>1.64</td>
</tr>
<tr>
<td>Zn 41</td>
<td>755.2</td>
<td>0.92</td>
<td>10.1</td>
<td>49/1</td>
<td>1.58</td>
</tr>
</tbody>
</table>

*Zn 93 is a benzene carrier run.*
run to run appears to have little effect on the reaction rate. Although several high pressure runs were completed, low pressure runs in this temperature range were almost all oxide catalysed with the exception of run Zn 4).

RATÉ CONSTANT CONSIDERATION

The Arrhenius plot (fig. 7) for the thermal decomposition of diethylzinc under the experimental conditions can be represented by the equation

$$\log k \ (\text{sec}^{-1}) = 14.2 - \frac{48500 \pm 2000}{23RT}$$

Although this equation undoubtedly results in considerable errors in the A factor and Ea values as a result of the uncertainty in choosing the correct slope, the values themselves do not seem unreasonable upon comparison with the values obtained for dimethylzinc (log k = 13.3- 

\(-54,000 \pm 2,000/2.3RT\)), or to the related compound diethylmercury (log k = 15.4 - (45,700/2.3RT)). Unfortunately, although other studies have been done on the decomposition of diethylzinc, including a thermal decomposition study in a static system, no rate constants are available for comparison.

BOND DISSOCIATION ENERGIES

Assuming \( \Delta H_f^{\circ} 298^\circ_A (C_2H_5) \cdot g = 25.3 \text{ kcal./mole} \), \( \Delta H_f^{\circ} 298^\circ_A (Zn, g) = 31.19 \text{ kcal./mole} \), and \( \Delta H_f^{\circ} 298^\circ_A (Zn(C_2H_5)_2, g) = 12.1 \text{ kcal./mole} \), one can then calculate the sum of the bond dissociation energies:

\[
D_1(C_2H_5-Zn-C_2H_5) + D_2(Zn-C_2H_5) = 31.2 + (2 \times 25.3) - 12.1
\]

\[
= 69.7 \text{ kcal./mole}
\]

If the activation energy Ea is then equated to the \( C_2H_5Zn-C_2H_5 \) bond strength, then the following result ensues:
\[ D_2 = (D_1 + D_2) - D_1 \]
\[ = (D_1 + D_2) - E_a \]
\[ = 69.7 - 48.5 \]
\[ = 21.2 \text{ kcal./mole.} \]

It must however be kept in mind that \( D_1 + D_2 \) for the reaction

\[
\text{Zn(C}_2\text{H}_5)_2\text{g} \rightarrow \text{Zn,g} + 2\text{C}_2\text{H}_5\text{.g} \]

is only approximately equal to \( \Delta H^\circ_{\text{A}} \) for the process, although the difference between the two is not expected to exceed 2 kcal./mole.

SUGGESTIONS FOR IMPROVEMENTS

It is apparent from the scatter of points obtained in the Arrhenius plot (fig. 7) that in the majority of cases the reaction occurring was a surface catalysed reaction and that the uncatalysed process had not been totally isolated. If more accurate and meaningful results are to be obtained from any future study, it is imperative that all possible sources of oxide contamination must be eliminated. It is therefore suggested that the number of taps in the system be drastically reduced as this is the most logical locality for leakage. Another possible improvement would be the consideration of the use of a stronger reducing agent in removing water from the toluene, perhaps lithium aluminum hydride would be better. Lastly, it is suggested that more careful cleaning of the reaction vessel be undertaken, as any traces of zinc nitrate adhering to the vessel would undoubtedly yield zinc oxide when the furnace was heated. It is expected that a hydrofluoric acid wash following the fuming nitric acid would suffice to remove any adhering zinc nitrate from the quartz.
It was rather disconcerting to discover a methyl containing impurity in the original compound, especially after the bulk of the work had been completed. A large part of this impurity was removed by vigorous degassing (see Fig. 8). However, in order to check the validity of the proposed methyl radical displacement reaction, the diethylzinc should be purified by fractionation under vacuo. It is hoped that implementation of these few suggestions will resolve this question and greatly improve the quality of the results from any future study.
Figure 8: Vapour Pressure of Diethylzinc after Vigorous Degassing.

○ Literature Values $^{27}$

○ Found in the present study
BIBLIOGRAPHY


VITA AUCTORIS

Born:

May 20, 1948; Toronto, Ontario, Canada. Son of Mr. August and Mrs. Aune Koski.

Primary School:

Sir James Dunn Public School, Wawa, Ontario, Canada.

Secondary School:

Michipicoten High School, Wawa, Ontario, Canada.

University:


Awards:

1966 Great Lakes Power Company Award.

Professional Society:

Chemical Institute of Canada.