THE THERMAL DECOMPOSITION OF AZOMETHANE OVER A LARGE RANGE OF PRESSURE

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In a previous research by the author,[1] the thermal decomposition of azomethane was found to be homogeneous and unimolecular over small pressure ranges. There was some evidence that the rate constants were slightly lower at pressures of about 4 cm. than at pressures of 20–40 cm. It was thought likely that the rate constants would become considerably smaller at very low pressures. A collision theory of activation had been worked out by Rice and the author[2] which would require a decrease in the rate at somewhat lower initial pressures. Recently Hinshelwood and Thompson[3] and Hinshelwood[4] found two reactions which deviate from the unimolecular rate at low pressures. In this research the rate of decomposition of azomethane has been studied over a 3000-fold pressure range.

Experimental Method

Previous research[1] had shown the decomposition of azomethane to be almost entirely represented by the equation $CH_3NNCH_3 = C_2H_6 + N_2$. A small amount of side reaction accounted for an increase in pressure of 104% of the original pressure, instead of exactly 100% as determined by the equation. The reaction chamber and thermostat were the same as those used previously. Experiments at high pressures were performed exactly as before, the increase in pressure being measured by the height of a mercury column. Pressure measurements at low pressures were made with a small McLeod gage. Between the reaction chamber and the McLeod gage was a mercury trap which consisted of a glass float inside of a larger tube. When the mercury was let into the gage for a reading, the float would rise and fit tightly into a ground-glass joint at the top of the trap. The mercury will not rise above the ground-glass joint, thus permitting the mercury to be raised to any desired height in the gage without flowing into the reaction chamber. The volume of the trap and tubing connecting the trap to the gage was 2.8 cc. Two different McLeod gages were used. That used in Expts. 51 to 64 had a volume of 8.87 cc., and that used in Expts. 65 to 72 had a volume of 11.14 cc. The reaction chamber had a volume of 210 cc. without tubing and 168 cc. when filled with tubing. The volume of tubing connecting the reaction chamber to the trap was small and was neglected in the calculations.

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

[2] Rice and Ramsperger, article in press.

[3] Hinshelwood and Thompson, *Proc. Roy. Soc.*, **113A**, 221 (1926).

[4] Hinshelwood, *Proc. Roy. Soc.*, **114A**, 84 (1927).

In starting an experiment, the thermostat was brought to constant temperature and the desired amount of azomethane was let into the highly evacuated reaction cell and trapped off from the supply and from vacuum by mercury traps. The pressure was then read on a McLeod gage. The mercury was allowed to remain in the trap until nearly time for the next pressure reading. At that time the mercury was lowered and sufficient time was allowed to obtain pressure equilibrium before the pressure was again read on the gage. Generally, six to eight such readings were made during the course of the reaction. Constants were calculated until the reaction was 60 to 85% complete. The pressure of azomethane in the reaction cell had to be known at the beginning and end of each time interval for which a rate constant was to be calculated. This calculation was made as follows.

Let P be the pressure read on the gage. Let the pressures in the reaction cell be designated as follows: P', the pressure before the reading was made; P'', the pressure after the reading was made; P'_A, the partial pressure of azomethane before each reading; P''_A, the partial pressure of azomethane after each reading. Let V be the volume of the reaction chamber, V_1 the volume of the trap, and V_2 the total volume of the McLeod gage. Let T_1 be the temperature of the trap and gage, and T_2 the temperature of the reaction cell. Let N_1 be the number of moles of gas in the trap and N_2 the number of moles in the reaction cell. We can calculate P'' in terms of P and the temperature and volume constants as follows. $PV_1 = N_1RT_1$, $PV = N_2RT_2$, $P''V = (N_1 + N_2) RT_2$. Eliminating N_1 and N_2 we find $P'' = P(V_1T_2/VT_1 + 1)$. P' may be calculated as follows. Let N_3 be the number of moles passing into the gage only, when the mercury is lowered for a reading. Let ΔP be the increase in pressure read on the gage in two successive readings. Then $\Delta PV_2 = N_3RT_1$ and $P_1'V = (N_1 + N_2 + N_3)RT_2$; $P' = P'' + \Delta PV_2T_2/VT_1$. Now the increase in pressure in the reaction cell, after one reading was made at time t and before the next reading at time t', is $P'_{t'} - P''_t$. If this increase be divided by 1.04, we get the change in azomethane pressure. Therefore we have the relation $P'_{At'} = P''_{At} - (P'_{t'} - P''_t)/1.04$; also, $P''_{At} = P'_t\, P''_t/P'_t$. The first-order rate constants were then calculated from the relation $K = \log_{10}\ P''_{At}/P'_{At'} \times 2.303/(t' - t)$, where t and t' are given in seconds. The corrections which were necessary on account of the use of a McLeod gage are small. The pressures read on the gage are all corrected by about 3% to obtain P''. The increase in pressure (ΔP) during each time interval is about nine-tenths of the actual pressure increase in the reaction cell. The accuracy of the measurements is, therefore, nearly as good as a direct pressure measurement on a manometer. A small correction of at most a few per cent. for the decomposition occurring before the first reading was necessary only at the highest temperature and highest pressures used.

