indicate that an accuracy of about 2% in the velocity and heat of reaction is obtained.

Investigation by means of this calorimeter of the sucrose inversion supports the conclusion that this reaction is quite strictly monomolecular.

Measurements of the velocity of decomposition of diacetone alcohol check the results of French and Murphy rather than those of La Mer and Miller and Koelichen.

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[CONTRIBUTION FROM M. W. KELLOGG COMPANY RESEARCH LABORATORY]

The Thermal Decomposition of Azomethane

BY E. W. RIBLETT AND L. C. RUBIN

The thermal decompositions of aliphatic azo compounds, particularly that of azomethane, have been considered as examples of simple unimolecular reactions. Ramsperger and Rice[1,2] and Kassel[3] have presented theories of unimolecular reactions and have found that azomethane decomposition furnished the best test of the theories.

The comparison of the theory with the experimental data has been made upon the supposition that the pressure increase in the decomposition was directly proportional to the extent of the decomposition. This was in line with Ramsperger's statement[4] that the decomposition of azomethane is almost entirely represented by the equation $CH_3NNCH_3 = C_2H_6 + N_2$.

In the course of some work upon azomethane in this Laboratory, evidence was obtained that the above equation of Ramsperger did not represent the true course of the reaction. The importance that has been attached to the decomposition of azomethane was thought to warrant a description of the results obtained from analyses of the gaseous products from the decomposition.

Experimental

Azomethane was prepared by Thiele's[5] method as modified by Allen and Rice.[6] It was purified by five distillations, each distillation being followed by a thorough evacuation at liquid nitrogen temperatures. Combustion analyses showed the product to be pure azomethane.

The decomposition apparatus consisted of a 200-cc. Pyrex reaction vessel connected to a large storage vessel through an auxiliary, calibrated filling vessel of 200-cc. capacity. The purpose of the filling vessel was (1) to prevent an explosion spreading to the storage vessel, and (2) to enable a more accurate determination of the initial pressure in the reaction flask. The reaction vessel was also connected to a Toepler pump and to the usual pumping system.

The reaction bulb was placed in an electrically heated air-bath provided with a temperature controller. The temperature was determined from millivolt readings of an iron–constantan thermocouple located in a glass thermowell near the center of the reaction vessel.

Each experiment was conducted by admitting azomethane from the storage bulb to the filling vessel, noting the pressure in the filling vessel, opening the filling vessel to the reaction bulb for two seconds, and closing the stopcock which isolated the reaction chamber. The reaction was followed by means of a manometer until the desired decomposition was obtained, whereupon the contents of the reaction vessel were removed quickly by expansion into a previously evacuated flask at room temperature. The gas was subsequently forced out of this flask by means of mercury into a graduated gas buret, where the quantity was measured. The gas quantities used for an analysis varied from 100 to 175 cc.

The gas was then passed into a small fractionating column, the bottom of which was cooled with carbon dioxide–acetone mixture to about −78°. The top of the column was cooled with liquid nitrogen. A portion of the sample passed through the two condensing media and consisted largely of nitrogen. The remainder of the sample was then fractionated into four portions, the last portion being obtained by opening the column (about 4 cc. total capacity) to an evacuated 400-cc. flask.

Each of the five fractions was then analyzed by combustion with oxygen over a heated platinum spiral. The first fraction was mostly nitrogen with small amounts of methane. The second fraction contained methane with small quantities of nitrogen. The third fraction was ethane with small amounts of methane and possibly traces of ethylene. The fourth fraction contained the remainder of the ethane and, in experiments involving partial decomposition, azomethane. The last fraction, in the case of complete decomposition, showed the same analysis as the fourth fraction. Where azomethane was present, the last fraction was largely azomethane.

At the end of each distillation a small amount of liquid was observed on the walls near the bottom of the column. This was not volatilized by boiling water at a pressure of about 20 mm. In this connection, a pronounced fog was observed when the sample from the reaction vessel was brought to atmospheric pressure. This fog usually disappeared during the transfer to the gas buret.

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[1] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

[2] Rice and Ramsperger, *ibid.*, **50**, 617 (1928).

[3] Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

[4] Ramsperger, THIS JOURNAL, **49**, 1495 (1927).

