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The thermal decomposition of gaseous aluminum trimethyl, in the absence of hydrogen, is nearly 94 percent homogeneous and of kinetic order three-halves over the pressure range 10 to 85 mm measured at room temperature. The reaction products consist largely of methane and to a lesser extent ethane, ethylene, and hydrogen and a solid deposit on the walls of the reaction vessel. A reaction mechanism involving methyl radicals is proposed. The apparent energy of activation, calculated on this basis, is found to be 45 kcal., in agreement with the experimentally determined figure. The high ratio of methane produced to alkyl decomposed suggests that aluminum trimethyl in the vapor state at room temperatures must consist at least of tetrameric molecular complexes. In the presence of hydrogen, both the decomposition rate and the energy of activation are reduced as compared to the decomposition of the pure alkyl, a puzzling effect for which no satisfactory explanation can at present be offered. Photochemically, the presence of hydrogen seems to have little effect on the over-all decomposition but enhances the relative amount of methane slightly. In this, aluminum trimethyl appears to differ from mercury dimethyl which is known to decompose faster thermally and photochemically in the presence of hydrogen than in its absence.

SINCE the recent[1] publication of more precise data on the physical properties of aluminum trimethyl, such as vapor pressure, molecular weight, and molecular association, attention of research workers has been drawn to the study of the compound, particularly with regard to the structure of its fairly stable dimeric molecules.[2] No kinetic study, however, of gaseous aluminum trimethyl, has, up to date, been published. It was thought to be of interest to investigate the kinetics of its decomposition and compare the behavior of this trivalent metal alkyl with that of divalent mercury dimethyl[3] and tetravalent alkyls like silicon tetramethyl[4] and tin tetramethyl,[5] and obtain at the same time some information which would throw light on the molecular structure of polymeric aluminum trimethyl, which is still in question. Investigation has, therefore, been made of the thermal and photochemical decomposition of the compound in the gas phase in absence and in presence of hydrogen. The kinetic behavior of aluminum alkyl appears to be, in many respects, dissimilar to that of the corresponding divalent and tetravalent alkyls.

* Abstract from the thesis presented by C. C. Schubert in partial fulfillment of the requirements for the Master's degree.

[1] A. W. Laubengayer and W. F. Gilliam, J. Am. Chem. Soc. **63**, 477 (1941).

[2] N. R. Davidson, J. A. C. Hugill, H. A. Skinner, and L. E. Sutton, Trans. Faraday Soc. **36**, 1212 (1940); L. O. Brockway and N. R. Davidson, J. Am. Chem. Soc. **63**, 3287 (1941); R. S. Wiswall, Jr., and C. P. Smyth, J. Chem. Phys. **9**, 352 (1941); Kohlrausch and Wagner, Zeits. f. physik. Chemie **B52**, 185 (1942).

[3] John P. Cunningham and H. S. Taylor, J. Chem. Phys. **6**, 357 (1938).

[4] Helm and Mack, J. Am. Chem. Soc. **59**, 60 (1937).

[5] Chas. E. Waring and William S. Horton, J. Am. Chem. Soc. **67**, 540 (1945).
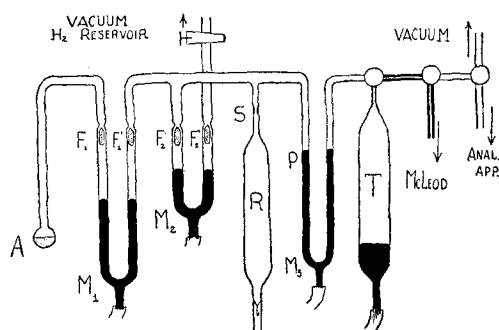
FIG. 1.

