[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Effect of Ethyl Radicals on the Thermal Decomposition of Azomethane. The Kinetics of the Thermal Decomposition of Tetraethyllead. Ethyl Radicals and Hydrogen

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Certain theories of homogeneous, unimolecular reactions[2] have been quite successful in interpreting the rates of decomposition of a number of compounds.[3] Although the excellent agreement of these theories with experiment, as well as certain experimental observations *per se*, practically excludes the existence of long reaction chains in those reactions which are termed homogeneous and unimolecular, yet there is no definite proof that very short chains do not occur in such reactions. For example, if such short chains did exist and if the chain propagating reactions were very fast compared to the unimolecular reaction and were initiated by it, the unimolecular reaction would be the rate determining step and the over-all reaction would have unimolecular characteristics. It was the purpose of this investigation to obtain experimental evidence for the existence or non-existence of short chains in one well-established homogeneous, unimolecular reaction.

It is not possible to test the existence of short chains by the introduction of surface, since there is no absolute assurance that such short chains would be terminated at that surface. It was thought that information of the kind desired might be obtained by introducing into the gas under investigation the molecular species most probably capable of initiating chains and then observing any acceleration in the rate of decomposition of that gas.

Azomethane, whose thermal decomposition has been quite thoroughly studied,[4] was chosen for this investigation for two reasons. First, the products of its decomposition are quite simple and very stable; and, second, there is good evidence that the decomposition of azomethane results in the liberation of methyl radicals,[5] which might initiate chains by reacting with the undecomposed azomethane.

It was hoped to introduce methyl radicals into a system containing azomethane and then to observe quantitatively any effect due to the radicals reacting with the azo compound. It was considered advisable to carry out the investigation at a temperature at which the azomethane itself slowly decomposes, and was, therefore, necessary to find a substance which would act as a supply of radicals at about 275°. No such material was found which would conveniently produce methyl radicals. Tetra-

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[1] National Research Fellow in Chemistry.

[2] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); Kassel, *J. Phys. Chem.*, **32**, 225 (1928); *ibid.*, **32**, 1065 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 114, 118 (1928).

[3] See, for example, Kassel, "The Kinetics of Homogeneous Gas Reactions," the Chemical Catalog Company, New York, 1932.

[4] Ramsperger, THIS JOURNAL, **49**, 912, 1495 (1927).

[5] Leermakers, *ibid.*, **55**, 3499 (1933).

ethyllead, however, answers all the requirements except that it gives ethyl rather than methyl radicals. The reactions of methyl and ethyl radicals are practically identical, and the activation energies of reaction between, say, azomethane and the two different radicals, respectively, would probably be almost the same. Hence the results obtained with ethyl radicals can very likely be considered, at least qualitatively, to be the results which would be obtained with methyl radicals. The evidence for the production of ethyl radicals from tetraethyllead is sufficiently well known to make it unnecessary to review the work here.[6]

The method of investigation consisted first in measuring the rate of decomposition of tetraethyllead and later measuring the same rate when azomethane was present in the system with the lead compound. The presence of any chains initiated by the ethyl radicals should be manifest by an apparent increase in the rate of decomposition of the tetraethyllead. It was necessary to study the thermal decomposition of tetraethyllead since no quantitative data are known concerning its kinetics. This study will be first described. In addition to the work with azomethane, several experiments were made to see if hydrogen reacts with ethyl radicals. The results of these experiments will be briefly given.

I. The Kinetics of the Thermal Decomposition of Tetraethyllead.

Geddes and Mack,[7] in a study principally concerned with the decomposition of germanium tetraethyl, reported that some preliminary investigations had shown that the thermal decomposition of tetraethyllead was a largely homogeneous reaction. They did not report any rate measurements. Meinert[8] studied the products of the decomposition of tetraethyllead, but did not investigate the kinetics of its decomposition. In the research here reported the kinetics of the decomposition were studied at temperatures of 245.0, 260.0 and 275.0°, and from pressures of 13 to 52 mm.

Apparatus and Materials.—The tetraethyllead was an Eastman product, and was purified by the method recommended by Calingaert.[9] It was further purified by distillation as described below.

