[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Thermal Decomposition of Ethyl Azide: A Homogeneous Unimolecular Reaction

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An examination of the homogeneous reactions which are accepted as being unimolecular[2] discloses the fact that in each reaction the molecule studied disrupts at several bonds located near the center of the molecule. This behavior is interpreted by recent theories of homogeneous unimolecular reactions[3] as being due to a flow of energy from the entire molecule to the comparatively weak bonds at its center, followed by the rupture of the bonds. A molecule which breaks up at one end would likewise require that there be a flow of energy from all its parts to that end, or it would, due to the impedance of energy transfer through its parts, behave as a more simple molecule made up essentially of the isolated reacting group at that end. Intermediate conditions could, of course, be realized. O. K. Rice[4] has discussed the effect of these possibilities on the dependence of the first order rate constant upon pressure.

Because of the absence of any relevant data on unimolecular reactions characterized by primary decompositions of groups removed from the centers of the molecules, the present investigation was undertaken. The Curtius rearrangement of acid azides which occurs through the loss of a molecule of nitrogen from the azide group is well known, but the simple aliphatic acid azides have not been isolated. Curtius[5] has studied a somewhat similar reaction in solution, the decomposition of benzil azide, and postulated that the reaction proceeded through the splitting out of a molecule of nitrogen from the azide group, the residue rearranging. Ramsperger[6] made some preliminary experiments on methyl azide, and found that this compound decomposed into hydrazoic acid and ethylene, leaving the azide group intact. Ethyl azide, as being the next most simple aliphatic azide and as promising to behave like benzil azide, was chosen for the present study. Ethyl azide has been found to decompose in the gas phase with measurable rate at 200°.

Nature of the Reaction

Various experiments were made to determine the products of the decomposition of ethyl azide. When this compound decomposes at constant volume and constant temperature the final pressure is 1.81 times the initial

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[1] National Research Fellow in Chemistry.

[2] See, for example, Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1932.

[3] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

[4] Rice, *Z. physik. Chem.*, **B7**, 226 (1930).

[5] Curtius, *J. prakt. Chem.*, **63**, 428 (1901).

[6] Ramsperger, THIS JOURNAL, **51**, 2134 (1929).

pressure. This ratio is independent of temperature over the range here investigated (200–240°) and is also independent of initial pressure in our experiments (from 0.08 to 19.5 cm.). For example, the experimentally determined ratio was 1.808 at 219.4°, 1.812 at 229.4° and 1.805 at 239.6°. At 219.4° it was 1.800 at 19.5 cm. initial pressure, 1.815 at 7.45 cm., 1.808 at 3.64 cm. and 1.810 at 0.08 cm. The ratio was not dependent on the preparation of ethyl azide, since two entirely independently prepared samples, one of which was somewhat more carefully fractionated than the other, gave identical results. Also, the ratio did not change during the course of the experiments, during which time over half of the original sample was exhausted. These latter facts tend to indicate that the compound used was comparatively pure.

Freezing out experiments were made after complete decomposition of several samples of ethyl azide at 230°. The procedure was briefly as follows. The initial pressure was measured at 23°, the reaction vessel was surrounded by an air-bath and the sample decomposed. The air-bath was removed and the reaction vessel was allowed to cool to room temperature, at which point some solid condensed out. During decomposition condensation of solid products in the side tubes leading to the flask was prevented by the use of 30 cm. of capillary tubing of one and one-half mm. bore which was also heated in the bath. A tube of 15 mm. diameter, sealed to the bottom of the reaction vessel, was surrounded by a carbon dioxide–ether mixture; subsequently by liquid air. Pressures were read repeatedly until equilibrium had been apparently established. The cooling bath was left in position for a longer period of time, up to several hours, and the final reading made. This agreed within several per cent. with the equilibrium reading previously taken.

The data in Table I are the results of these experiments, numbers 1 and 2 being made with the first prepared sample of ethyl azide, number 3 with the second preparation. Pressures have been corrected for the volume of the tube immersed in the baths.