EXPERIMENTAL

Materials

Aluminum trimethyl was prepared[6] by heating together aluminum metal foil and mercury dimethyl in a sealed tube on a boiling water bath, the mercury alkyl having been obtained according to the method indicated by Marvel and Gould.[7] Since the aluminum alkyl is highly and spontaneously inflammable in air, decomposing even in traces of oxygen, it was distilled in an oxygen-free nitrogen atmosphere in an all-glass set-up. The aluminum alkyl fraction collected boiled at 126–127°C at atmospheric pressure. It was further purified by distillation in vacuum *in situ* in the gas kinetic apparatus and stored in a bulb coated with carbon black and kept in a bath of acetone and dry-ice mixture.[8]

Hydrogen from commercial cylinders was purified by passage over platinized asbestos, then through a phosphorus pentoxide tube, and finally through a trap cooled in liquid air. A quartz mercy lamp of the Uviarc type, run hot so as completely to reverse the mercury resonance lines, served as the source of illumination in photochemical experiments. An electrical furnace

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[6] Buckton and Odling, Ann. Chim. Phys. **4**, 492 (1865).
[7] Marvel and Gould, J. Am. Chem. Soc. **44**, 153 (1922).
[8] Mention may be made of a new alkyl of aluminum and mercury which was by accident prepared in this connection. When the sealed tube containing aluminum foil and mercury dimethyl was heated in the water bath for several hours beyond the stage at which most of the mercury in the alkyl was displaced by aluminum, most of the resulting liquid, on fractionation, distilled off at 49–51°C at atmospheric pressure, This liquid, from preliminary tests, appears to be, not a molecular mixture, but a true molecular compound of aluminum-mercury alkyl and is more highly and spontaneously inflammable than the pure aluminum trimethyl. Further study of it is in progress.

of block aluminum core provided with a quartz window for illumination was used for maintaining temperature. In the thermal runs, various constant boiling baths of organic compounds were employed.

Apparatus and Procedure

The essential features of the apparatus for the handling of aluminum alkyl vapor are indicated in Fig. 1. The F's are ground-glass float valves by means of which not only could the compound be stored in the bulb A out of contact with mercury of manometer M_1 but also prevented from contamination by the grease of the stopcocks of the vacuum system.

The reaction vessel for the thermal runs consisted of a cylindrical Pyrex tube of 1.9 cm inner diameter and 22 cm in length, with a surface to volume ratio of about 2. When initially sealed at one end to the manometric system, the reaction vessel carried at its free extremity a capillary inner seal, as shown in Fig. 1. The volume of the reaction vessel, and that of any portion of the dead space of the manometric system whose value was required to be known in order to calculate the absolute amount of the alkyl in the reaction chamber, could be evaluated by admitting air or nitrogen into the system and measuring the pressures with the help of the calibrated McLeod gauge.

To fill the reaction tube with the desired amount of the aluminum alkyl, the storage bulb A was maintained at a temperature below room temperature so as to avoid condensation of the vapors during the subsequent pressure measurements, and the vapor admitted into the space confined between F_1, F_2, P, and the reaction vessel R, and its pressure was read on the manommeter M_3. It was then condensed completely into R with the help of an ether-dry-ice mixture, and the reaction vessel was sealed off from the system at S. Knowing the volume of the alkyl vapor whose pressure was read on the manometer and that of the reaction vessel, the pressure of the vapor in the vessel could be calculated. When hydrogen was to be added initially to the alkyl, the reaction tube was filled first with the latter and then with the required amount of hydrogen. Similar procedure was adopted in the case of the quartz reaction tube

which was provided at its two ends with graded seals. After the completion of the decomposition, the reaction tube was re-sealed to the manometric system, at the end carrying the inner capillary seal which could be broken by an iron-in-glass plunger propelled by an electromagnet, in order to study the nature of the reaction products.

It may be noted that before breaking the capillary seal as well as before initially filling the reaction vessel with the alkyl, the whole manometric system was flushed with some aluminum trimethyl vapor and then completely evacuated. This precaution was found necessary in the light of preliminary experiments which revealed decomposition, to varying degree, of the alkyl vapor at first contact with clean glass walls. The reaction tubes before use were cleaned, always in a uniform manner, with warm chromic acid solution, followed by distilled water.

