[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE DECOMPOSITION OF AZOMETHANE. A HOMOGENEOUS, UNIMOLECULAR REACTION

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Azomethane was found by Thiele[1] to be a very light yellow liquid boiling at 2°. He found that it exploded if the tube in which it was contained was heated to red heat, or if a spark was passed through the mixture. The products were nitrogen, hydrogen and a mixture of hydrocarbons. If the gas was mixed with carbon dioxide and the mixture passed through a red-hot tube no explosion occurred, but the azomethane was decomposed. Nitrogen and ethane were the principal products, but some ethylene, methane and hydrogen were also formed. The main reaction can therefore be represented by the equation

$$CH_3NNCH_3 = N_2 + C_2H_6 \qquad (1)$$

Two possible side reactions may be represented by the equations

$$2CH_3NNCH_3 = 2N_2 + C_2H_4 + 2CH_4 \qquad (2)$$

$$CH_3NNCH_3 = N_2 + C_2H_4 + H_2 \qquad (3)$$

In the experiments about to be described the gas was decomposed at constant temperature and constant volume. The final pressure varied from 2.03 to 2.05 times the initial pressure. The amount of ethylene formed by Reaction 2 or 3 determines the final pressure to be expected. Some of the gas produced by complete decomposition was analyzed for ethylene by shaking with bromine water of known concentration. The bromine reacts to form ethylene dibromide; the excess of bromine was treated with potassium iodide solution, and the iodine liberated was titrated with standard thiosulfate solution. The gas was found to contain 1.7% of ethylene, which corresponds to a final pressure of 2.034 times the initial pressure if the divergence from Equation 1 is attributed to either Equation 2 or Equation 3. Small deviations from the gas law would cause an additional increase in the final pressure. The calculation of the velocity constants is based on the average value for the final pressure of 2.04 times the initial pressure.

The Preparation of Azomethane

A good many preliminary experiments indicated that the impurities in the azomethane had a small but noticeable effect on the velocity of decomposition. The rate was in general decreased. The procedure of preparation which was finally adopted produced reaction-velocity constants which did not vary with the sample. The liquid was clear and gave a vapor pressure of 758 mm. at 2° for both the first and last fractions.

The method of preparation was that of Thiele.[1]

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[1] Thiele, *Ber.*, **42**, 2575 (1909).

Diformyl hydrazine was methylated with dimethyl sulfate and hydrolyzed in strong hydrochloric acid. The dimethyl hydrazine formed was separated by steam distillation and absorbed in hydrochloric acid solution. It was separated from solution by concentrating the solution to a small volume and dissolving the monohydrochloride salt in absolute alcohol. A slight excess of hydrogen chloride dissolved in alcohol was added to precipitate the dimethylhydrazine dihydrochloride. This salt was washed with alcohol containing hydrogen chloride and finally with ether. It was necessary to dry this salt very thoroughly in the presence of hydrogen chloride gas to prevent loss of hydrogen chloride and subsequent decomposition. It was placed in a flask and dried at 110° with a stream of dry hydrogen chloride passing through the flask. The salt was recrystallized from absolute alcohol and dried again in the presence of hydrogen chloride gas. The preparation of azomethane from this salt and the thermal decomposition of the azomethane were carried out on a high-vacuum line.

Twenty g. of potassium chromate was dissolved in 40 cc. of water and put into a 100cc. distilling flask which was immersed in an ice-bath. A ground-glass joint attached to the outlet tube permitted shaking of the flask during the preparation. Eight g. of the dimethylhydrazine dihydrochloride was dissolved in 15 cc. of water and allowed to drop very slowly from a dropping funnel into the neutral chromate solution. The pressure was reduced to about 25 cm. The evolved gas passed through ground, c. p., fused calcium chloride and was condensed in a receiving flask immersed in a carbon dioxide and ether mixture at —78°. After the solution had been added, the pressure was gradually reduced to 3 cm. The ether-carbon dioxide mixture was removed and the liquid azomethane allowed to evaporate through a 50 × 2cm. tube filled with soda lime and calcium chloride, a long mercury U-trap, a second receiver, a second U-trap, and into a 250cc. flask which was separated from the vacuum line by one stopcock and from the decomposition bulb by another stopcock. The azomethane was recondensed in the first receiver and re-evaporated several times. It was then separated from the first receiver by mercury in the first U-trap, condensed in the second receiver, separated from the flask by the second U-trap, and the flask was evacuated. Small amounts of air and other volatile substances were removed by evaporation into the evacuated flask, recondensation in the second receiver and evacuation of the flask. This process was repeated several times. Finally the flask was highly evacuated, filled with azomethane gas and trapped off from the second receiver. The pressure in the flask was at least 50 cm. This was the supply for the decomposition experiments.

