

concentration range 0.0004580 to 3.698 molal. The potential of the cell (E_0) when the ion activities of cadmium sulfate are hypothetically one molal has been found to be 0.00142 volt at 25° and 0.01652 volt at 0°.

The experimental results furnish excellent confirmation of the extension of the Debye-Hückel theory as given by Gronwall, La Mer and Sandved for the region 0.0006 to 0.01 molal, since their extension yields constant and positive, physically plausible values of " a " (3.6 Å.) where " a " is the distance of closest approach of the ions. The Debye-Hückel approximation gives steadily drifting and physically absurd, negative values of " a ." This extension furnishes an excellent control on the extrapolation to infinite dilution, since constant values for E_0 are obtained up to 0.01 molal.

The activity coefficients and the partial molal free energies of transfer of cadmium sulfate have been computed at 25 and 0° for the concentration range 0.0005 molal to saturation.

If cadmium sulfate is incompletely dissociated in the classical sense, this influence on the activity coefficient is too small to be detected below 0.01 molal.

It has been shown by direct measurement that $(\partial'a'/\partial T)$ is very small, if not actually zero. This may be taken as support for the view that hydration of the ions is not involved in the value " a ."

The mean heat of the cell reaction, Cd (solid, satd. with Hg) + PbSO₄ (solid) = CdSO₄ (M) + Pb (solid, satd. with Hg), for 12.5° and the corresponding excess electrical heats of transfer of cadmium sulfate have been computed using the Gibbs-Helmholtz equation.

NEW YORK, N. Y.

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THE THERMAL DECOMPOSITION OF DIMETHYL-TRIAZENE. A HOMOGENEOUS UNIMOLECULAR REACTION

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During the past four years a considerable amount of experimental data has given support to certain theories of unimolecular reaction velocity which postulate that activation occurs by kinetic theory collisions. The rate of production of activated molecules by collisions is a second order process but if only a very small fraction of those molecules which become activated decompose spontaneously the rate of decomposition is first order. At sufficiently low pressures collisions can no longer maintain the Maxwell-Boltzmann quota of activated molecules; consequently the rate falls off until finally at still lower pressures the rate approaches the rate of activation and is second order.

Now that the rate of decomposition of nitrogen pentoxide has at last also been shown to decrease at very low pressures,^{1,2} every example of a homogeneous unimolecular reaction shows such a decrease or else theory does not require it in the pressure range studied.

We have now studied the decomposition of dimethyl-triazene and find that this reaction also is first order at high pressures but falls off in rate at pressures below about one centimeter. Rate measurements have been made at temperatures from 200 to 230° and at pressures from 0.02 to 8.0 cm. of mercury.

Preparation of Dimethyl-triazene.—Dimethyl-triazene was prepared by the method of Dimroth.³

The copper salt of dimethyl-triazene was first prepared. Methyl azide was formed by dropping dimethyl sulfate upon a stirred and refluxed aqueous solution of sodium azide. The gas was passed through a warm tube containing calcium chloride and into an ice cooled solution of methylmagnesium iodide ($\text{CH}_3\text{—N=N=N} + \text{CH}_3\text{MgI} = \text{CH}_3\text{—N=N—NCH}_3\text{MgI}$). The resulting ether solution was hydrolyzed at zero degrees with an aqueous solution of ammonium chloride and ammonium hydroxide, and the dimethyl-triazene so formed was converted to its copper salt by shaking with ammoniacal cuprous chloride solution. The copper salt was separated from the water layer by repeated extraction with ether; the ether solution was dried with anhydrous sodium sulfate and the ether distilled from the salt. The solid green copper salt was recrystallized from warm anhydrous ether and dried over concentrated sulfuric acid.

The free dimethyl-triazene was prepared from its copper salt by warming it with solid diazoaminobenzene prepared according to Fischer.⁴ The liberation and purification of the dimethyl-triazene was carried out on a vacuum line.