TABLE I

RESULTS OF FREEZING OUT EXPERIMENTS

	1	2	3
$P_{\text{initial}, 23°}$, cm.	6.46	2.12	2.90
$P_{23°}$, cm.	8.72	2.81	
$P_{-78°}$, cm.	7.29	2.45	3.33
$P_{-183°}$, cm.	5.46	1.76	2.52
$\frac{P_{23°} - P_{-78°}}{P_{\text{initial}}}$	0.22	0.17	
$\frac{P_{-78°} - P_{-183°}}{P_{\text{initial}}}$	0.28	0.32	0.28
$\frac{P_{-183°}}{P_{\text{initial}}}$	0.85	0.83	0.87

These results indicate that for every mole of ethyl azide decomposed there is formed 0.20 mole of product which condenses between room temperature and −78°, 0.29 mole which condenses between −78 and −183°, and 0.85 mole which does not condense at −183°. By difference, since each initial mole gives 1.81 moles of product, 0.48 mole is condensed out at 23°.

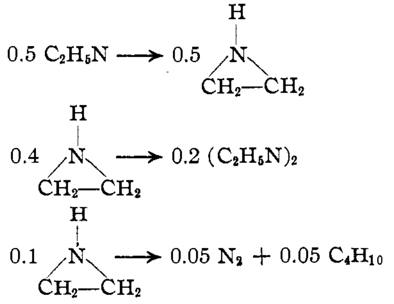
In addition to these experiments several samples of ethyl azide were completely decomposed and the products were frozen out with liquid air and titrated with 0.01 normal hydrochloric acid, using methyl orange as indicator. Two such experiments gave 0.64 and 0.655 equivalent of base per mole of ethyl azide decomposed. Hydrazoic acid was tested for by freezing out, neutralizing the base present, acidifying with acetic acid, and adding silver nitrate solution. A precipitate, presumably silver azide, resulted. To another neutral solution, prepared by freezing out as above and neutralizing with dilute hydrochloric acid, a solution of ferric nitrate was added. The deep, cherry red color due to ferric azide immediately formed. Finally, some of the solid product which condensed out upon pumping out the reaction cell was collected and its melting point taken. The substance softened at 84° and melted at 85.5°.

From these data it is possible to write down reactions which are consistent with all the facts, but which are not necessarily the only reactions which can explain them. The momentary formation of a radical such as C_2H_5N introduces into the reaction system many possibilities for reaction of its rearrangement product, such as polymerization and further decomposition. It must be emphasized that these subsequent reactions do not affect in the least the kinetics or interpretation of the unimolecular decomposition of ethyl azide. We can write the following stoichiometric equations

$$0.2\ C_2H_5N_3 \longrightarrow 0.2\ C_2H_4 + 0.2\ HN_3 \qquad (1)$$

$$0.8\ C_2H_5N_3 \longrightarrow 0.8\ C_2H_5N + 0.8\ N_2 \qquad (2)$$

$$0.3\ C_2H_5N \longrightarrow 0.3\ CH_3{-}CH{=}NH \qquad (3)$$



(4)

(5)

(6)

Reaction (1) is plausible, since we have definitely proved the presence of HN_3 and since methyl azide behaves in similar fashion. Ramsperger[5] has investigated the thermal decomposition of hydrazoic acid and finds that it decomposes slowly at 290°. Only a very small fraction of that present would decompose at the temperature of our experiments during the time required for complete decomposition of ethyl azide. Reaction (2) is undoubtedly the principal reaction. It is analogous to the first step of the Curtius rearrangement, and corresponds to the first step in the decomposition of benzil azide. Reaction (3) is definitely known to occur. Ethylidene imine exists in the solid state as a trimer[7] with melting point of 85°. It is monomolecular at 260° as Delépine has determined by vapor density measurements. On hydrolysis it would yield acetaldehyde ammonia and would titrate one equivalent of acid per nitrogen atom present. The melting point of the solid product isolated from the decomposition of ethyl azide agrees with that given for ethylidene imine, and the independence of the ratio 1.81 on temperature and pressure indicates that in the gas phase there is no equilibrium between monomer and polymer. Reaction (4) leads to a product which has been arbitrarily written as ethylene imine. It might be any unsaturated nitrogen compound other than ethylidene imine which results from the instantaneous rearrangement of the C_2H_5N radical. Since reaction (3) is unimolecular and reactions (5) and (6) are bimolecular it has been necessary to introduce reaction (4) to account for the independence of the final–initial pressure ratio upon pressure. Reactions (5) and (6) are very fast bimolecular reactions between the unstable product of (4). Reaction (6) results in further decomposition, reaction (5) in polymerization. The polymerization is a very likely reaction, due to the nature of the unsaturated compound formed in (4). What the polymer is cannot be said, but it could very probably be the stable six-membered ring compound, piperazine. It is known that in the preparation of N-methylethylene-imine there is always formed some dimethylpiperazine.[8] Piperazine is dibasic and would titrate one equivalent of acid per atom of nitrogen.