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

[6] Allen and Rice, THIS JOURNAL, **57**, 310 (1935).

Experimental Results

Reaction Velocity.—The rate constants for the first 10% decomposition of the azomethane are given in Table I.

TABLE I

REACTION VELOCITY CONSTANTS

			$K \times 10^4$ (sec.$^{-1}$)			
				Corrected for		
Expt.	T, °C.	P_i, mm.	No correction	External volume	External volume & self-heating	Ramsperger's values
75	311	94	0.8	0.9	0.9	0.7
74	314	96	.9	0.9	0.9	.8
76	314	119	.9	1.0	1.0	.8
65	325	108	1.9	1.9	1.9	1.8
66	327	68	2.1	2.1	2.1	2.0
85	337	136	5.6	5.6	4.3	4.3
84	337	142	5.9	6.0	4.6	4.3
83	339	84	6.0	6.1	5.2	4.8
96	339	107	6.3	6.4	5.1	4.8
95	339	114	6.0	6.1	4.8	4.8
94	339	120	6.1	6.2	4.8	4.8
93	339	127	6.4	6.5	5.0	4.8
92	339	134	6.8	6.9	5.2	4.8
91	339	142	6.8	7.1	5.2	4.8
82	339	159	6.8	6.9	4.7	4.8
79	340	80	6.2	6.3	5.3	5.2
78	340	90	6.3	6.4	5.2	5.2
77	340	102	5.4	5.5	4.4	5.2
109	340	111	6.8	6.9	5.3	5.2
108	340	116	6.6	6.7	5.1	5.2
107	340	120	6.8	6.9	5.2	5.2
106	340	125	6.8	6.9	5.1	5.2
105	340	130	6.8	6.9	5.0	5.2
104	340	135	6.9	7.0	5.0	5.2
103	340	140	7.0	7.1	5.0	5.2
102	340	144	7.1	7.2	4.9	5.2
101	340	150	7.1	7.2	4.8	5.2
100	340	154	7.3	7.4	4.8	5.2
99	340	160	7.3	7.4	4.7	5.2
98	340	167	7.3	7.4	4.6	5.2
97	340	171	7.4	7.5	4.5	5.2
90	340	146	7.9	8.0	5.0	5.2
89	341	166	8.6	8.8	4.8	5.4
81	340	180	8.0	8.1	4.6	5.2
88	340	187	8.9	9.1	4.8	5.2

The values in column 4 were calculated by the method of Ramsperger,[7] except that the ratio of the final to the initial pressure was taken as 2.1, in conformity with the present findings. Comparison of the values in column 4 with those in the last column (estimated from Ramsperger's curve) shows good agreement below about 330°.

Above 330° the constants given in column 4 are considerably higher than those of Ramsperger. This is due to the fact that in our experiments around 340° the initial pressures are sufficiently high to cause appreciable increase in the rate constant, due to self-heating of the azomethane.

Since the thermal decomposition of azomethane is an exothermic reaction, the reaction mixture becomes heated up as the reaction proceeds. As the reaction mixture becomes heated, the rate of decomposition is increased until, under suitable conditions, the rate becomes infinite and an explosion results. Consequently, as the explosive conditions are approached, the reaction rate constants for the slow decomposition are higher than where the self-heating is negligible.

According to Rice and Sickman[8] the rate constant may be corrected for the self-heating from a knowledge of the ratio of the initial pressure to the critical explosion pressure. The critical explosion pressure at 341° was found to be 187 mm. in our particular apparatus. This is to be compared with 191 mm. determined by Allen and Rice[6] for a similar apparatus. Assuming a parallelism between the critical explosion pressure in the two set-ups, the ratio of initial pressure to the critical explosion pressure has been calculated for those experiments where a correction would be significant.

The rate constants were corrected for the effect of external volume according to Allen,[9] and these constants are given in column 5 of Table I. From the ratio of initial pressure to the critical explosive pressure and the data listed by Rice and Sickman,[8] the constants of column 5 were corrected for self-heating, and the corrected rate constants are given in column 6. By comparison of the data in column 6 with those in column 7 it is evident that the constants found here agree quite well with those of Ramsperger.

The agreement of the constants only after the correction was applied is further evidence of the accuracy of the correction as outlined by Rice and Sickman.