Analysis

The reaction vessel containing the products of the thermal or photochemical decomposition was first surrounded with a liquid-air bath; the mixture of non-condensable methane and hydrogen was transferred by means of the Toepler T into the McLeod gauge and its absolute total amount measured. The liquid-air bath was then replaced by an ether-dry-ice mixture in order to remove the two-carbon hydrocarbons and measure their amount after transference into the McLeod gauge. Since the amounts of the gases were extremely small, particularly in the case of the two-carbon hydrocarbons at low percentage decompositions, their analyses were conducted in the microchemical gas analysis apparatus of Blacet and Leighton.[9] In the hydrogen-methane mixture, hydrogen was determined by oxidation over an alkaline copper oxide bead and the methane calculated by difference. In the hydrocarbon mixture, ethylene was estimated by absorption by fuming sulfuric acid in a porous glass bead and the ethane evaluated by difference. Tests in this mixture for acetylene by means of an alkaline cuprous chloride bead did not give positive results.

[9] F. E. Blacet, P. A. Leighton, and G. D. MacDonald, Ind. Eng. Chem. Anal. Ed. **3**, 266 (1931); **5**, 272 (1933); **6**, 334 (1934).

Experimental Results

The analytical data on the thermal and photochemical decomposition of aluminum trimethyl both in absence and in presence of hydrogen are presented in Table I. The pressures of gases are given in mm Hg at room temperature. The reaction time in all cases was 60 min., except in a few instances as indicated in the footnotes to the table. The last column gives the amount of methane produced per unit of alkyl decomposed. The zero values represent in some cases traces of the particular component. The bracketed experiments are meant to show the reproducible character of a run, which from other data, not given in the present table, was quite satisfactory. Average values of these experiments will later be utilized for calculating specific reaction constants. Experiments 40 and 39 give the data for the decomposition in packed reaction vessels with increased surface to volume ratios. The unpacked vessels used in all the other experiments had a ratio of about 2.

In every run, besides the gaseous reaction products recorded in the table, there was a solid deposit on the walls of the reaction vessel which was in some cases a thin film with a bluish metallic sheen, soluble in dilute acid and alkali,

TABLE I.

Expt.	T°C	Init. alkyl mm	Init. H₂ mm	Final alkyl mm	CH₄ mm	C₂H₆ mm	C₂H₄ mm	H₂ mm	CH₄/Alkyl
				Thermal					
40ᵃ	298	14.7		12.7	9.16	0.69	0.06	0.34	4.6
39ᵇ	298	14.9		12.6	12.55	0.92	0.10	0.40	5.4
38	298	9.1		8.4	3.60	0.49	0.01	——	5.1
32	298	15.4		13.5	6.72	0.57	0.02	0.19	3.6
34	298	14.8		13.1	6.85	0.51	——	0.21	4.0
66ᶜ	298	15.7		14.4	4.93	0.49	0.02	0.03	3.8
67ᵈ	298	15.2		0.0	61.70	0.55	0.00	0.00	4.1
37	298	29.2		24.6	16.60	——	——	0.20	3.6
45	298	29.8		25.0	17.36	0.39	0.02	0.54	3.6
47	298	48.0		37.8	40.30	0.27	0.00	——	4.0
48	298	50.9		39.8	43.50	0.43	0.00	0.52	3.9
49	298	85.5		63.1	205.20	0.60	0.00	0.00	9.2
70	313	15.1		10.9	17.40	0.52	0.02	0.90	4.3
65ᵉ	334	15.1		9.1	27.20	0.58	0.02	——	4.5
51	334	15.1		4.8	46.20	0.44	0.01	1.10	4.5
57	298	15.2	14.8	13.8	8.13	0.32	0.01	15.2	5.8
62	298	15.1	15.5	13.9	8.90	0.33	0.01	15.0	7.4
71	313	14.7	15.5	12.6	10.70	0.51	0.01	16.4	5.1
58	334	14.7	15.1	9.8	28.00	0.38	0.01	13.9	5.7
59	334	14.8	26.6	9.6	29.40	0.40	0.02	26.4	5.7
				Photochemical					
68ᵉ	29	13.8		13.1	0.52	1.47	0.00	0.03	
61ᶠ	120	13.6		13.1	0.76	0.98	0.00	0.03	
60ᶠ	120	13.7	15.7	13.1	1.26	1.06	0.00	15.00	