To summarize, according to the above reactions one mole of ethyl azide gives, on decomposition, 0.85 mole of nitrogen, 0.20 mole of hydrazoic acid, 0.20 mole of ethylene, 0.05 mole of butane, 0.30 mole of ethylidene imine, and 0.20 mole of polymer. The ratio of initial to final pressure is 1.80. If the polymer is dibasic, as, for example, piperazine is, each mole of ethyl azide would give 0.70 equivalent of base. Titration gives 0.65. With methyl orange as indicator the hydrazoic acid should at most neutralize only a few per cent. of the base present. A correction for this might raise the experimental value to 0.70 equivalent per mole. At room temperature the ethylidine-imine and the polymer would condense out. They constitute 27.8% of the products and experimentally 26.6% is found. From 23 to −78° the hydrazoic acid would come out. It is 11% of the products and experimentally 11% is obtained. Between −78 and −183°, the butane and ethylene, 14% according to the equations above, condense.

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(7) Delépine, *Compt. rend.*, **125**, 951 (1927).

(8) Knorr, Hörlein and Roth, *Ber.*, **38**, 3137 (1905).

Experiment gives 16%. The nitrogen, 47.3%, would remain as a gas at −183°. This agrees with the 47.0% found in the experiments. No claim is made that all of the reactions given above certainly occur as written.

The Preparation of Ethyl Azide

Ethyl azide was prepared according to the directions of Staudinger and Nauser.[9] The material was dried over calcium chloride and fractioned several times, the fraction boiling from 48.6–49.0° being retained. This constituted over half of the original sample. The only impurity likely to be found in this preparation is ethyl alcohol which boils some 28° higher. The ethyl azide was contained in a trap which was sealed to the high vacuum line and separated from it by a capillary stopcock. It was freed of dissolved gases by freezing it with liquid air, pumping out the trap, allowing it to warm up, and repeating the operation several times.

Kinetics of the Reaction

Apparatus and Procedure.—The rate of decomposition was followed by the increase of pressure at constant volume. The Pyrex reaction flask of 300 cc. volume was kept in an oil-bath, the temperature of which was automatically controlled to 0.05°. The thermometer was graduated into 0.2° intervals and was read through a magnifying lens.

Since some of the products of the reaction are solid at room temperature, it was necessary to provide against their condensation in the side tubes leading to the high vacuum line and to the clicker system used in measuring the pressure. This was successfully accomplished by using capillary tubing as leads to the capillary stopcock to the vacuum line and to the clicker. In each of these leads about 30 cm. of capillary tubing, joined directly to the reaction vessel and in the shape of a U-tube, was heated in the oil-bath. It was found that shorter lengths of capillary tubing so heated were equally effective since with 10-cm. lengths there was also no evidence of condensation. The independence of the 1.81 ratio upon pressure is good evidence of this, since the rate of diffusion of products into the cold tubing would vary considerably over the pressure range studied. Solid products condensed out upon pumping out the reaction vessel, and it was necessary occasionally to replace the capillary tubing leading to the vacuum line. Pressure measurements were made with a clicker system. Such a system is described elsewhere.[10] In experiments 1 to 31 pressures were read directly on a mercury manometer. In experiments 31 to 44 the clicker with click constant of 1.103 cm. was placed in series with a small McLeod gage having magnifications of 10 and 20 fold in the pressure readings. This clicker appeared to be reproducible to 0.001 cm. The supply was connected by capillary tubing to the lead to vacuum on the reaction vessel side of the stopcock. Since the total volume outside of the bath was only about 1% of the volume of the reaction vessel, no corrections have been applied in the pressure readings.

In making a run the cell was evacuated to 10^{-4} mm. or better, the stopcock to the vacuum line was closed, and the stop watch started when the stopcock to the supply was opened. The latter was closed when sufficient pressure had been judged to be built up in the reaction vessel; air was then let in upon the clicker. When this clicked, the time was taken and the pressure read. Pressure readings were taken at intervals thereafter, the intervals being chosen to give roughly the same amounts of decomposition and therefore lengthening out as the run progressed. The first measurement usually took from twenty to thirty seconds. Initial pressures were obtained by extrapolation when necessary. The extrapolation was usually only about 2 or 3% even at the higher tem-

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(9) Staudinger and Nauser, *Helv. Chim. Acta*, **4**, 872 (1921).