Many experiments were continued until reaction was complete. The pressure of azomethane as calculated was always within 1 or 2% of zero at the end of the reaction, thus confirming the accuracy of the corrections and showing that the increase in pressure is, even at low pressures, very close to 1.04 times the original pressure.

Experimental Results

A summary of all of the experiments is given in Table I.

TABLE I

SUMMARY OF EXPERIMENTS

Expt. No.	Temp., °C.	Initial pressure, cm.	Average $K \times 10^3$	Expt. No.	Temp., °C.	Initial pressure, cm.	Average $K \times 10^3$
62	290	0.0309	0.032	64	330	0.1267	0.60
60	290	.0879	.045	54	330	.1510	.69
52	290	.1989	.053	63	330	.2648	.79
61	290	.2587	.058	51	330	.2870	.75
53	290	.5818	.069	55	330	.4531	.84
72	290	1.203	.090	69	330	.7507	1.10
71	290	2.351	.097	68	330	1.439	1.31
67	290	4.407	.118	65	330	1.621	1.45
81	290	19.10	.132	70	330	3.328	1.76
74	290	32.00	.137	66	330	5.646	2.13
79	290	37.50	.137	82	330	14.36	2.65
77	290	70.79	.135	76	330	20.00	2.69
59	330	0.0259	.31	75	330	23.53	2.82
58	330	.0380	.36	80	330	26.96	2.76
57	330	.0505	.40	73	330	39.26	2.82
56	330	.0873	.48	78	330	48.68	2.96

TABLE II

COMPLETE DATA OF THREE EXPERIMENTS

Expt. 58. $V_1T_2/VT_1 = 2.8 \times 603/210 \times 298 = 0.027$. $V_2T_2/VT_1 = 8.87 \times 603/210 \times 298 = 0.086$

Decomposition in filling cell $= 0.001$ cm.

t, min.	0	16	30	47	73	109	164
P, cm.	0.0380	0.0480	0.0541	0.0594	0.0642	0.0686	0.0711
P''	.0390	.0493	.0556	.0610	.0659	.0705	.0730
P'	.0390	.0502	.0561	.0615	.0663	.0709	.0732
P'_A	.0370	.0262	.0192	.0133	.0081	.0032	.0006
P''_A	.0370	.0257	.0190	.0132	.0080	.0032	.0006
$K(\times 10^3)$		.36	.35	.35	.31	.42	

Expt. 53. $V_1T_2/VT_1 = 2.8 \times 563/168 \times 298 = 0.0315$. $V_2T_2/VT_1 = 8.87 \times 563/168 \times 298 = 0.10$

t, min.	0	24	64	105	151	202	242
P, cm.	0.5640	0.6036	0.6762	0.7470	0.8070	0.8640	0.8994
P''	.5818	.6226	.6975	.7705	.8325	.8912	.9277
P'	.5818	.6266	.7048	.7776	.8385	.8969	.9312
P'_A	.5818	.5387	.4563	.3746	.3058	.2417	.2017
P''_A	.5818	.5353	.4516	.3712	.3036	.2402	.2009
$K(\times 10^3)$		.054	.066	.076	.070	.075	.073

TABLE II (Concluded)

Expt. 69. $V_1T_2/VT_1 = 2.8 \times 603/210 \times 298 = 0.027.$ $V_2T_2/VT_1 = 11.14 \times 603/$
$210 \times 298 = 0.107$

t, min.	0	3	6	10	15	74
P, cm.	0.731	0.859	0.961	1.061	1.156	1.399
P''	.7507	.8822	.9869	1.090	1.187	1.437
P'	.7507	.8959	.9979	1.101	1.197	1.440
P'_λ	.7507	.6111	.4911	.3765	.270	.005
P''_λ	.7507	.6023	.4861	.373	.268	.005
$K(\times 10^3)$		1.14	1.13	1.07	1.08	