The vacuum system was of Pyrex glass and consisted of a 30-cc. flask connected in series with a 3 × 1-cm. tube filled with c. P., ground, fused calcium chloride; a receiver of 3-cc. capacity; a 12 × 1-cm. tube filled with calcium chloride; and a small combination distilling flask of 3-cc. capacity and water-cooled reflux column. The exit tube of the reflux column led to another 3-cc. receiver which was separated from the high-vacuum line by a stopcock. Equivalent quantities, 2 g. of the copper salt and 3 g. of diazoaminobenzene, were mixed and introduced into the flask and the latter was sealed off at the neck. The system was evacuated and the flask heated slowly to a temperature of 90° by means of a glycerin bath. The dimethyl-triazene vapor was allowed to pass through the first tube of calcium chloride and was condensed in the first receiver by a mixture of solid carbon dioxide and ether at -78°. When the vapor had all been condensed the receiver was sealed off from the flask and its contents were allowed to distil through the second larger calcium chloride tube into the distilling flask, where they were recondensed with the ether-carbon dioxide mixture. The liquid was allowed to distil back to the receiver in the same manner, this process was repeated several times, and with the liquid finally frozen out in the distilling flask the latter was sealed off from the calcium chloride tube. The amount of liquid dimethyl-triazene was about 1.5 cc. Air was then let into the system at a pressure of 75 mm. and the liquid was slowly distilled into the second receiving flask, which was cooled as before to -78°. During the distilla-

¹ Ramsperger and Tolman, *Proc. Nat. Acad. Sci.*, 16, 6 (1930).

² Schumacher and Sprenger, *ibid.*, 16, 129 (1930).

³ Dimroth, *Ber.*, 39, 3905 (1906).

⁴ Fischer, *ibid.*, 17, 641 (1884).

tion a glycerin bath served to control the temperature of the distilling flask, and water was run into the condenser around the reflux column to insure careful fractionation. About three drops of a liquid which did not solidify at -78° came over below 40° . These were pumped out and rejected. With the exception of the last several drops, which were also rejected, the remainder of the liquid boiled between 43.0 and 43.1° under 75 mm. pressure. The distilling flask was finally sealed off from the receiver. The solid in the receiving flask melted fairly sharply at about -12.0° to give a perfectly clear, colorless liquid. In order to free the dimethyl-triazene from any dissolved air, the liquid was distilled into the top of the container by means of a bath of solid carbon dioxide and the flask was evacuated. This process was repeated several times. The sample was used for the rate determinations without further treatment.

Nature of Reaction

When dimethyl-triazene is completely decomposed at constant volume, the final pressure is 2.175 times the initial pressure. This fact, together with a titration for basic constituents and some freezing-out data, make possible a rough estimate of the reaction products.

The gas resulting from the complete decomposition of dimethyl-triazene was collected in a 120-cc. bulb at 9.60 cm. pressure. A tube sealed to the bottom of the bulb was surrounded with baths at various temperatures and the pressure was read on an attached mercury manometer. The following readings (corrected for the lower temperature of the gas in the cold bath) were obtained.

$t, ^{\circ}\text{C.}$	$P, \text{cm.}$	% Uncondensed
20	9.60	100
-20	9.05	94
-79	6.80	71
-111	6.25	65
-183	5.25	55

Titration with 0.01 *N* hydrochloric acid and phenolphthalein showed that 29.6% of the gas was basic, assuming one equivalent of acid per mole of base.

When dimethyl-triazene spontaneously decomposes it may be expected to break up into various radicals which may combine with one another or react with one another so as to give the reaction products. We shall try to represent the reaction products which seemed likely to form from such a process by stoichiometric equations and then test these equations with the above data.

- (a) $0.82 \text{ CH}_3\text{—N=N—NHCH}_3 = 0.82 \text{ N}_2 + 0.41(\text{CH}_2)_2\text{NH} + 0.205 \text{ C}_2\text{H}_6 + 0.205 \text{ CH}_3\text{—NH—NH—CH}_3$
- (b) $0.18 \text{ CH}_3\text{—N=N—NHCH}_3 = 0.18 \text{ CH}_4 + 0.27 \text{ N}_2 + 0.09 \text{ C}_2\text{H}_6$
- (c) $0.18 \text{ CH}_3\text{—N=N—NHCH}_3 = 0.18 \text{ C}_2\text{H}_6 + 0.27 \text{ N}_2 + 0.09 \text{ H}_2$