The thermal decomposition was carried out in an apparatus similar to that used by Smith.[2] The reaction chamber had a capacity of 210 cc. and was surrounded by a chamber containing mercury vapor boiling under a known pressure. The mercury was condensed by a water condenser and returned to the bottom of the flask. This chamber was connected with a 20-liter carboy and a mercury manometer. The large capacity of the system made automatic pressure control unnecessary. A thermometer was used in some of the experiments to determine the constancy of the temperature. The variation was at most 0.1°. The mercury vapor-pressure measurements of Smith and Menzies[3] were used to determine the temperature. Between the reaction chamber and the gas supply was a U mercury trap of small-bore tubing and on the opposite side of the reaction chamber

[2] Smith, This Journal, 47, 1862 (1925).

[3] Smith and Menzies, *ibid.*, 32, 1434 (1910).

was a similar U-trap which was connected to the mercury diffusion pump. The volume of gas outside the reaction chamber was small compared to the total volume. Before each experiment the thermostat was brought to constant temperature and the reaction chamber was evacuated to a pressure of less than 10^{-5} cm. The U-trap on the high-vacuum side was filled with mercury, the desired amount of azomethane gas was let in through the stopcock, and the U-tube on the supply side filled with mercury. The pressure was then read on a meter stick attached to the U-tube on the high-vacuum side. At the higher temperatures and higher pressures a small correction for the decomposition, which occurred before the first pressure reading was made, was necessary. It was usually only 1% of the total pressure. The pressures were calculated for mercury at 0°. Pressure readings were made until the reaction was from 60–80% complete. The partial pressure of azomethane (P_{A}) was calculated from the expression $P = P_{\mathrm{A}} + 2.04\ (P_i - P_{\mathrm{A}})$, where P is the measured pressure and P_i is the initial pressure. This equation can be rearranged to give $P_{\mathrm{A}} = (2.04\ P_i - P)/1.04$. The unimolecular reaction-velocity constants were calculated by using the equation $K = \log_{10}[P_{\mathrm{A}_t}/P_{\mathrm{A}_{t'}}][2.303/(t'-t)]$,

Table I

Summary of All Experiments

Expt. no.	Temp., °C.	Initial press., cm.	$K \times 10^3$, av.	Surface
25	278.6	15.97	0.050	Large
26	287.3	16.49	.100	
27	294.1	11.26	.172	
1	295.9	11.41	.217	Small
15	296.8	11.63	.227	
6	298.1	3.76	.225	
16	298.2	10.66	.252	
17	298.2	10.73	.253	Large
18	298.3	10.03	.250	
4	298.3	4.80	.232	Small
2	298.4	12.05	.257	
3	298.4	24.65	.248	
5	298.4	15.21	.252	
20	298.4	43.46	.263	Large
21	298.4	3.62	.223	
14	298.7	3.99	.235	Small
8	305.0	5.75	.408	
10	305.0	7.13	.440	
9	305.3	16.16	.457	
11	311.6	10.33	.727	
19	313.7	6.26	.747	Large
12	316.3	10.15	1.03	Small
13	319.6	6.84	1.25	
22	320.4	21.80	1.30	Large
23	323.7	11.28	1.58	
24	327.4	17.65	2.08	

where P_{A_t} corresponds to the pressure of azomethane at one reading and $P_{A_{t'}}$ is the pressure of azomethane at the following reading. From five to eight pressure readings were made during each experiment and constants were calculated for each time interval. No trend in the constants of a given experiment occurred which was greater than the experimental error, and there was no trend which was common to all of the experiments. All of the experiments but one (in which some gross error was made) which were made from five different preparations of azomethane after the above method of preparation was first used, are included in this paper. A large number of experiments were made at approximately 298.4°. In these experiments the initial pressure was varied as much as 12-fold, the surface was varied 6.5-fold by placing small Pyrex tubing in the reaction chamber, and several different preparations of azomethane were used. Experiments were made at temperatures ranging from 278.6–327.4° in order to determine the temperature coefficient. A summary of all of the experiments is given in Table I.