The complete data, including the calculated values of all pressures, are given for three typical experiments in Table II.
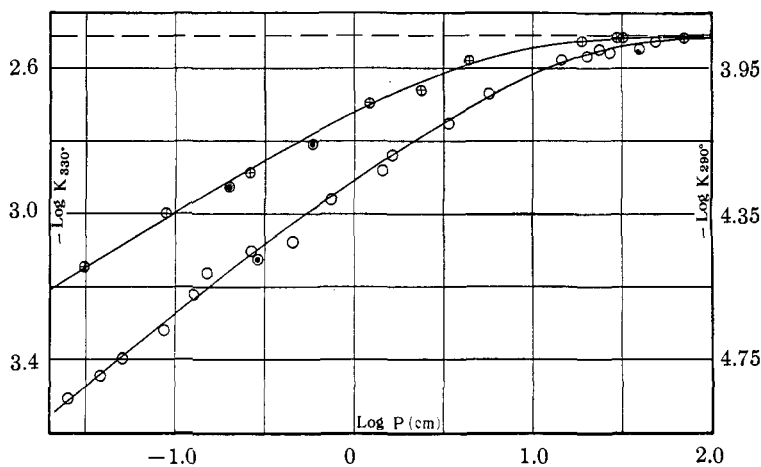

Fig. 1.—O, 330°; ⊕, 290°; ⦿, Large surface.

All of the results are plotted in Fig. 1. It is convenient to plot the logarithm of the initial pressure against the logarithm of the velocity constant. It is apparent that the curves for both temperatures would approach a constant value of the rate constant at high pressures. In order to bring out the relationship of the two curves they have been drawn as nearly as possible to a common asymptote, with the ordinate at the right giving the negative of the logarithm of the rate constant at 290° and the ordinate on the left the negative of the logarithm of the rate constant at 330°. Within experimental error the asymptote for 330° is log $K = -2.51$, $K = 3.09 \times 10^{-3}$, and for 290° log $K = -3.86$, $K = 0.138 \times 10^{-3}$.

Discussion

It is apparent that the reaction is strictly first order only at high pressures and that it remains first order to lower pressures at the lower temperature. Comparison of experiments at several low pressures and at 330°

shows that a five-fold change in the initial pressure only doubles the first-order rate constant. The reaction at these pressures is, therefore, far from being second order with respect to initial pressure. Furthermore, the first-order rate constant is reasonably constant from one time interval to the next in any given experiment, as is shown by the three experiments in Table II. This indicates that the rate velocity is not dependent on the partial pressure of azomethane in the presence of its decomposition products, but that these products exert about the same influence in maintaining the rate as their equivalent of azomethane would. Experiments in the presence of larger amounts of various inert gases will be tried.

The reaction is still homogeneous at low pressures since the three experiments made with increased surface fall on the curve within experimental error. The heat of activation calculated by means of the Arrhenius equation for the temperature coefficient had been found in the previous research to be 51,200 cal. per mole. The value obtained by using the rate constants at high pressures for 290 and 330° is 52,500 cal. This value is not to be chosen in preference to the earlier value, since it is determined from only two points. Nevertheless, the earlier value is likely to be low since the experiments at higher temperatures should have been made at somewhat higher pressures to be comparable with low-temperature points.

Theoretical Part

There are known, at present, several unimolecular reactions for which the rate becomes lower at low pressures. This suggests that a sufficiently high rate of activation is not being maintained to keep the reaction strictly first order. Any theory in which the activation energy is obtained by collision of molecules will require a reduction in the rate at sufficiently low pressures. The two theories of Rice and the author[2] give equations for the way in which the rate should fall off with pressure. In a forthcoming article by Rice and the author, these theories will be further tested with the data on azomethane and other unimolecular reactions.

Summary

The rate of decomposition of azomethane was determined at pressures from 0.0259 cm. to 70.79 cm., and at temperatures of 290 and 330°.

The reaction was found to be homogeneous at all pressures. It is strictly unimolecular only at high pressures and is unimolecular to lower pressures if the temperature is low. The velocity constant at the lowest pressure was reduced to less than one-fourth of its high-pressure value when the temperature was 290°, and to one-tenth of the high-pressure value at 330°.

An explanation of the results on a collision hypothesis developed by Rice and the author is forthcoming.

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