The number of moles in each equation (0.82 and 0.18) has been so chosen that a combination of equation (a) with (b) or of (a) with (c) will give the correct ratio of final to initial pressure. Equation (a) gives some dimethyl-hydrazine (supposedly by a combination of two CH_2NH radicals) and thus

accounts for the gas which freezes out at -20° . With phenolphthalein it would neutralize an equivalent of acid and together with the $(\text{CH}_3)_2\text{NH}$ accounts for 27% of the gas which is nearly equal to the 29.6% observed. The combination of (a) with (b) gives 58% non-condensable with liquid air ($\text{N}_2 + \text{CH}_4$), while (a) with (c) gives 54% ($\text{N}_2 + \text{H}_2$), both of which are close to the value found (55%). Evidently no choice can be made between (b) and (c). It is not claimed that the agreement found with these stoichiometric equations is a very accurate description of the nature of the reaction.

Apparatus and Procedure

The rate of decomposition was followed by the increase in pressure at constant volume. The 250-cc. Pyrex reaction flask was placed in an oil-bath the temperature of which was automatically controlled to 0.05° . The thermometer used was calibrated against a Bureau of Standards thermometer.

In the high-pressure runs Nos. 39 to 50 the supply bulb was connected to a metal stopcock of the Bodenstein type,⁵ which was connected directly to the cell. One arm of a mercury U-trap was sealed to this connecting tube and the other arm led to the high-vacuum line. The stopcock and mercury trap were surrounded by a cardboard structure containing a glass window. Warm air was circulated through this structure so as to maintain a temperature of about 50° . This was necessary to prevent condensation of dimethyl-triazene in the system outside the thermostat. The volume outside the thermostat was at most 1% of the total volume. In making a run the cell was evacuated to about 1×10^{-5} mm., mercury was let up into the trap, the desired amount of gas let into the reaction vessel through the metal stopcock and the stop watch started. The pressure in the U-trap was read immediately and at intervals during the course of the run.

The low-pressure measurements were made with a clicker system.⁶ The supply was connected to an ordinary vacuum stopcock. This led to one arm of a mercury trap, the other arm of which was connected directly to the cell. A lead to vacuum was sealed in about 3 cm. above the bottom of the U-tube on the reaction vessel side. This lead had a stopcock separating it from the vacuum line. The clicker of about 0.5-cc. capacity and having a click constant of 0.150 cm. pressure was sealed by a small tube to the reaction vessel. A larger tube fitting around the clicker, and sealed to it by a ring seal at its base, was connected to a McLeod gage of 130-cc. capacity and to a number of capillary tubes. By evacuating through these capillary tubes it was possible slowly to change the pressure on the clicker as the critical clicking pressure was approached. Air could be let in through another capillary to reset the clicker. The limit of accuracy of this pressure measurement system was the reproducibility of the clicker,

⁵ Bodenstein and Dux, *Z. physik. Chem.*, **85**, 305 (1913).

⁶ Smith and Taylor, *THIS JOURNAL*, **46**, 1393 (1924).

which appeared to be better than 0.001 cm. The outside volume was less than 1% of the total volume of the reaction vessel. After letting the desired amount of gas into the reaction cell the mercury was raised in the U-trap and the air pressure surrounding the clicker was adjusted to get the click. Due to the fact that a short time was required to obtain the first click it was necessary to extrapolate the pressure readings back to zero time. The extrapolation was usually only about 2 to 3%, even at the higher temperatures. A similar extrapolation was sometimes necessary for the high pressure experiments.

Experimental Data

The partial pressure of dimethyl-triazene (P_T) was calculated for each reading by the expression $P_T = (2.175P_0 - P)/1.175$, where P_0 is the initial pressure at zero time and P is the total pressure at that reading. The factor of 2.175 is required because the final pressure is 2.175 times the initial pressure. First order rate constants were calculated by the interval method, that is, by using the equation

$$k_1 = \log_{10} P_{T_t}/P_{T_{t'}} \times 2.303/(t' - t)$$

where P_{T_t} is the partial pressure of dimethyl-triazene at time t , and $P_{T_{t'}}$ is its partial pressure at the following reading taken at time t' . First order