The complete data of three typical experiments are given in Table II.

TABLE II

COMPLETE DATA OF THREE EXPERIMENTS

Experiment 20

Time, min	0	10	20	33	46	65
P_A, cm	43.08	37.18	31.36	25.19	20.52	15.51
$K \times 10^3$, sec.$^{-1}$		0.245	0.283	0.282	0.263	0.245

Experiment 21

Time, min	0	15	30	48	75
P_A, cm	3.62	3.00	2.49	1.93	1.31
$K \times 10^3$, sec.$^{-1}$		0.208	0.207	0.237	0.240

Experiment 22

Time, min	0	3	6	9	12	17	25
P_A, cm	21.23	16.77	13.03	10.20	8.06	5.55	3.15
$K \times 10^3$, sec.$^{-1}$		1.31	1.40	1.36	1.31	1.24	1.18

The heat of activation, Q, is given by the Arrhenius expression for the temperature coefficient of reaction rate which is $d\ ln\ K/d(1/T) = Q/R$. If $\log_{10} K$ be plotted against $1/T$, all points should fall on a straight line. The slope of this line multiplied by 2.303 R gives the heat of activation. Fig. 1 shows this plot. The intercepts of the straight line are at $1/T = 0.0016595$ and $1/T = 0.0018205$. Q is found to be 51,200 cal.

Discussion of Results

That the reaction is homogeneous is proved by increasing the surface 6.5-fold without increasing the rate. This is evident if we compare Expts. 16 and 17 or Expt. 18 with 2 and 5. There is, however, a definite but small difference in the constant of experiments at the lowest and highest initial pressures. This difference is greatest in Expts. 20 and 21, which were also the experiments of highest and lowest initial pressure. Some experiments show a reduction in the rate constant toward the end of the decomposition when the partial pressure of azomethane has become small, but this is not true of all of them, as is shown by Expt. 21. Furthermore, the experimental error becomes greater and the uncertainty of the final pressure has an influence. The question of the small effect, if any, of the initial pressure can only be determined by going to much lower pressures. Experiments at lower pressures are now in progress.

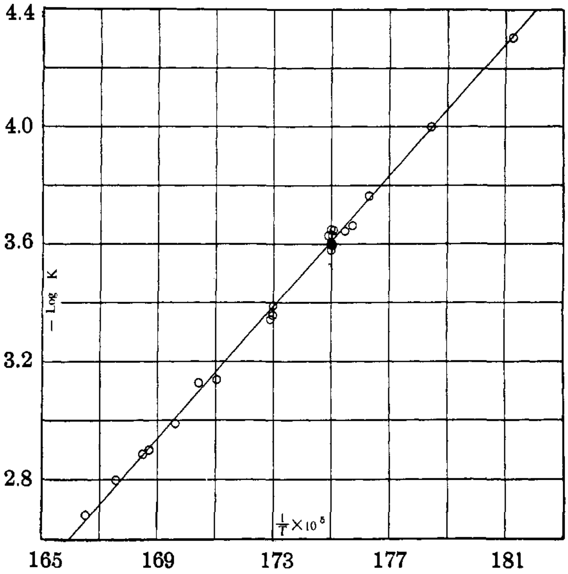

Fig. 1.

Photochemical Decomposition

Azomethane was found to be decomposed by the light from a quartz mercury arc. The pressure was doubled when decomposition was complete. The rate of decomposition was two-thirds as great in a Pyrex vessel as in a quartz vessel. Quantitative photochemical experiments with ultraviolet light will be undertaken.

Summary

The rate of thermal decomposition of azomethane was studied at temperatures from 278.6–327.4°, at pressures from 3.62 cm. to 43.46 cm. and with 6.5-fold variations in surface.

The decomposition was found to be homogeneous and unimolecular. The heat of activation was found to be 51,200 cal. per mole.

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