ᵃ In a packed vessel with surface to volume ratio 5.3; ᵇ 10.8.
ᶜ Decomposition time—40 minutes.
ᵈ Complete decomposition—several hours.
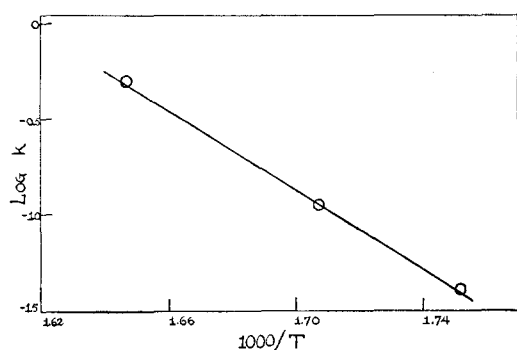ᵉ Decomposition time—180 minutes; ᶠ 90 minutes, current being 4 amp.

FIG. 2.

and in cases of higher temperature and pressure and longer reaction period, a complex of metallic and brownish polymeric material. At the highest pressure investigated, 85.5 mm, a heavy yellowish deposit was formed at the two ends of the reaction vessel; it reacted vigorously with water yielding gases which seemed to contain, as judged by the smell, some ethylene; the main component of these gases might be methane, since aluminum carbide, yellowish in color, is known to decompose with water into methane and aluminum oxide.

It may be remarked that the chief source of error in the data was the measurement of the alkyl pressure manometrically, which could not be accurate to more than 0.5 mm, so that in cases of low percentage decompositions, as in Experiment 38, a large error could creep into the value of alkyl decomposed, obtained as the difference between initial and final pressures recorded in the table. It may be well also to add that the tediously long procedure involved in the completion of a run is partly responsible for the lack of more abundant data at different initial pressures of alkyl at 334°C and in the presence of hydrogen.

DISCUSSION OF RESULTS

Thermal Decomposition in Absence of Hydrogen

Surface Effect

From the amounts of alkyl decomposed, Experiments 39 and 40, in packed vessels with a surface to volume ratio of 5.3 and 10.8, respectively, calculation, according to the method

indicated by Geddes and Mack,[10] leads to about 6 percent heterogeneity for the reactions conducted in unpacked vessels employed in our experiments whose surface to volume ratio was about 2. Consequently the thermal decomposition of aluminum alkyl is mainly a homogeneous reaction.

Order of Reaction

Preliminary calculations for the order of the alkyl decomposition at varying initial pressures, employing the expression

$$\Delta x_1 / \Delta x_2 = (p_1/p_2)^n,$$

where Δx_1 and Δx_2 are the decrease in pressure per unit time and p_1 and p_2 are the average of initial and final pressures in the two cases, gave an average value of about 1.5 for n, the order of the reaction. On the basis of three-halves kinetic order, the specific reaction rate constants for various initial pressures at 298°C were calculated using the rate expression in its integrated form,

$$k = \frac{2}{t}\left[\frac{1}{(a-x)^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}}\right],$$

where a and $(a-x)$ are the initial and final concentration, after time t sec., concentration being expressed in moles per cc, so that k has the dimensions of $cc^{\frac{1}{2}}$ $mole^{-\frac{1}{2}}$ $sec.^{-1}$. The constants are presented in Table II at three temperatures. The slope of the plot of log k versus reciprocal of absolute temperature T, in Fig. 2, yields, for the apparent activation energy E of the process, a value of about 45 kcal. The frequency factor A, in the rate expression,

$$k = A \times e^{-45000/RT}$$

has a value of 8.1×10^{15}, quite comparable as to

TABLE II. Percentage composition of gaseous products at 334°C with an initial alkyl pressure of 15 mm.