(10) Smith and Taylor, THIS JOURNAL, **46**, 1393 (1924). For a diagram, see Leermakers and Ramsperger, *ibid.*, **54**, 1837 (1932).

peratures. At 239.6° it was often more convenient and more accurate to allow the reaction to go to completion and obtain the initial pressure from the final pressure.

Experimental Data

The partial pressure of ethyl azide, P_A, was calculated for each reading by the expression $P_A = (1.81\,P_0 - P)/0.81$, where P_0 is the initial pressure at zero time and P is the total pressure at that reading. The factor 1.81 is required because the final pressure is 1.81 times the initial pressure. First order constants were calculated by the interval method, using the equation

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

where P_{A_t} is the partial pressure of ethyl azide at time t and $P_{A_{t'}}$ is its partial pressure at time t'. First order rate constants were calculated for from 3 to 9 intervals (depending on the temperature) and until decomposition was from 40 to 90% complete. Since the earlier experiments showed that there was no trend in the individual constants up to 90% decomposition, the slow runs were in some cases not carried beyond 40%. In Table II are given the data for several typical runs.

TABLE II

DATA FOR RUNS

Run Number 2; $P_{\text{final}}/P_0 = 1.815$; $T = 219.4°$; $P_0 = 7.45$ cm.

p, cm.	P_A	t, sec.	$k_1 \times 10^4$
7.54	7.33	35	4.47
7.87	6.93	161	5.01
8.21	6.50	287	4.48
8.60	6.03	451	4.56
9.12	5.39	701	4.71
9.67	4.71	985	4.58
10.37	3.86	1419	4.67
11.12	2.94	2000	4.58
11.77	2.14	2693	4.75
12.51	1.23	3856	
13.51	0.00	∞	

Run number 39; $P_{\text{final}}/P_0 = 1.808$; $T = 219.4°$; $P_0 = 0.0810$ cm.

p, cm.	P_A	t, sec.	$k_1 \times 10^4$
0.0815	0.0802	15	2.88
.0855	.0754	235	2.24
.0900	.0698	577	4.23
.0970	.0611	890	2.99
.1035	.0531	1360	2.95
.1090	.0463	1793	
.1465	.0000	∞	

Table III is a summary of all the runs.

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 with the exception of number 33 has been given. In number 33 some unaccountable irregularities occurred; this run has been excluded.

As can be seen from Table II there is no trend in the individual first order rate constants during an experiment. This is true for all of the runs, even though some were carried as far as 85% to completion. In experiments 23 to 30 inclusive, and in 43 and 44, the surface to volume ratio was increased 13-fold by packing the reaction vessel with Pyrex tubing.

TABLE III

SUMMARY OF ALL EXPERIMENTS

Number	Temp., °C.	Init. press., cm.	% decomposed	Number of constants	Average devn., × 10^4	$k_1 \times 10^4$, sec.$^{-1}$
20	199.4	7.98	61	7	0.04	0.75
21		7.50	43	6	.03	.97
22		7.16	30	5	.02	.82
19	209.4	10.11	58	7	.07	2.09
14		7.76	76	7	.04	1.80
17		6.19	62	6	.07	2.17
16		5.82	42	7	.12	1.87
18		3.98	61	8	.19	1.98
15		3.77	62	8	.04	2.25
3	219.4	19.46	85	9	.14	4.93
6		16.70	72	7	.13	4.60
4		9.89	69	7	.07	4.77
2		7.45	84	9	.12	4.65
31		4.70	50	6	.05	4.54
1		3.64	77	7	.23	4.62
5		3.01	55	6	.15	4.66
34		1.76	50	6	.17	4.57
35		0.948	48	5	.13	4.43
32		.513	49	5	.16	4.16
36		.318	56	7	.39	3.92
38		.230	59	4	.32	3.71
37		.091	46	5	.60	3.08
39		.081	43	5	.47	3.06
7	229.4	13.20	92	9	.13	10.53
9		5.67	73	4	.06	10.49
8		1.48	79	6	.75	10.49
12	239.6	17.48	73	4	.50	23.3
13		14.75	75	4	.35	23.3
10		5.73	85	7	1.3	22.3
11		4.28	66	5	0.88	21.5
42		1.17	85	3	.31	19.6
41		0.658	83	3	1.18	19.0
40		.139	80	3	1.80	15.5
Added Surface, 13 Times Original						
27	209.4	13.56	35	5	0.08	1.75
28		10.73	38	4	.02	1.92
26		9.45	42	5	.04	1.64
23	219.4	11.35	73	9	.07	4.32
24		8.74	71	9	.11	4.28
44		0.634	42	4	.11	3.96
43		.382	24	3	.39	3.87
25	229.4	10.34	65	7	.09	9.64
29	239.4	9.93	83	4	.5	21.3
30		9.04	83	5	.6	21.3