Analyses

The products from four partial decompositions, four complete decompositions, and two explosive decompositions have been analyzed.[10] In order to obtain sufficient sample for analysis, it was necessary in some instances to make several decomposition experiments and composite the products. The experiments from which the samples were taken were made in as nearly iden-

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[7] Ramsperger, THIS JOURNAL, **49**, 914 (1927).

[8] Rice and Sickman, *J. Chem. Phys.*, **4**, 247 (1936).

[9] Allen, THIS JOURNAL, **56**, 2053 (1934).

[10] The gas analyses were made by Mr. A. G. Davis of this Laboratory.

TABLE II

DECOMPOSITION PRODUCTS

				Moles products per 100 moles azomethane reacted							% decomposed	
Expt.	T, °C.[a]	P_i, mm.[a]	P_t/P_i[a]	H_2	N_2	CH_4	C_2H_4	C_2H_6	Liquid	Total	Manometer[a]	Analysis
103–109	340	125	1.3	..	68	38	..	27	40	173	34	47
97–102	340	158	1.3	..	66	38	..	27	38	169	38	56
91–96	339	124	1.6	..	72	51	..	32	30	185	57	71
89–90	340	156	1.7	..	66	51	..	24	39	180	63	83
77–79	340	91	2.1	..	81	60	10	30	23	204	100	100
81	340	181	2.1	..	81	71	1	29	26	208	100	100
82–83	340	122	2.1	..	81	74	2	23	27	207	100	100
84–85	337	139	2.1	..	79	82	2	25	22	210	100	100
86[b]	340	238	2.9	79	95	52	56	..	1	283	100	100
87[b]	341	212	2.9	77	99	49	57	..	..	282	100	100

[a] Average. [b] Explosive reactions.

tical manner as possible. In each case the rate was followed in the usual manner up to the time the reaction was interrupted. The rate constants have been given in a previous table.

Table II shows the results of the analyses expressed as moles of products per 100 moles of azomethane decomposed. The data given in columns 2, 3, 4, and 12 represent averages of the individual experiments indicated by the numbers given in column 1. The temperature and pressure for the individual experiments were given in Table I.

As the pressure on the sample was raised to atmospheric, a condensation was noted as fog. This, of course, caused a contraction in the volume of gas measured. Also, when the distillation had been completed, small amounts of a liquid could be seen on the lower part of the distillation column. This again represented a loss of products. The total of these two losses has been given in Table II as "liquid."

These data show that in all cases methane was formed to a larger extent than ethane, contrary to the conclusion of Ramsperger but in qualitative agreement with a note by Forbes and Heidt.[11] Furthermore, the presence of appreciable quantities of material heavier than azomethane casts some doubt upon the decomposition of azomethane being a simple, straightforward, unimolecular reaction. The production of the heavy material is apparently just sufficient to offset the methane production, so that, over all, the volume increase upon completion of the reaction is 1.1. The data in column 11, however, indicate that the lower the extent of the decomposition the lower is the number of molecules of products per molecule of azomethane decomposed. If such a trend was maintained down to 10% decomposition, the rate constants given previously may be seriously in error, since it was assumed in the calculation that each molecule of azomethane always gave 2.1 molecules of products regardless of the extent of the decomposition.

Comparison of the last two columns of Table II shows that the actual amount of azomethane reacted is larger than that indicated by the pressure changes for the four cases of partial decomposition.

Apparently in the range from 50 to 80% decomposition somewhat less than 70% of the nitrogen of the decomposed azomethane is evolved as such. Presumably the remainder of the nitrogen is combined in the liquid. Likewise, a carbon and hydrogen balance shows that carbon and hydrogen were lost to the liquid. A microanalysis of the accumulated liquid showed: carbon 63%; nitrogen 29%; hydrogen 8%. Assuming the liquid to be a single compound the formula $C_5H_8N_2$ is indicated.

The yield of methane appears to increase with the extent of the decomposition, while ethane remains about constant. The liquid production appears to decrease with increase in decomposition of azomethane. Ethylene was found only in the case of complete decomposition, and then in very small amounts, with the exception of experiment 77–79. In the latter experiment the disproportionately large ethylene yield was undoubtedly due to analytical error, since the methane production was also out of line.