Expt.	Time in min.	CH₄	C₂H₆	C₂H₄	H₂
53	5	91.34	8.03	0.63	Traces
54	10	93.36	6.16	0.48	Traces
52	15	95.07	4.80	0.12	Traces
65	40	97.84	2.09	0.07	Traces
51	60	97.00	0.90	0.04	1.9
9	180	98.00	0.50	0.00	1.5

[10] Geddes and Mack, J. Am. Chem. Soc. 52, 4372 (1930).

the order of magnitude with the values of frequency factors for other three-halves order reactions.[11] The slight increase over the normal value of 10^{15} is not unexpected in view of the probably high entropy of activation which can be accounted for by the polymeric nature of the reactant in its initial state, as will be presently indicated. The three-halves order might, at first sight, appear to hold only within the pressure range recorded in Table I, namely 10 to 85.5 mm. Actually, however, since aluminum trimethyl is known to exist completely in the dimeric form even at 70°C,[1] and since the experimental pressures were measured at room temperature at which the alkyl might be in a higher polymeric state, the effective pressure range, in reference to the decomposition temperatures at which the polymer molecules would be completely dissociated into simple monomeric molecules, would be about 20 to 170 mm. Over this whole range, therefore, the kinetic order of the reaction would seem to be three-halves.

Reaction Products

The predominant component of gaseous reaction products is methane, with smaller amounts of hydrogen, ethane, and ethylene, besides a complex solid deposit on the walls of reaction vessel, which might be composed of metallic aluminum, aluminum carbide, and some polymer material. The variation of the percentage composition of gaseous products with time at 334°C is expressed by the data in Table III. Impossibility of obtaining measurable and analyzable amounts of products prevented the performance of runs with shorter periods than 5 min., and at temperatures below 334°C. The general trend of the results obtained is nevertheless quite clear. Methane percentage, and in a smaller degree that of hydrogen, increase with time, whereas the percentages of ethane and ethylene suffer a regular decrease. This may be attributed to progressive pyrolysis with time of ethane to give methane, thus increasing total methane percentage. The gradual decrease of ethylene and its final disappearance in three hours, Experiment 9, might be due, partly, to its hydrogena-

TABLE III.

T°C	298	298	298	298	313	334
Init. alkyl mm	15.1	29.5	49.5	85.5	15.1	15.1
$k_{1.5}$	0.042	0.040	0.044	0.042	0.110	0.476

tion, and partly to pyrolysis and subsequent polymerization.

It is of interest to note the high ratio of methane to alkyl, about 9, in the last column of Table I, at the highest initial pressure of alkyl employed, namely 85.5 mm. The repetition of another high initial pressure run gave also a similar high methane to alkyl ratio. This presupposes at least a tetrameric form of the aluminum alkyl in the vapor at room temperature, as will be evident from the following stoichiometric relation,

$$[Al(CH_3)_3]_4 \rightarrow Al_4C_3 + 9CH_4.$$
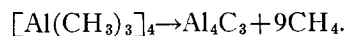
The possibility of such a relatively high polymeric form of aluminum trimethyl is suggested by the nature of the molecular weight *versus* temperature curve of Laubengayer and Gilliam,[1] and also by the ability of this alkyl to form associated complexes with other compounds.[12] Hence aluminum trimethyl seems to exist in the vapor phase at room temperatures in a more complex molecular state than dimeric, probably in a tetrameric form.

Reaction Mechanism

To account for the above facts, the following mechanism is suggested. The thermal decomposition of aluminum trimethyl being of three-halves order, must, by analogy with other similar reactions, involve a chain mechanism, the initial step being the splitting of a methyl radical according to the equation,

$$Al(CH_3)_3 \rightarrow Al(CH_3)_2 + CH_3. \qquad (1)$$
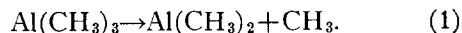
The complex radical Al(CH$_3$)$_2$ might break down further into methyl radicals or alternately could be the source of ethane which appears in relatively high percentages in the early stages of the reaction, before it has time to decompose as in the long period runs in which it is present in smaller percentages. This would also account for

[11] See R. N. Pease, *Equilibrium and Kinetics of Gas Reactions* (Princeton University Press, Princeton, 1942), p. 133.