Discussion and Interpretation of the Results

This reaction exhibits the behavior of a true unimolecular reaction, *i. e.*, a true first order rate constant independent of pressure only at high pressures, and at sufficiently low pressures a decrease in rate constant with decreasing pressure.

In Fig. 1 is plotted the usual log k_1–$1/T$ relationship. Only those experiments carried out at high pressures where the rate constant has become independent of pressure have been used in this plot. The high pressure value has been taken as the average, for a given temperature, of all experiments made above 3 cm. initial pressure, except at 239.6°, where it has been taken as the value found at 15 cm. At the lower temperatures, 199.4 and 209.4°, the average rate constants do not agree very well from run to run, although during the run the individual constants are fairly steady; no reason is known for this behavior. Air was let into the cell twice during the experiments at 209.4°; this may account for part of the fluctuations although at the higher temperatures the condition of the reaction vessel appeared not to affect the rates. The average rate constants of the experiments at each of these two temperatures is taken as the high pressure rate constant. All of the high pressure rate constants may be slightly lower than the true asymptotic values. The upper line in Fig. 1 is for the unpacked reaction vessel, the lower line is for the vessel whose surface–volume ratio has been increased 13-fold. The two lines are, within the experimental error, parallel, and give a heat of activation of 39,740 calories. The equation for the high pressure rate in the unpacked vessel is $k_\infty = 2.00 \times 10^{14}e^{-39,740/RT}$

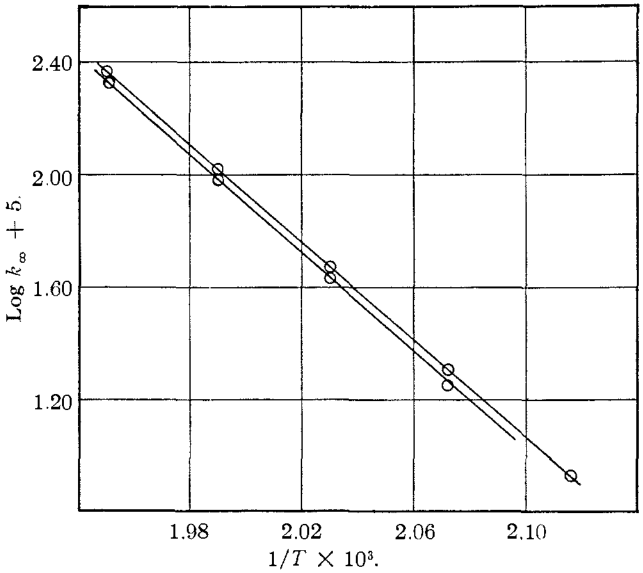

Fig 1.—Plot of reciprocal temperatures against logarithms of the high pressure rate constants. The upper line is for the unpacked reaction vessel; the lower line is for the vessel whose surface to volume ratio has been increased 13-fold.

One of the most striking features of this reaction is the effect of surface upon the rate. There is a definite, small decrease in rate upon increasing the surface. This effect is independent of temperature and, within experimental error, of pressure; the latter is shown by experiments 43 and 44. At the pressures of these two experiments the rate constants would be 4.30 and 4.01×10^{-4}, respectively, in the unpacked vessel. That the decrease in rate is not accidental is shown by experiments 31 and 34, in which the added surface had been removed. The rate constant came up to its previous value. It dropped again when the surface was added in experiments 43 and 44. The ratio of initial to final pressure was found to be 1.805 in experiment 25. The individual constants did not drift during a given experiment, even when in some instances decomposition was allowed to proceed 80% to completion. In all respects the behavior was the same in the packed and unpacked vessels. The decrease in rate here observed is about 9%, so that doubling the surface should (assuming proportionality between rate and surface) cut down the rate of decomposition less than one per cent. The author can think of no explanation for this behavior. It cannot be due to the conduction of heat from the hot decomposing gas by the added surface, since the effect should be greater at higher temperatures. This is not true as can be seen from Fig. 1.

