4. These results substantially confirm the observations previously made in this Laboratory [Barry, THIS JOURNAL, **44,** 933 (1922)] which yielded the approximate value for the total heat similarly developed on a gold-plated surface of 0.035 cal. per sq. cm.

5. The phenomenon, which is certainly not an adsorption in the usual sense of the term, awaits full explanation. It appears to involve the occlusion of water vapor by gold, and to be affected, at least, by capillary imbibition.

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The Thermal Decomposition of Methyl Azide. A Homogeneous Unimolecular Reaction

BY JOHN A. LEERMAKERS[1]

The author has recently studied the thermal decomposition of ethyl azide[2] and has found it to be a homogeneous, unimolecular reaction. It seemed advantageous to study the next lower homolog in the series of azides, methyl azide. Ramsperger[3] made some preliminary experiments on the decomposition of methyl azide and reported that it was homogeneous and unimolecular. He did not find it feasible to continue the investigation over a range of temperatures and pressures because of his experimental method. His work was confined to five experiments at 245° at initial pressures from 5.7 to 0.05 cm. The present investigation was conducted over the temperature range 200–240° and from initial pressures of 46.6 to 0.078 cm.

Nature of the Reaction.—When methyl azide decomposes at constant volume and constant temperature the final pressure is 1.66 times the initial pressure. This ratio is independent of temperature and pressure. Ramsperger reported that in his experiments the ratio was 1.55. It was found in the present investigation that the ratio for the first several experiments was 1.54 but that after these experiments it was 1.66, where it remained practically constant. In the last experiments performed the ratio slightly increased to 1.68.

In order to determine the products of the reaction, freezing out experiments were made after complete decomposition of methyl azide at 240°. The procedure was exactly as described in the previous work on ethyl azide.[2] The results are given in Table I. Pressures have been corrected for the volume of the tube immersed in the cold baths.

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[1] National Research Fellow in Chemistry.

[2] Leermakers, THIS JOURNAL, **55**, 2719 (1933).

[3] Ramsperger, *ibid.*, **51**, 2134 (1929).

TABLE I

RESULTS OF FREEZING OUT EXPERIMENTS

Experiment	1	2	3	Average
P_{initial}, cm.	9.77	4.07	2.86	
P_{24°, cm.	13.95	6.23	4.27	
P_{-78°, cm.	12.60	5.57	3.84	
P_{-183°, cm.	9.38	3.90	2.78	
$P_{24^\circ}/P_{\text{initial}}$	1.43	1.53	1.49	1.48
$P_{-78^\circ}/P_{\text{initial}}$	1.29	1.39	1.34	1.34
$P_{-183^\circ}/P_{\text{initial}}$	0.96	0.96	0.97	0.96

The pressures for experiment 1 at 24 and -78° may be slightly low due to the solubility of uncondensed gases in the condensed products. It is significant that the ratio $P_{-183^\circ}/P_{\text{initial}}$ is the same for this experiment as for the others. Upon cooling the reaction vessel from 240 to 24° white crystals appeared on the walls of the flask in all the experiments. From the data above it is seen that for each mole of methyl azide decomposed there is formed 0.14 mole of products which condenses between 24 and -78°, 0.38 mole which condenses between -78 and -183° and 0.96 mole which does not condense at -183°. Since each mole of methyl azide gives 1.66 moles of product upon complete decomposition, by difference 0.18 mole condenses out between 240 and 24°.