[12] Norman Davidson and Herbert C. Brown, J. Am. Chem. Soc. **64**, 316 (1942).

the metallic deposit observed on the walls of the reaction vessel.

The formation of methane probably occurs by the reaction,

$$Al(CH_3)_3 + CH_3 \rightarrow CH_4 + Al(CH_3)_2 \cdot CH_2. \quad (2a)$$
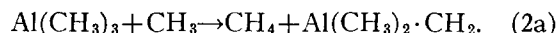
The latter radical, by analogy with other complex radicals, like propyl, etc., may tend to lose a methyl radical and revert to a stable molecule.

$$Al(CH_3)_2 \cdot CH_2 \rightarrow CH_3 + Al(CH_3) \cdot CH_2. \quad (2b)$$
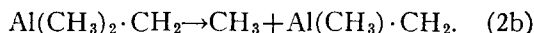
Actually compounds of the type $BrAl:CH_2$ have been prepared from aluminum and CH_2Br_2. It seems probable therefore that $Al(CH_3) \cdot CH_2$ could be stable and could deposit out in this or in a polymerized form on the walls of the reaction vessel, thus accounting for some of the solid deposit which has been remarked earlier.

Steps (2a) and (2b) would together constitute a chain. The chain breaking step must be the recombination of the radicals into ethane,

$$CH_3 + CH_3 \rightarrow C_2H_6, \quad (3)$$
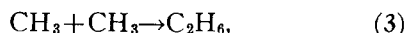
in order to account for three-halves order. Further reactions of the type (2a) and (2b) with the eventual production of aluminum carbide, the presence of which in the deposit was indicated by its vigorous reaction with water, as has already been remarked, would kinetically be similar. The molecule in step (2b) in its simple or polymeric form would probably also react with water to yield some methane and plausibly also unsaturated hydrocarbons. For all these reactions a constant k_2 may be assigned, which would evidently be a complex of the rates of several reactions of the type (2a).

The steady-state concentration of methyl radicals, on this basis, is given by steps (1) and (3), as the steps (2a) and (2b) mutually cancel.

$$[CH_3] = \left(\frac{k_1}{k_3}[A]\right)^{\frac{1}{2}}$$

[A] standing for aluminum alkyl concentration. The over-all rate of disappearance of the alkyl is given by

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A][CH_3].$$

Substitution for concentration of methyl radicals yields

$$-\frac{d[A]}{dt} = k_1[A] + k_2\left(\frac{k_1}{k_3}\right)^{\frac{1}{2}}[A]^{\frac{3}{2}}.$$

The initial rate $k_1[A]$ will be negligible in comparison with the rate of chain reactions, and therefore the observed three-halves order for the over-all decomposition is accounted for.

On this basis, the apparent energy of activation E observed will be

$$E = E_2 + \tfrac{1}{2}(E_1 - E_3).$$

E_2 the energy of activation of reaction (2a) is that of a radical-molecule reaction, which seems to have in general a value of 15 kcal. or less. E_3, the energy of activation of recombination of two methyl radicals is very small and may be neglected. E_1, essentially the strength of the $Al - C$ bond in the alkyl is not known. A probable estimation can be made from a knowledge of related alkyl compounds. For the $Hg - C$ bond in mercury dimethyl, Terenin[13] gives a value of 40–50 kcal. Sodium methyl decomposes rapidly at 100°C, and mercury dimethyl would decompose rapidly around 400°C.[3] This would mean a value of 20 to 25 kcal. for the $Na - C$ bond. The $C - C$ bond energy is about 85 kcal. A value of about 60 kcal. for the bond between C and an element like Al in group III of the Periodic Table seems reasonable. Substitution of this value for E_1 in the expression will give for E of the over-all decomposition

$$E = 15 + \tfrac{1}{2}(60) = 45 \text{ kcal.}$$

a value in agreement with the experimental value of ~45 kcal.