TABLE I
DATA FOR RUNS

Run number 17; $P_{\text{final}}/P_0 = 2.175$; $T = 210.0^\circ$; $P_0 = 0.2340$ cm.			
p , cm.	P_T	t , sec.	$k_1 \times 10^4$ (sec. ⁻¹)
0.2340	0.2340	0	
.2410	.2280	120	
.2648	.2078	645	1.76
.2935	.1835	1510	1.38
.3128	.1670	2190	1.39
.3298	.1525	2865	1.35
.3623	.1250	4380	1.41
.3815	.1088	5415	1.37
.4010	.0915	6675	1.37
.4348	.0560	9750	1.59
.5090	.0000	∞	
Run number 35; $P_{\text{final}}/P_0 = 2.175$; $T = 200.0^\circ$; $P_0 = 2.987$ cm.			
p , cm.	P_T	t , sec.	$k_1 \times 10^5$ (sec. ⁻¹)
2.987	2.987	0	
3.087	2.902	290	
3.550	2.508	1710	10.25
4.006	2.119	3360	10.21
4.438	1.752	5320	9.71
4.791	1.451	7290	9.56
5.106	1.187	9340	9.80
5.400	0.937	12060	8.68
5.700	0.682	15300	9.78

TABLE I (Concluded)

Run number 31; $P_{\text{final}}/P_0 = 2.175$; $T = 230.0^\circ$; $P_0 = 0.0400$ cm.

p , cm.	P_T	t , sec.	$k_1 \times 10^4$ (sec. ⁻¹)
0.0400	0.0400	0	
.0413	.0389	75	
.0475	.0336	635	2.62
.0528	.0291	1070	3.28
.0571	.0254	1600	2.58
.0619	.0214	2185	2.94
.0663	.0176	2855	2.88
.0711	.0135	3600	3.57
.0750	.0107	4595	2.79

rate constants were calculated for from five to twelve intervals so chosen as to give nearly equal pressure increases and until decomposition was 70 to 80% complete. The complete data of three typical runs are given in Table I.

In Table II is a summary of all of the runs with the exception of the first thirteen and runs 45 to 48, inclusive.

TABLE II
SUMMARY OF ALL RUNS

Number	Temp., °C.	Initial press., cm.	Number of constants	Average deviation	k_1 (sec. ⁻¹)
35	200.0	2.987	7	0.31×10^{-5}	9.71×10^{-5}
36	200.0	1.595	6	.56	9.98
37	200.0	0.2995	8	.21	6.62
34	200.0	.1464	6	.24	5.19
38	200.0	.0794	8	.23	4.27
33	200.0	.0317	5	1.08	4.15
18	210.05	1.520	11	0.14×10^{-4}	2.07×10^{-4}
16	210.0	0.956	9	.12	1.97
19	210.05	0.5825	12	.10	1.70
17	210.0	.2340	8	.11	1.45
21	219.9	1.520	7	.21	4.03
20	219.9	0.2620	10	.17	2.60
14	225.4	.763	7	.21	4.54
15	225.4	.111	5	.26	3.06
26	230.0	2.946	9	.42	8.35
25	230.0	1.505	6	.27	8.62
24	230.0	0.683	7	.26	7.40
29	230.0	.2945	7	.50	6.25
23	230.0	.2500	7	.26	5.23
27	230.0	.1652	6	.57	6.05
28	230.0	.0980	7	.34	4.59
22	230.0	.0560	4	.16	3.44
31	230.0	.0400	7	.24	2.95
32	230.0	.0296	5	.24	2.88
30	230.0	.0192	5	.23	2.93

TABLE II (Concluded)

Number	Temp., °C.	New Compound		Average deviation	k_1 (sec. ⁻¹)
		Initial press., cm.	Number of constants		
44	200.0	4.84	8	0.99×10^{-5}	9.12×10^{-6}
43	200.0	2.10	7	1.01	9.28
42	230.0	8.00	4	0.62×10^{-4}	7.02×10^{-4}
41	230.0	2.25	5	1.01	6.71
40	230.0	2.18	4	1.54	7.03
39	230.0	1.75	4	0.59	7.11
Added Surface 11.5 Times Original					
49	200.0	2.46	5	1.05×10^{-5}	8.93×10^{-6}
50	230.0	2.24	7	0.87×10^{-4}	7.09×10^{-4}

The first thirteen preliminary runs were carried out with an impure sample and a rough method of following the pressure. They differed but little from the later runs. Runs 45 to 48 will be discussed later.

While no trend in the constants during a given run was common to all of the runs, there seems often to have been a slightly higher rate at the start of the run as shown by run 17.