The rate of the decomposition was measured by the change of pressure with time at constant volume in the apparatus diagrammatically presented in Fig. 1. C is the reaction vessel of about 210-cc. capacity, which was maintained at the desired constant temperature by the mercury boiler A of the type described by Ramsperger and Waddington.[10] B is a click gage used in measuring the pressures which were read on a mercury manometer. D and E are all-metal, sylphon type, needle valves designed so that they could be heated to 175°; they were vacuum tight. G is the supply of tetraethyllead and F is a small U-trap of about 1.5 cc. capacity. K is the stopcock leading to the usual high vacuum line. In order to keep the volume of the system outside of the thermostat as small as possible all tubing was capillary of 1.5 mm. bore. The valves D and

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(6) For leading references see Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

(7) Geddes and Mack, *ibid.*, **52**, 4372 (1930).

(8) Meinert, *ibid.*, **55**, 979 (1933).

(9) Calingaert, *Chem. Rev.*, **2**, 56 (1925).

(10) Ramsperger and Waddington, THIS JOURNAL, **55**, 214 (1933).

E were enclosed in an asbestos box which was heated electrically to 150° and all of the capillary tubing on the reaction vessel side of E, with the exception of the trap F and the supply G, was heated electrically to 180°. The clicker gage B was also heated to 180°.

Procedure.—In making a run, the cell was brought to the desired temperature by the mercury boiling in A and was thoroughly pumped out through K and E. The trap F was cooled to −78°, the supply G was warmed to about 60° by means of a water-bath, and the valve D was opened. The tetraethyllead distilled into F, where it was condensed. When sufficient liquid had collected, the valve D was closed, the pumping was continued for several minutes, and the valve E was then closed. The cooling bath at F was removed and the trap was quickly warmed with a smoky gas flame until the liquid had vaporized. At this time the stop watch was started and a small electrically heated furnace was placed around F. Pressures in the reaction cell were then read at the desired times, readings being taken at such periods as to give approximately equal pressure increments. During the vaporization of the lead alkyl into the reaction cell a slight amount of decomposition occurred. This was apparently negligible since the ratio of final to initial pressure was fairly constant from experiment to experiment. Initial pressures were obtained by extrapolation where this was necessary; otherwise the initial pressure was assumed to be the pressure of the first reading.

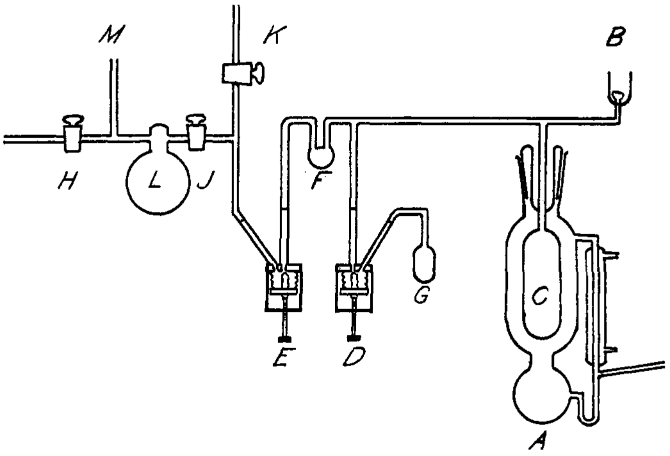

Fig. 1.—Diagram of apparatus used in the experiments.

Experimental Results.—After complete decomposition of tetraethyllead at constant volume the pressure of the products was approximately double the initial pressure of the tetraethyllead. This ratio of final to initial pressure was found to vary somewhat with the temperature of the decomposition. For any given temperature the ratio was fairly constant; the fluctuations were due, probably, to the inaccuracy in the determination of the initial pressure, which resulted from the method of introduction of the lead alkyl into the reaction vessel. At 275.0° the average ratio of final to initial pressure was 2.00, at 260.0° the average ratio was 2.19, and at 245.0° the average ratio was 2.14. From Meinert's data,[8] the ratio of final to initial pressure at 275.0° is calculated to be 1.9. The agreement of the present data with this figure is satisfactory when it is considered that the surface of the reaction vessel used by Meinert was clean glass, while the surface here used was the lead mirror formed by successive decompositions. It is entirely possible that the various reactions involving the radicals would occur to a different extent on the two different surfaces.