Compared to tin and silicon tetramethyls, aluminum trimethyl appears to be different as regards both kinetic order and apparent energy of activation. Waring and Horton[5] report for thermal decomposition of tin tetramethyl a first-order constant above 80 mm of initial alkyl pressure and below this pressure an order approaching 2, and an energy of activation for the first-order reaction of 82 kcal., which high value is interpreted as evidence of a decomposition mechanism through molecular rearrangement. Silicon tetramethyl[4] too decomposes according to first order, with an energy of activation of 79 kcal. For dimethyl mercury,[3] similar data are not available; but it is known that it decomposes readily only at a higher temperature than

[13] A. Terenin and N. Prilezhaeva, Acta Physicochimica 1, 759 (1934).

does aluminum trimethyl. An adequate explanation of these differences would require further research and examination

Thermal Decomposition in Presence of Hydrogen

The effect of hydrogen, as is seen from the last section of the data in Table I, is to decrease the over-all rate of decomposition of the alkyl and to increase the ratio of methane to alkyl decomposed. An approximate doubling of hydrogen pressure for the same initial alkyl pressure of about 14.7 mm, cf. Experiment 59, produces little change over the value of Experiment 58. With this piece of evidence, in spite of the absence of data on the effect of varying initial pressure of alkyl in presence of a constant pressure of hydrogen, it might tentatively be assumed that the kinetic order of alkyl decomposition is three-halves as in the case of the pure alkyl. The specific reaction rate constants calculated on this basis are presented in Table IV at three temperatures, and the plot of log k versus reciprocal of absolute temperature is given in Fig. 3. The slope of this straight line yields for the apparent energy of activation E a value of 30.5 kcal. Calculation of E on the basis of a first-order reaction, just as a check, gave a value of 29 kcal., not materially different from the previous one. This is rather puzzling in that the presence of hydrogen should reduce both the rate of decomposition and the apparent energy of activation. At present we are not able to offer any satisfactory explanation. The fact that the presence of hydrogen increases the ratio of methane to alkyl decomposed from about 4 to 5, does not throw much light on the above mentioned problem. It might well be that the kinetics in the two cases are quite different and can be elucidated only by further investigation of the problem.

It must be noted that the behavior of aluminum alkyl in presence of hydrogen is markedly
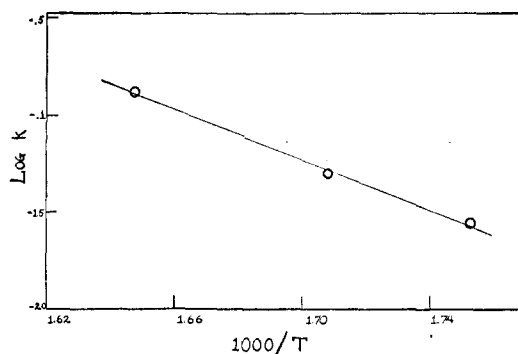

FIG. 3.

different from that of mercury dimethyl[3] which decomposes faster in presence of hydrogen than in its absence, the accelerated rate increasing with increase in hydrogen pressure and consuming hydrogen in the process. In the case of aluminum, the adverse effect of hydrogen becomes constant after a pressure value of 15 mm, further increase of hydrogen making little difference, as can be seen from Experiments 58 and 59, though no hydrogen is used up.

Photochemical Decomposition

The few photochemical experiments whose results are presented in Table I were performed primarily to verify whether the difference which was observed in the thermal decomposition of aluminum and mercury alkyls would hold also in the photodecomposition. The effect of hydrogen in Experiment 60 as compared with its absence in Experiment 61, is not appreciable at all, whereas in the case of dimethyl mercury, hydrogen noticeably accelerated the rate of decomposition of the alkyl. No definite conclusions can now be drawn regarding the nature of the photochemical decomposition of aluminum alkyl in absence of exhaustive data. Still the difference in behavior of aluminum and mercury alkyls is evident. Further photochemical study of aluminum trimethyl will soon be undertaken in this laboratory.

ACKNOWLEDGMENT

TABLE IV.

T°C	298	313	334
Init. alkyl mm	15.1	14.7	14.7
$k_{1.5}$	0.028	0.050	0.140