The white solid which resulted from the decomposition in a number of runs and which condensed out in the capillaries upon pumping out the reaction cell was collected and found to be mostly hexamethylenetetramine. It also probably contained some ammonium azide. The solid was dissolved in water and a portion of the solution gave positive tests for azide ion by the silver nitrate and ferric nitrate tests. It had been observed that upon pumping out the system between runs part of the white solid disappeared. This is good indication that the azide present was in the form of ammonium azide since the dissociation pressure of the latter compound is relatively high at room temperature. Hexamethylenetetramine was identified by its melting point and by a specific test given by Mulliken.[4]

It is possible to write stoichiometric equations which are consistent with the freezing out data and which yield the identified products. The reactions here proposed are almost identical in nature with those which were postulated to occur in the decomposition of ethyl azide. We write the equations

$$0.25\ CH_3N_3 \longrightarrow 0.25\ CH_2^- + 0.25\ HN_3 \qquad (1)$$
$$0.75\ CH_3N_3 \longrightarrow 0.75\ N_2 + 0.75\ CH_3N \qquad (2)$$
$$0.75\ CH_3N \longrightarrow 0.75\ CH_2{=}NH \qquad (3)$$
$$0.35\ CH_2{=}NH \longrightarrow 0.058\ (CH_2)_6N_4 + 0.117\ NH_3 \qquad (4)$$
$$0.40\ CH_2{=}NH \longrightarrow 0.20\ C_2H_6 + 0.20\ N_2 \qquad (5)$$
$$0.25\ CH_2^- \longrightarrow 0.125\ C_2H_4 \qquad (6)$$

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[4] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1916, Vol. II, p. 129.

Reactions (1), (2), (3), (4) and (5) are essentially the reactions which were advanced to explain the decomposition of ethyl azide.[2] They correspond to equations (1), (2), (4), (5) and (6) for that reaction. Since there is no stable rearrangement product for CH_3N the reaction (3) as given for ethyl azide cannot occur here. Equation (6) is the only innovation in this mechanism. It is of interest that the relative amounts of the decomposing substances which break up according to reactions (1) and (2) are practically the same for the two aliphatic azides according to our mechanism. Although it is highly probable that the radical CH_3N would instantly rearrange to the unstable $CH_2{=}NH$ before undergoing collisions, it is impossible to say by just what mechanism the latter polymerizes to give hexamethylenetetramine.

According to the above reactions one mole of methyl azide decomposes to give 0.25 mole of hydrazoic acid, 0.95 mole of nitrogen, 0.058 mole of hexamethylenetetramine, 0.117 mole of ammonia, 0.20 mole of ethane and 0.125 mole of ethylene. The ratio of final to initial pressure is 1.70 if the hexamethylenetetramine does not condense out in the reaction flask. This compound has a high sublimation pressure at the temperature of the experiments, and since the ratio was not measured at the very high pressures nor at the lowest temperature it would probably remain in the gas phase for those experiments where the ratio was determined. Since in the other experiments the reaction was seldom carried more than 40% to completion, it would probably not condense out during the rate measurements. In the freezing out experiments the white solid did not appear on the walls of the reaction vessel until the latter had cooled to below 150°. At room temperature the hexamethylenetetramine and the ammonia in the form of ammonium azide would be condensed out. These total 0.18 mole and experimentally 0.18 was found. Between 24 and $-78°$ the rest of the hydrazoic acid, 0.13 mole, would condense. The experiments gave 0.14 mole. Between -78 and $-183°$ the ethylene and ethane, 0.33 mole, would come out and 0.38 mole was found to condense. The nitrogen, 0.95 mole, would be left as a gas at $-183°$ and the experiments gave 0.96.

The author does not claim that all of these reactions certainly occur as written. The fact that the mechanisms which best fit the experimental facts are practically identical for the decompositions of the two azides is considered evidence in their favor.

Preparation of Methyl Azide.—Methyl azide was prepared by dropping dimethyl sulfate upon an alkaline solution of sodium azide heated on a steam-bath. The evolved gas was passed through a tube containing C. P. fused calcium chloride and was collected at $-78°$. It was allowed to distil at room temperature into another cold trap, the first and last fractions being rejected. It was freed of dissolved gases by freezing with liquid air, pumping out the trap, allowing the latter to warm up and repeating the operation several times.

Apparatus and Procedure.—The apparatus and the procedure were the same as in the previous investigation.