Due to the uncertainty in the initial pressures, decomposition was allowed to proceed to completion in all of the experiments. First order rate constants were calculated by the interval method, using the equation

$$k_1 = \frac{2.303}{(t_2 - t_1)} \log \frac{(P_f - P_1)}{(P_f - P_2)}$$

where P_f is the final pressure and P_1 and P_2 are the total pressures at times t_1 and t_2, respectively. Rate constants were calculated until decomposition was from 50 to 75% complete. Beyond about 75% decomposition there was a distinct drop in the constants calculated during a run. In several cases there was a slight trend in the constants from the start; this was not common to all of the runs. The percentage deviation of the individual constants from the average constant for a run varied from 2 to 10%, depending on the run; the grand average of such deviations for all the runs was 7.2%. Table I gives the data of a typical experiment.

TABLE I

DATA FOR TYPICAL EXPERIMENT

Expt. no. 6; P_{initial} = 19.0 mm.; P_{final} = 38.8 mm.; T = 275.0°

P_{total}, mm.	$P_{\text{final}} - P_{\text{total}}$, mm.	t, sec.	$k_1 \times 10^4$, sec.$^{-1}$
21.5	17.3	60	22.0
23.3	15.5	110	24.2
24.9	13.9	155	22.6
27.1	11.7	231	18.1
29.9	8.9	382	21.0
33.1	5.7	594	
38.8	0	∞	

Table II is a summary of all the experiments.

TABLE II

SUMMARY OF ALL EXPERIMENTS

Number	Temp., °C.	P_{initial}, mm.	$P_{\text{final}}/P_{\text{initial}}$	$k_1 \times 10^4$, sec.$^{-1}$
8	275.0	52.7	2.06	22.1
9		41.1	1.99	21.8
10		36.1	2.00	23.1
7		20.8	1.87	21.6
6		19.0	2.04	21.6
4	260.0	44.0	2.17	8.42
2		28.0	2.24	8.45
3		22.7	2.27	8.58
1		13.9	2.15	8.51
11		13.2	2.14	8.41
14	245.0	39.8	2.18	3.27
13		25.2	2.05	2.93
15		21.4	2.18	3.06

TABLE II (*Concluded*)

Surface–volume ratio increased 7.5 times

Number	Temp., °C.	P_{initial}, mm.	$P_{\text{final}}/P_{\text{initial}}$	$k_1 \times 10^4$, sec.$^{-1}$
32	275.0	66.6	[a]	28.5
33		58.1	1.98	28.1
31		39.1	2.08	28.5

[a] Ratio not determined because of long extrapolation to initial pressure.

Discussion of the Results.—It is seen from Table I and Table II that the reaction is unimolecular in character. Over the rather narrow pressure range investigated, the rate constants do not decrease with decreasing pressure; it is very probable that the rates have been measured in the so-called high pressure region. In experiments 31, 32 and 33 the surface–volume ratio of the reaction cell was increased 7.5-fold by packing it with Pyrex tubing. In the first experiment with the packed cell, before the surface of the tubing had become coated with lead, the rate was slightly faster than it was found to be in experiments 31, 32 and 33. On the assumption that the rate of any heterogeneous reaction occurring in the system was proportional to the surface, the reaction in the unpacked cell was between 96 and 97% homogeneous. Geddes and Mack[7] reported that the reaction was 98% homogeneous. Because of the slight heterogeneity it was not thought advisable to measure rates at lower pressures.

A plot of reciprocal temperatures against the logarithms of the rate constants gives a very good straight line. From the slope of this line the energy of activation of the reaction is calculated to be 36,900 calories per mole. The rate constants given in Table II are quite accurately represented by the equation $k_1 = 1.2 \times 10^{12}e^{-36,900/RT}$.

It is interesting to note that within the experimental error the factor A, in the equation $k_1 = Ae^{-Q/RT}$, is the same for the decompositions of tetraethyllead and germanium tetraethyl. Geddes and Mack[7] find that A has the value 3×10^{12} sec.$^{-1}$ for the decomposition of germanium tetraethyl, while the present investigation leads to a value of $A = 1.2 \times 10^{12}$ sec.$^{-1}$ for tetraethyllead.