In runs 45 to 50 the surface was increased by adding Pyrex tubing, thus increasing the surface to volume ratio by 11.5 fold. The first run made after introducing the extra surface (Run 45) was 12% higher in rate but this effect disappeared gradually during the next three runs and then the rate constants were identical with runs made without extra surface. Earlier preliminary runs had likewise shown that opening the cell to the air or washing it out gave a slightly higher rate for the next two or three runs, so that apparently some conditioning of the surface or removal of impurities was necessary to eliminate catalysis completely. We conclude that the reaction rates reported were not influenced by the extent of wall surface and that the reaction is therefore homogeneous.

Runs 39 to 50 were made with a different sample of dimethyl-triazene and were made with the arrangement of apparatus described for the high-pressure measurements, while all the others reported were made with the low-pressure arrangement. Although the initial pressure to final pressure ratio was uniformly 2.175 for the first sample, it was not constant for these later runs but varied from 2.06 to 2.19. The experimental accuracy was not quite as good and they are all uniformly lower in rate than the earlier runs at similar pressures. It seems likely that this sample was impure. The metal stopcock became discolored and may have affected the sample. These runs show, however, that the first order rate constant has become independent of pressure above about 1 cm.

Interpretation of the Data

This reaction has the same characteristics as many other unimolecular reactions, namely, a true first order rate only at high pressures and a

falling of the first order rate constant at lower pressures. In Fig. 1 is plotted the log of the rate constant against the reciprocal of the absolute temperature. Only the rate constants at the higher pressures where the first order rate is independent of pressure have been used in this plot. From the slope of the best straight line through the points we find for the heat of activation $Q = 33,800$ cal. per mole. The equation for the high pressure rate constant is given by the expression $k_{\infty} = 4.05 \times 10^{11} e^{-33,800/RT}$

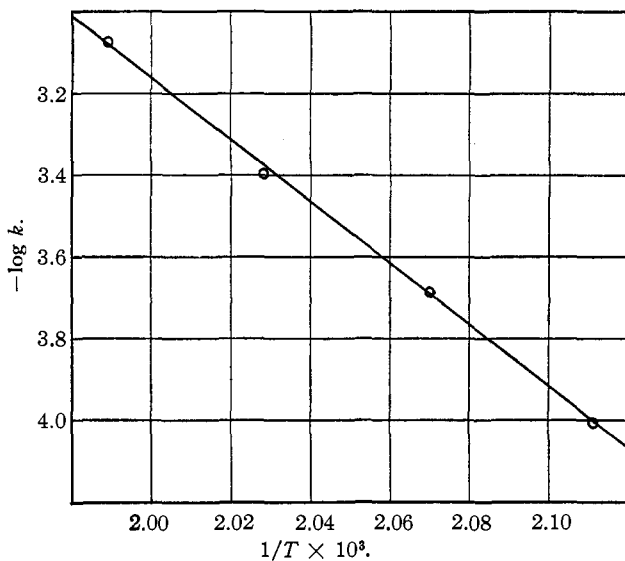


Fig. 1.

Figure 2 shows the usual plot of $\log k/k_{\infty}$ against $\log P$. The curves are theoretical and the points are the experimental values for the runs at 200 and 230° with the first sample. The lower curve is for Theory I and the upper two curves are for Theory II.⁷ The uppermost curve is for 200° and the other one close to it is for 230°. The number of squared terms chosen to fit the data best was 14 and the diameter of the molecule 10.0×10^{-8} cm. for Theory I and 6.0×10^{-8} cm. for Theory II. For Theory I the critical energy ϵ_0 is 39,800 cal. per mole and for Theory II $\epsilon_0 = 33,300$ cal. per mole. It is evident that it is not possible to decide definitely between the two theories on the basis of the data shown.

Discussion

During the past six years the experimental data on unimolecular reactions have been increased from one single reaction, namely, the decomposition of nitrogen pentoxide, to at least thirteen reactions that are

⁷ Rice and Ramsperger, *THIS JOURNAL*, 49, 1617 (1927).

now definitely recognized as being of this type. These reactions are listed in Table III. The pressure and temperature range over which they have been investigated are given and the constants in the rate expression $k_{\infty} = Ae^{-Q/RT}$ are listed. The values given for n designate the number of squared terms required to fit the data with either Theory II⁷ or Theory III.⁸ Ordinary kinetic theory diameters are used throughout.