Experimental Data

The partial pressure of methyl azide (P_A) was calculated for each reading by the expression $P_A = (1.66\,P_0 - P)/0.66$, where P_0 is the initial pressure at zero time and P is the total pressure at that reading. First order constants were calculated by the interval method, using the equation

$$k_1 = 2.303/(t' - t) \times \log P_{A_t}/P_{A_{t'}}$$

where P_{A_t} is its partial pressure of methyl azide at the time t and $P_{A_{t'}}$ is its partial pressure at the time t'. Intervals were chosen to give roughly the same amounts of decomposition. First order constants were calculated for from 3 to 7 intervals, depending on the temperature and pressure, and until decomposition was from 20 to 60% complete. In most of the runs the rates were measured up to 30% decomposition. In order to avoid the production of large amounts of hexamethylenetetramine which would clog the capillary upon pumping out the cell, the experiments were not carried farther than was necessary to obtain the rate constants. Since there was no drift in the individual constants up to 60% decomposition, the average constant obtained during the first 20 or 30% of the run may be taken as the true average for the experiment. In Table II are given the data for several typical experiments.

TABLE II

DATA FOR RUNS

Run number 10; $P_{\text{final}}/P_0 = 1.66$; $T = 240.0°$; $P_0 = 15.03$ cm.

p, cm.	P_A	t, sec.	$k_1 \times 10^4$, sec.$^{-1}$
15.22	14.80	32	9.60
15.75	13.99	90	9.83
16.15	13.38	135	9.39
16.75	12.49	210	9.65
17.82	10.87	354	9.55
18.85	9.30	516	
24.98	0.00	∞	

Run number 32; $T = 240.0°$; $P_0 = 0.251$ cm.

p, cm.	P_A	t, sec.	$k_1 \times 10^4$, sec.$^{-1}$
0.2520	0.2490	20	3.55
.2655	.2285	261	3.76
.2940	.1856	817	3.50
.3275	.1348	1729	

The column headings are self-explanatory. The column entitled Average Deviation is simply the arithmetical average of the deviations of the individual constants from the average constant. Every experiment made except the first five and number twelve has been included in Table III. During the first experiments the final–initial pressure ratio was changing. After experiment five it remained constant. Number twelve gave an

TABLE III

SUMMARY OF ALL EXPERIMENTS

Number	Temp., °C.	Initial press., cm.	Number of constants	Average devn. $\times 10^{-4}$	$k_1 \times 10^4$ sec. $^{-1}$
16	200.0	16.50	3	0.027	0.231
15		13.30	7	.018	.230
17	213.0	19.70	4	.033	.917
18		13.20	5	.074	.866
21		12.50	4	.048	.847
22		9.15	5	.021	.795
23		4.13	4	.038	.674
26[a]		2.86	6	.080	.604
24		2.08	5	.080	.600
27[a]		1.29	5	.039	.554
25		0.509	3	.078	.506
28[a]		.310	5	.067	.512
29		.110	2	.002	.463
19	226.0	16.47	5	.10	2.91
20		15.50	5	.17	2.79
6	240.0	46.61	3	.60	9.23
8		35.25	4	.43	9.23
7		28.78	3	.10	9.11
10		15.03	5	.11	9.60
9		14.77	5	.18	9.17
13		12.90	3	.08	9.47
11		8.80	4	.37	9.13
14		7.30	4	.57	7.87
36		4.24	4	1.17	7.49
35		2.73	3	0.12	7.12
37		1.33	5	.25	5.89
30		1.13	6	.33	5.06
31		0.896	5	.19	4.88
34		.534	4	.12	4.63
32		.251	3	.10	3.60
33		.0785	6	.40	2.70

[a] Surface–volume ratio of reaction vessel increased thirteen-fold.

average constant that was very low. No reason is known for this behavior and this run has been excluded from the table.

As can be seen from Table II there is no drift in the individual first order constants during an experiment. In experiments 26, 27 and 28 the surface–volume ratio of the reaction cell was increased thirteen-fold by packing the reaction vessel with Pyrex tubing. From these experiments it is seen that the reaction is not influenced by the addition of surface, and is therefore homogeneous.