II. Azomethane and Ethyl Radicals

The experimental procedure in this part of the work consisted of measuring the rate of decomposition of tetraethyllead in the presence of azomethane. By making the necessary corrections for the slow decomposition of the azomethane, rate constants for the tetraethyllead decomposition were calculated from the observed pressure changes. In the computations it was assumed that the ratios of final to initial pressures for the tetraethyllead decomposition had the values found in Part I; the final pressures were not used. By this method of calculation any reaction of ethyl radicals with azomethane would result in rate constants which would be greater than those found in Part I. Several of the experiments were allowed to continue until all of the tetraethyllead had decomposed. By correcting for the azomethane decomposition, the final pressures due to the lead compound were found and the final–initial pressure ratios determined. Any reaction of ethyl radicals with azomethane should increase the ratios beyond those found for tetraethyllead when decomposed alone.

Apparatus and Materials.—Azomethane was prepared by the method of Thiele as described by Ramsperger.[4] The material was freed of inert gases by several times expanding into a bulb, freezing down and pumping out non-condensed gases. The tetraethyllead was the same as used in Part I.

The apparatus is shown diagrammatically in Fig. 1. The only additions to the set-up as described in Part I are the two stopcocks J and H, the 300-cc. flask L and the mercury manometer M. The stopcock H leads to the supply of azomethane which was contained in a trap kept at −78°.

Procedure.—Before a run was started, azomethane was allowed to evaporate into the flask L until the desired pressure, as read on the manometer M, was obtained. The stopcock H was then closed. Tetraethyllead was introduced into the reaction vessel and its pressure determined exactly as described in Part I. After the initial reading of the tetraethyllead pressure had been made, the stopcock K was closed and the stopcock J and the valve E were opened. After about five seconds the valve E and the stopcock J were closed, the time being noted. The pressure in the reaction system for this time was read on the manometer M at a convenient later time. The other pressure readings were taken at the desired time intervals by means of the clicker system as previously described. Measurements for the most part were made until about 80% of the tetraethyllead had decomposed. Several experiments were continued until all of the lead alkyl had decomposed.

Experimental Results.—In order to be certain that azomethane did not decompose catalytically on the lead surface of the reaction vessel, several samples of the gas were decomposed under conditions identical with those which existed during the later experiments except that the tetraethyllead was not present. The results, when compared with those of Ramsperger,[4] indicate that there is no appreciably heterogeneous reaction of azomethane on a lead surface at temperatures around 275°. An experiment was performed immediately following those described above to determine if the products of the azomethane decomposition affected the surface in a way to cause heterogeneous decomposition of tetraethyllead. Tetraethyllead at an initial pressure of 45.7 mm. was decomposed at 275.0° and the rate constant found was 22.8×10^{-4} sec.$^{-1}$. This is the value found in Part I.

The results of the experiments with azomethane and ethyl radicals were calculated as outlined above. From the initial reading of the pressure of tetraethyllead and from the time of that reading, the pressure at zero time was calculated. Similarly, the partial pressure of the tetraethyllead and its products was calculated for the time of the introduction of the azomethane. From the observed total pressure at this time, that of the azomethane was obtained by difference. The partial pressure of the azomethane and its products was calculated for each subsequent reading from the rate constants reported by Ramsperger,[4] and this was subtracted from the total. The resulting pressures were used to calculate first order rate constants for the decomposition of the tetraethyllead. In the latter calculations the ratio of final to initial pressure was assumed to be 2.00 for 275.0° and 2.19 for 260.0°. Table III gives the data of a sample experiment.