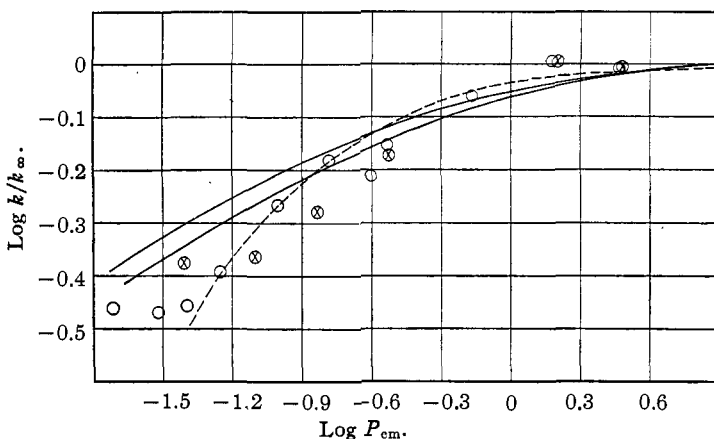


Fig. 2.

All but three of these thirteen reactions show a falling off in rate at low pressures. Of these three, ethylene oxide and pinene have not been investigated at sufficiently low pressures and azoisopropane is sufficiently complex a molecule that it is not required that its rate of decomposition fall off until very low pressures are reached. Thus from a qualitative point of view the experimental data are in complete accord with the present theoretical method of treatment. Furthermore, with the possible exception of the decomposition of nitrogen pentoxide, there is no quantitative disagreement with Theories II or III or their modified quantum treatments. As Kassel⁹ has indicated, it is possible even to account for the rate of decomposition of nitrogen pentoxide if one uses Kassel's quantum treatment¹⁰ and permits the use of a vibrational specific heat of at least 20 cal./mole and a molecular diameter of 17×10^{-8} cm. There are no specific heat data for nitrogen pentoxide but it seems likely that 20 cal./mole of vibrational specific heat will be found too high. In this connection it must be remembered that the requirement of an exact numerical agreement can be carried too far, since any actual molecule is not exactly of the type postulated either by the classical or quantum theory.

⁸ Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

⁹ Kassel, *THIS JOURNAL*, **52**, 3972 (1930).

¹⁰ Kassel, *J. Phys. Chem.*, **32**, 1065 (1928).

TABLE III
 DATA FOR UNIMOLECULAR REACTIONS

Substance reacting	P, cm.	T, °C.	A	Q, cal./mole	n
C ₂ H ₅ CHO ¹¹	2.0 to 40.0	450 to 600	$>1.38 \times 10^{12}$	54000	11
C ₂ H ₅ -O-C ₂ H ₅ ¹²	2.5 to 50.0	426 to 588	$>3.09 \times 10^{11}$	53000	6-8
CH ₃ -O-CH ₃ ¹³	3.0 to 90.0	422 to 552	1.52×10^{13}	58500	11-12
CH ₃ -O-C ₂ H ₅ ¹⁴	2.6 to 54.0	386 to 460	$>9.23 \times 10^{11}$	47000	9
CH ₃ -O-C ₃ H ₇ ¹⁴	2.2 to 33.6	400 to 450	$>2.21 \times 10^{12}$	49000	12
CH ₃ -N=N-CH ₃ ^{15,16}	0.026 to 70.79	278 to 327	1.07×10^{16}	51200	25
CH ₃ -N=N-C ₃ H ₇ ¹⁷	0.0058 to 13.12	250 to 332	2.80×10^{15}	47480	33
C ₃ H ₇ -N=N-C ₃ H ₇ ¹⁸	0.025 to 4.60	250 to 290	5.6×10^{13}	40900	>40
CH ₃ -N=N- NHCH ₃ ¹⁹	0.019 to 8.0	200 to 230	4.05×10^{11}	33800	14
d-Pinene ^{20,21}	17.0 to 116.0	184 to 237	5.40×10^{14}	43700	>20
Ethylene oxide ²²	2.4 to 90.5	378 to 445	9.9×10^{12}	52000	>14
N ₂ O ₅ ^{23,24,25}	0.00056 to 70.0	0 to 65	4.5×10^{13}	24700	30 ⁹
N ₂ O ^{26,27}	8.1 to 800	560 to 667	4.0×10^9	53000	2

The mass of evidence so far presented indicates strongly that activation is by collision and that reaction occurs when the critical energy becomes localized in a particular part of the molecule.