Figure 1 is a plot of the moles of product per 100 moles of azomethane decomposed against the percentage decomposition. Experiment 77–79 has been omitted from the graph, and the points for 100% decomposition are averages for the other three experiments.

[11] Forbes and Heidt, THIS JOURNAL, 57, 2331 (1935).

An interesting possibility brought out by Fig. 1 is that the extrapolation of the liquid production to zero decomposition indicates about 0.5 mole of liquid per mole of azomethane. Similarly, nitrogen production approaches the same limit. On the basis of these two products it might appear that the initial act is the bimolecular combination of two molecules of azomethane with simultaneous splitting off of a molecule of nitrogen. The other products could be accounted for as further degradation products of the heavy molecule from the bimolecular combination. Such a scheme is compatible with the disappearance of the heavy compound. The ethane production, however, is apparently independent of the extent of the decomposition and cannot thus be accounted for.

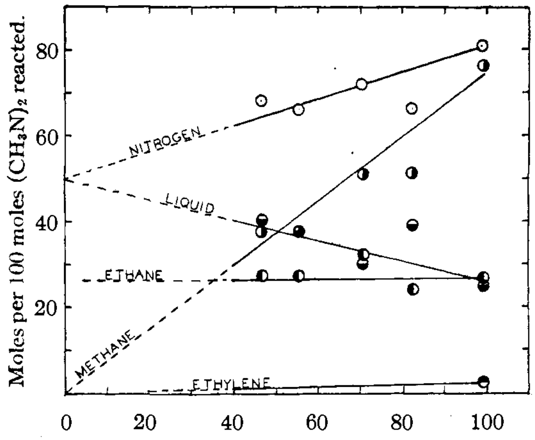

Fig. 1.—Decomposition products of azomethane: ○, nitrogen; ◑, methane; ◓, ethylene; ◐, ethane; ◒, liquid.

Of interest in this connection is a statement made by Emmett and Harkness[12] with regard to the thermal decomposition of *sym*-dimethylhydrazine at 350°. "The products of the thermal decomposition indicated a very complex reaction. They were principally methane and nitrogen together with considerable quantities of ethane, and of some water soluble material." They determined the products at complete decomposition, and the above quotation accurately describes the corresponding results with azomethane, except that what they have called "water soluble material" has been found here to be a liquid at room temperature. Emmett and Harkness concluded that, based on pressure changes, the decomposition was a first-order reaction, but abandoned work upon it due to its apparently complex nature.

Reaction velocity constants have been calculated for the partial decomposition experiments from the azomethane disappearance as determined by analysis. For comparison, the rate constants calculated from the manometric observations have been averaged. Table III shows these several values, together with the ratios of the constants.

Table III

Reaction Velocity Constants

Expt.	P_i	K_p	K_A	K_A/K_p	% decomposed (analysis)
103–109	125	6.7	10.1	1.51	47
97–102	158	7.5	12.7	1.70	56
91–96	124	6.4	9.1	1.42	71
89–90	156	7.8	13.5	1.73	83

K_p Constant calculated from pressure change.
K_A Constant calculated from azomethane remaining.

It appears that, while appreciably higher, the K_A values are about as constant as the K_p values in the four experiments. There is no apparent relation between the extent of decomposition and any of the constants, so that so far as these experiments show the decomposition of azomethane conforms to the unimolecular law.

There is, however, a curious relationship between the constants calculated in the two different ways. If K_p is plotted against K_A an excellent straight line is obtained which has a slope of 3.2. This relation may be fortuitous.

Summary

The reaction velocity constants of the thermal decomposition of azomethane have been determined at 340° by following (a) the pressure changes (K_p), and (b) the composition of the reaction mixture (K_A). The constants calculated from the amount of azomethane decomposed are about 50% higher than the constants calculated from pressure measurements.

The composition of the reaction mixtures at 50 to 100% decomposition has been determined. The decomposition is apparently complex, the products being nitrogen, methane, ethane, and a higher molecular weight compound containing nitrogen. In spite of the complexity, the decomposition at 340° apparently follows the unimolecular law.

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[12] Emmett and Harkness, This Journal, 54, 543 (1932).