Discussion and Interpretation of Results

This reaction exhibits the characteristics of a true unimolecular reaction, *i. e.*, a first order rate constant independent of pressure at high pressures and a decrease in rate constant with decreasing pressure at sufficiently low pressures. In Fig. 1 is plotted the usual log k_1–$1/T$ relationship. Only those experiments performed at high pressures where the rate constant has become independent of pressure have been used in this plot. These high pressure constants have been taken as the averages, for the various temperatures, of all experiments made above 10 cm. initial pressure. All of these experimentally determined high pressure constants may be slightly lower than the true asymptotic values. From the slope of the line in Fig. 1 the heat of activation is found to be 43,500 cal. per mole. The high pressure rate is given by the expression

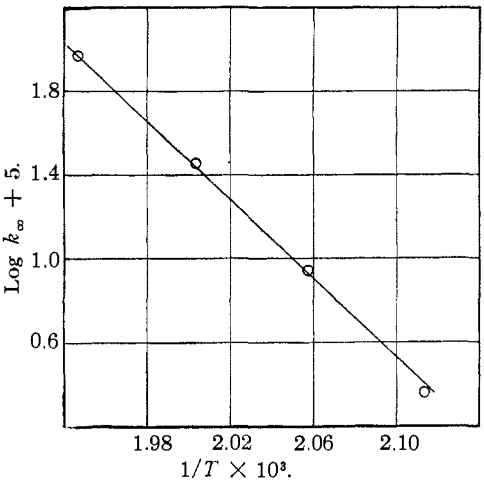

Fig. 1.—Plot of log k_∞ against $1/T$.

$$k_\infty = 3.02 \times 10^{15} e^{-43,500/RT} \text{ sec.}^{-1}$$

Figure 2 is a plot of log k/k_∞ against log P for the experiments at 213.0 and 240.0°. The circles are the experimental points for 213.0°, the circles enclosing crosses are for 240.0° and the solid circles are for the experiments

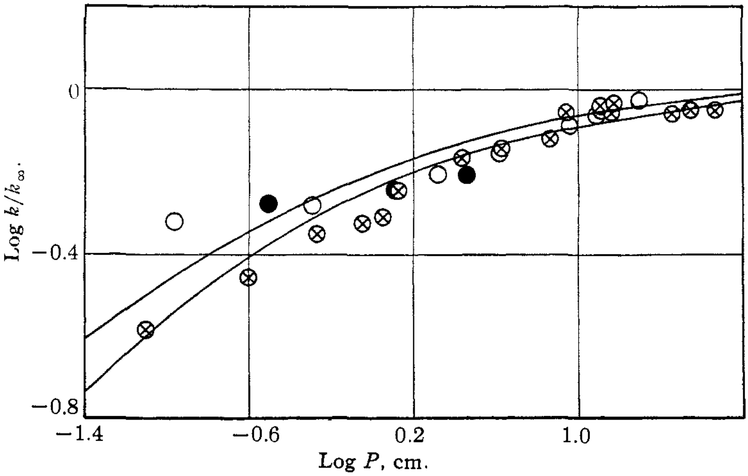

Fig. 2.—Plot of log k/k_∞ against log P. The circles are for the experiments at 213.0°, the circles enclosing crosses are for the experiments at 240.0° and the solid circles are for the experiments at 213.0° with the added surface. The curves are theoretical.

at 213.0° with the added surface. The theoretical curves are those obtained by integrating graphically the final expression derived by Kassel.[5] In this equation σ, the molecular diameter, has been taken as 4.9×10^{-8} cm. and S, the number of oscillators in the molecule, as 13. A is 3.02×10^{15} and E_0 is 43,500 cal. per mole. The upper curve is for 213.0° and the lower one for 240.0°.