TABLE III

DATA FOR SAMPLE EXPERIMENT ON AZOMETHANE AND ETHYL RADICALS

Expt. 19; $T = 275.0°$; $P_{\text{initial, Tet.}} = 30.7$ mm. (calcd.); $P_{\text{final, Tet.}} = 61.7$ mm. (obs.); $P_{\text{final, Tet.}} = 61.4$ mm. (calcd.); $P_{\text{final}}/P_{\text{initial}} = 2.01$; $P_{\text{initial, Azo.}} = 45.9$ mm. (obs.); $P_{\text{initial, Azo.}}/P_{\text{initial, Tet.}} = 1.50$.

p_{Total}	p_{Azo}	$p_{\text{T, P}}$	$p_{\text{Tet.}}$	t, sec.	$k_1 \times 10^4$, sec.$^{-1}$
35.1	0	35.1		73	
84.0	45.9	38.1 (cal.)		130	
87.3	45.9	41.4	20.0	182	
91.6	45.9	45.7	15.7	297	20.9
94.9	46.1	48.8	12.6	403	20.6
97.9	46.3	51.6	9.8	530	19.9
104.4	47.4	57.0	4.4	909	21.1
111.5	49.8	61.7	0	2455	

The pressures in columns 1, 2, 3 and 4 are in mm. The first column gives the observed total and the second column lists the calculated partial pressures of azomethane. Column three gives the partial pressures of the tetraethyllead and its decomposition products; column four, those of the tetraethyllead. Table IV is a summary of all the experiments.

TABLE IV

SUMMARY OF ALL EXPERIMENTS ON AZOMETHANE AND ETHYL RADICALS

No.	Temp., °C.	$P_{\text{Tet.}}$, mm.	$P_{\text{Azo.}}$, mm.	$P_{\text{Azo.}}/P_{\text{Tet.}}$	$(P_{\text{init.}}/P_{\text{fin.}})_{\text{Tet.}}$	$k_1 \times 10^4$
19	275.0	30.7	45.9	1.50	2.01	20.6
20		36.8	66.9	1.82	2.02	20.2
21		28.6	97.5	3.41		24.4
6–10		19–53	0	0	2.00	22.0
22	260.0	29.1	69.7	3.08		6.00
23		36.8	90.8	2.46		6.52
1–4		13–44	0	0	2.19	8.47

The column headings are self-explanatory. Experiments listed as numbers 6–10 and 1–4 are taken from Part I of this paper. Each of the other experiments was carried out with a higher pressure of azomethane than of tetraethyllead in order to provide favorable conditions for reaction of the ethyl radicals with azomethane.

Discussion of Results.—It is seen from Table IV that the first order rate constants calculated for the decomposition of tetraethyllead in the presence of azomethane are the same, at 275.0°, as those found in Part I. At 260.0° the constants of Part I are about 25% greater than those found here. At neither temperature are the calculated rates greater when azomethane is present. This fact is considered to be strong evidence that in the system here investigated there is no reaction between azomethane and ethyl radicals. The agreement of the final–initial pressure ratios found in experiments 19 and 20 with those found in experiments 6–10 is equally convincing evidence of this lack of reaction. The reason for the 25% drop in rate constant found in experiments 22 and 23 is not obvious. The more interesting observation for the present problem is that the rate is not increased over that found in numbers 1–4.

III. Hydrogen and Ethyl Radicals

Von Hartel and Polanyi[11] have found that methyl radicals react with hydrogen at temperatures above 300°. They calculate for the reaction $CH_3 + H_2 = CH_4 + H$ an activation energy of 8 kilocalories. Simons, McNamee and Hurd[12] argue from certain qualitative observations that there must be some reaction of hydrogen with methyl radicals, even at room temperature. Their arguments may be extended to apply to ethyl radicals, since Paneth and co-workers have shown methyl and ethyl radicals to behave very much alike. Geddes and Mack[7] made experiments at 442° on the decomposition of germanium tetraethyl in the presence of hydrogen; they concluded that there was some reaction of the hydrogen with the germanium alkyl or with its decomposition products. Since they found approximately the same rate of decomposition of the germanium tetraethyl in the presence of hydrogen as in its absence, it must be concluded that the reaction probably occurs with the products of the decomposition. This points to a reaction of hydrogen with ethyl radicals at 442°. In order to determine if hydrogen reacts with ethyl radicals at temperatures around 275°, several experiments were performed with hydrogen in the same manner as those carried out with azomethane.

Materials, Apparatus and Procedure.—The hydrogen used was commercial tank hydrogen. The tetraethyllead was the same as in Parts I and II. The apparatus was the same as in Part II except that stopcock H in Fig. 1 led to a 2-liter flask filled with hydrogen. The procedure was identical with that in Part II, hydrogen being substituted for azomethane.