Summary

The thermal decomposition of dimethyl-triazene has been studied at temperatures from 200 to 230° and at pressures of 0.019 to 8.0 cm.

The reaction has been found to be homogeneous and first order at high pressures, but the rate begins to decrease at pressures below about 1 cm. and has dropped to about one-third of the high pressure value at the lowest pressures studied. The high pressure rate constant is given by the expression $k_{\infty} = 4.05 \times 10^{11} e^{-33,800/RT}$.

¹¹ Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, A113, 221 (1926).

¹² Hinshelwood, *ibid.*, A114, 84 (1927).

¹³ Hinshelwood and Askey, *ibid.*, A115, 215 (1927).

¹⁴ Glass and Hinshelwood, *J. Chem. Soc.*, 1805 (1929).

^{15,16} Ramsperger, *THIS JOURNAL*, 49, 912, 1495 (1927).

¹⁷ Ramsperger, *ibid.*, 51, 2134 (1929).

¹⁸ Ramsperger, *ibid.*, 50, 714 (1928).

¹⁹ Ramsperger and Leermakers, *ibid.*, 53, 2061 (1931).

²⁰ D. F. Smith, *ibid.*, 49, 43 (1927).

²¹ Kassel, *ibid.*, 52, 1935 (1930).

²² Heckert and Mack, *ibid.*, 51, 2706 (1929).

²³ Daniels and Johnson, *ibid.*, 43, 53 (1921).

²⁴ Ramsperger and Tolman, *Proc. Nat. Acad. Sci.*, 16, 6 (1930).

²⁵ Schumacher and Sprenger, *ibid.*, 16, 129 (1930).

²⁶ Volmer and Kummerow, *Z. physik. Chem.*, 9B, 141 (1930).

²⁷ Nagasako and Volmer, *ibid.*, 10B, 414 (1930).

The data can be fitted equally well by either Theories I or II of Rice and Ramsperger by using fourteen squared terms.

A table summarizing the present data on unimolecular reactions is given and discussed.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE TEMPERATURE COEFFICIENT OF THE THERMAL DECOMPOSITION OF AMMONIA ON PLATINUM

BY J. K. DIXON¹

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The heat of activation of the thermal decomposition of ammonia on the surface of a number of metals is about 40,000 to 50,000 calories per mole up to 800°. In particular, Kunsman has found this to be true for tungsten, molybdenum, nickel, iron and supported iron catalysts.² The same value was found for a copper catalyst.³ At pressures below 25 mm. Schwab and Schmidt found 44,000 calories per mole for platinum; but above 25 mm. the value observed was 144,000.⁴ No intermediate values for the heat of activation were observed. Since facilities were at hand it seemed well worth while to confirm or correct this abnormally high temperature coefficient.

Experimental

Experiments were carried out by a dynamic method which has been described.³ The only changes made were in the catalyst and the tube which held the catalyst. A platinum wire gauze was made into a small roll, 6 cm. long, and placed in a fused quartz tube of 10-mm. bore. The platinum wire was 0.010 cm. in diameter and its total apparent surface 310 sq. cm. This catalyst approximates that used by Schwab and Schmidt. The quartz tubing was connected to the rest of the apparatus by means of graded quartz-Pyrex seals. The rate of decomposition of ammonia on this catalyst was determined in the way previously described, with and without added hydrogen or nitrogen, at the temperatures 776, 826 and 858°.

Results

A summary of a number of typical experiments is given in Table I. The first column gives the number of the experiment; the second the barometric pressure in centimeters of mercury; the third, fourth and fifth

¹ National Research Council Fellow.

² Kunsman, *THIS JOURNAL*, **50**, 2100 (1928); **51**, 688 (1929); see also Elöd and Banholzer, *Z. Elektrochem.*, **32**, 555 (1926).

³ Dixon, *THIS JOURNAL*, **53**, 1763 (1931).

⁴ Schwab and Schmidt, *Z. physik. Chem.*, **B3**, 337 (1929).