From Fig. 2 it is seen that the agreement between theory and experiment is good at 240.0°. At 213.0°, however, the experimental rate falls off more rapidly at the higher pressures than the theoretical curve for that temperature and then flattens off so that the latter exhibits a greater slope than the experimental curve. There is evidence that this same behavior is exhibited in two other reactions. This is seen in the experiments performed by Ramsperger[3] at 270° on the decomposition of methyl isopropyl di-imide, and in the measurements at 200° on the decomposition of dimethyltriazene.[6] In each of these reactions the temperatures here mentioned are the lowest at which rates were measured.

It should be pointed out that the rates here reported are somewhat lower than those given by Ramsperger for the decomposition of methyl azide.[3] It is not possible to make an accurate comparison since Ramsperger did not obtain the high pressure constant at the temperature of his experiments and because he reported the condensation of solid products during his measurements. The first measurements made here, which were rejected for reasons mentioned above, gave constants which were about 20% greater than the later accepted values. The consistency of our measurements at the various temperatures as shown by Fig. 1 may be considered evidence that our rates are not low due to extraneous causes, since it is not probable that any inhibiting factor would be independent of temperature.

The maximum number of classical oscillators possible in a molecule of methyl azide is 15. The number here chosen to best fit the data is 13. This seems high for a molecule having three very light atoms such as hydrogen atoms which would probably not be fully excited. However, there are four heavy atoms in a molecule of methyl azide, the same number that is present in a molecule of azomethane. The measurements on the decomposition of the latter require twelve or thirteen oscillators for their interpretation. This is the same as the number here needed for methyl azide. It is interesting to note that for the azo compounds and for the azides the numbers of classical oscillators needed to fit the experimental data are approximately three times the numbers of heavy atoms.

The author wishes to thank Professor G. B. Kistiakowsky for the interest and advice which have materially aided this research.

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

(6) Ramsperger and Leermakers, THIS JOURNAL, **53**, 2061 (1931).

Summary

1. The thermal decomposition of methyl azide has been studied at temperatures from 200.0 to 240.0°, and from pressures of 0.08 to 46.6 cm.

2. The reaction has been found to be homogeneous. It is first order at high pressures but the rate constants decrease with decreasing pressure below 10 cm. initial pressure. The high pressure rate constant is given by the expression $k_\infty = 3.02 \times 10^{15} e^{43,500/RT}$.

3. To best fit the data to the theoretical expression relating rate constant and pressure a molecular diameter of 5×10^{-8} cm. and 13 classical oscillators are required.

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The Adsorption of Hydrogen by Silica Gel at Elevated Temperatures

BY L. H. REYERSON

In a recent paper Alyea[1] has suggested interesting mechanisms for the explosive and non-explosive reactions occurring between hydrogen and oxygen at elevated temperatures. Experimental evidence is given for a large adsorption of hydrogen by Pyrex glass surfaces at temperatures above 500°. Alyea concludes that this marked adsorption of hydrogen is due to activated adsorption. In discussing the mechanisms of the slow and explosive reactions Alyea postulates that this hydrogen is attached to the surface of the glass in an activated form, which it is not at room temperatures. Suggestions are made as to the possible attachment of the hydrogen to the surface as well as to the mechanism by which the chain reaction is initiated. As a result of this work it was felt that marked adsorption of hydrogen by silica gel should be obtained at temperatures above 500°. Previous work in this Laboratory had given inconclusive evidence that hydrogen was somewhat better adsorbed by silica gel in the neighborhood of 400° than it was below 300°. The adsorption of hydrogen by silica gel was therefore studied in the temperature range of 400 to 600°.

Experimental Procedure

A sample of high-grade silica gel prepared by the method of Patrick was purified by digestion with concentrated nitric acid. This treatment was followed by prolonged dialysis. The gel was then dried in a current of air at about 300°. Finally the gel was electrodialyzed for about two weeks in an electrodialysis cell using cellophane membranes to separate the middle section, containing the gel, from the two electrode sections. The dialysis was continued until the resistance across the cell reached a constant maximum value. The gel was then dried slowly and finally heated to about 300°. The

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(1) Alyea, THIS JOURNAL, **53**, 1324–1336 (1931).