Experimental Results.—The calculations were made in the same manner as described in Part II except that it was not necessary to compute the pressures of hydrogen for each of the readings. The hydrogen pressure was assumed to remain constant and to have the value determined at the start of the run. All of the experiments were allowed to continue until the tetraethyllead was completely decomposed, and final–initial pressure ratios for the decomposition were calculated. Table V is a summary of all the runs.

The column headings have the significance they have in Table IV.

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(11) Von Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

(12) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 946 (1932).

TABLE V

SUMMARY OF ALL EXPERIMENTS ON HYDROGEN AND ETHYL RADICALS

No.	Temp., °C.	$P_{\text{Tet.}}$, mm.	P_{H_2}, mm.	$P_{H_2}/P_{\text{Tet.}}$	$(P_{\text{init.}}/P_{\text{fin.}})_{\text{Tet.}}$	$k_1 \times 10^4$
26	275.0	25.1	108.4	4.32	1.98	27.5
27		26.1	132.9	5.09	2.03	26.1
28		39.3	84.0	2.14	1.94	24.7
6–10		19–53	0	0	2.00	22.0
29	260.0	31.7	114.5	3.61	2.10	9.8
30		39.4	80.3	2.04	2.07	9.6
1–4		13–44	0	0	2.19	8.5

Discussion of the Results.—The most significant results of the experiments listed in Table V are the final–initial pressure ratios. At 275.0° these are the same, within the limits of error, for the experiments made with and without hydrogen. The ratios for the experiments at 260.0° in which hydrogen was present are slightly lower than those in experiments 1–4; the difference is not sufficiently great to be certain that it is real. The 15% increase in rate above that found in Part I, as shown in column 7, is more or less incompatible with the agreement shown in column 6. The discrepancy is very probably due to the presence of small amounts of oxygen in the hydrogen. Geddes and Mack[7] found that traces of oxygen markedly accelerated the rate of decomposition of germanium tetraethyl; it is likely that oxygen has the same effect on the decomposition of tetraethyllead. It should be pointed out that any reaction of ethyl radicals with hydrogen would cause a lowering of the rate constants as calculated here; this is due to the fact that the pressure increase would be less than that expected from the tetraethyllead decomposition alone.

Because of the sensitivity of the rate of decomposition of tetraethyllead to oxygen, less emphasis should be placed upon the constants of column 7 than upon the final–initial pressure ratios; this is particularly true because the presence of slight traces of oxygen would affect the latter very little. If all of the ethyl radicals reacted with hydrogen according to the equation $4C_2H_5 + 2H_2 = 4C_2H_6$ the ratio of final to initial pressure would be 4 to 3, or 1.33. Any reaction of hydrogen with ethyl radicals would thus lower the final–initial pressure ratio, the limiting value being 1.33. The results indicate that there is very little, if any, reaction of ethyl radicals with hydrogen in the system here investigated.

Conclusions

The experiments reported in Part II lead to the conclusion that in the system here investigated and at temperatures around 275° there is no reaction of ethyl radicals with azomethane. It would seem possible that the absence of this reaction could be due to a preferential reaction of the radicals with the undecomposed tetraethyllead. Meinert[8] obtained good evidence that in a system very similar to that used here the reaction of ethyl radicals with tetraethyllead was a wall reaction. If this is so, before diffusion of the radicals to the walls there must occur quite a large number of collisions between the radicals and the azomethane present in the reaction vessel. This indicates that the absence of a homogeneous reaction between ethyl radicals and azomethane is not due to a preferential reaction of the radicals with the lead alkyl; it must be concluded that the inertia is due to the comparatively high activation energy associated with the reaction.

It is quite probable that there would be no reaction of methyl radicals with azomethane under conditions identical with those employed for the investigation with ethyl radicals. If this is true, since the experiments on the decomposition of azomethane have been performed in reaction systems quite similar to that used here, we may conclude that there are no short reaction chains involving methyl radicals which accompany the unimolecular decomposition of azomethane as measured by Ramsperger.[4]

The results of Part III indicate that there is very little, if any, reaction of hydrogen with ethyl radicals at temperatures in the neighborhood of 275°.

Paneth and Lautsch[13] have measured the half-lives of ethyl radicals under various conditions. From their results we may conclude that an ethyl radical would retain its identity in the reaction system employed here for at least 10^{-3} sec. In 10^{-3} sec. an ethyl radical would collide about 10^7 times at 275° with hydrogen (or azomethane) which was at a partial pressure of 100 mm. From our experimental results the fraction of effective collisions must be smaller than 10^{-7}. Therefore, the activation energy of a bimolecular reaction between ethyl radicals and hydrogen or azomethane is calculated to be greater than 15 kilocalories.

I wish to thank Professor G. B. Kistiakowsky for the advice and help which have aided in this research.

Summary

1. The kinetics of the thermal decomposition of tetraethyllead have been studied at temperatures of 245.0, 260 and 275.0° and from initial pressures of 13 to 52 mm. The decomposition was found to be unimolecular and between 96 and 97% homogeneous. The rate constants measured in the system here used are quite well given by the equation $k_1 = 1.2 \times 10^{12} e^{-36,900/RT}$ sec.$^{-1}$.

2. Ethyl radicals were found not to react with azomethane at temperatures around 275°. It is concluded that there are no chains accompanying the unimolecular decomposition of azomethane.

3. Ethyl radicals were found to react very little, if any, with hydrogen at 275°.

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(13) Paneth and Lautsch. *Ber.*, **64**, 2708 (1931).

4. The activation energies of bimolecular reactions of ethyl radicals with hydrogen or azomethane are calculated to be greater than 15 kilocalories.

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The Dissociation of Water in Lithium Bromide Solutions at 25°

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The dissociation of water has been determined by means of electromotive force measurements in several salt solutions. A complete list of references on the subject and a discussion of the method is available.[1]

To afford a comparison with lithium chloride a similar determination in lithium bromide solutions has been undertaken.

The electromotive forces of the cells $H_2 \mid LiOH(m_1), LiBr(m_2) \mid AgBr \mid Ag$ are connected with the desired function through the equation

$$\log K_\gamma = \log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log m_2/m_1}{0.05915} + \log K_w + \log \gamma_H \gamma_{Br} \quad (1)$$

where K_w is the equilibrium constant for the dissociation of water.

By measuring the above cell with a constant value of m_1 and several values of m_2, and by determining $\gamma_H \gamma_{Br}$ ($m = 0$) in lithium bromide solutions of the same total ionic strength, we can evaluate K_γ if we know E_0 and K_w in pure water. E_0 has recently been determined to be 0.07172 v.,[2] and K_w has been found by electromotive force measurements to be 1.008×10^{-14}.[3] The associated functions $m_w = m_H = m_{OH}$, $\gamma_H \gamma_{OH}$, and $\gamma = \sqrt{\gamma_H \gamma_{OH}}$ can then be calculated if a_{H_2O} is obtainable.

Measurement of the Cells: $H_2 \mid LiOH(m_1), LiBr(m_2) \mid AgBr \mid Ag$.—The determinations were carried out in the usual type of cell. The silver bromide electrodes were protected from light and carbon dioxide was carefully excluded from the cells and solutions. Table I gives the results; column six the mean electromotive force.

In equation (3), rearranged to give

$$E - E_0 + 0.05915 \log m_2/m_1 = -0.05915 \log K_w a_{H_2O} - 0.05915 \log (\gamma_H \gamma_{Br}/\gamma_H \gamma_{OH}) \quad (1a)$$

it is seen that by plotting the left side against μ the function will extrapolate to 0.05915 log K_w at infinite dilution. Use was made of this equation to obtain values of E at round concentrations. Column seven of Table I gives the value of the left side of equation (1a) as determined and column two of Table III gives the value at round concentrations.

(1) Vance, THIS JOURNAL, **55**, 2729 (1933); Harned and Mason, *ibid.*, **54**, 3112 (1932).

(2) Harned and Hamer, *ibid.*, **55**, 4496 (1933).

(3) (a) Harned and Copson, *ibid.*, **55**, 2206 (1933); (b) Harned and Hamer, *ibid.*, **55**, 2194 (1933).