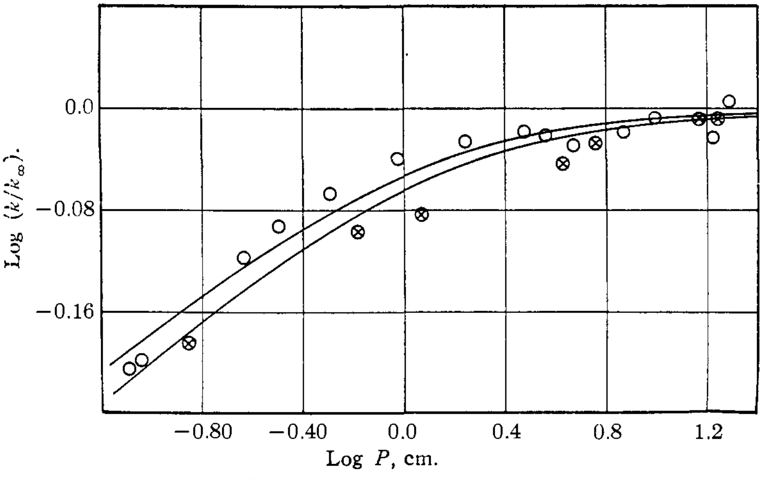

Fig. 2.—Plot of log k/k_∞ against log P. The circles are for the experiments at 219.4°; the circles enclosing crosses are for the experiments at 239.6°. The curves are theoretical.

Figure 2 is the usual log k/k_∞, log P plot for the experiments at 219.4 and 239.6°. The circles are the experimental points for the lower temperature, the circles enclosing crosses are for 239.6°. The values for k_∞ have been taken slightly higher (about 3%) than those used in determining the heat of activation in order better to fit the theoretical curves. This procedure is not unjustified. The theoretical curves are those obtained by graphically integrating the final expression given by Kassel.[3] In this equation σ, the molecular diameter, has been taken as 6.21×10^{-8} cm. and S, the number of oscillators in the molecule, as 14. A is 2.00×10^{14} and E_1 is 39,740 cal. per mole. The upper curve is for 219.4° and the lower one for 239.6°. Since the rate has fallen off only 40% at the lowest pressure studied the plot is very sensitive to experimental error; for example, the experiments at 239.6° and 0.3 and 0.6 cm. pressure differ from the theoretical curves by about five per cent. From the plot it may be seen that the rate falls off more rapidly at the higher temperature, in agreement with the theories. At 219.4° there is definitely a greater falling off at low pressures than is predicted by the theories although the discrepancy is not great. This discrepancy would appear to increase at still lower pressures.

The maximum number of oscillators possible in a molecule of ethyl azide is twenty-four. The number found best to fit the data is fourteen, approximately one-half of those possible. It has been found that to explain the decomposition of azomethane[11] twelve out of a possible twenty-four oscillators are required. The molecular diameter chosen was 6×10^{-8} cm. It is seen that in both molecules about one-half of the possible oscillators are excited. The difference in the structures of azomethane and ethyl azide, but particularly in the locations of their reactive parts makes this fact of some interest. The similarity of requirements necessary for the theoretical explanation of their decompositions adds support to the theories.

The author wishes to express thanks to Professor G. B. Kistiakowsky for the generous advice given by him during this investigation, and for the facilities which have made possible its prosecution.

Summary

1. The thermal decomposition of ethyl azide has been studied at temperatures from 199.4 to 239.6°, and from pressures of 0.08 to 19.5 cm.

2. The reaction has been found to be first order at high pressures, but the rate constants decrease with decreasing pressure below 2 cm. initial pressure. The high pressure rate is given by the expression $k_\infty = 2.00 \times 10^{14}e^{-39,740/RT}$.

3. Increasing the surface–volume ratio of the reaction vessel has been found to cause a slight but definite decrease in the rate constants.

4. To fit the data best to the theoretical expressions relating rate constant and pressure a molecular diameter of 6.2×10^{-8} cm. and fourteen classical oscillators are required.

5. The similarity between the numbers of oscillators required to explain the decompositions of ethyl azide and azomethane, two molecules which

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[11] Ramsperger, THIS JOURNAL, **49**, 1495 (1927); Rice and Ramsperger, *ibid.*, **50**, 617 (1928).

decompose in very different parts, is considered additional evidence in support of theories of homogeneous unimolecular reactions.

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The Dissociation of Water in Strontium Chloride Solutions at 25°

BY JOHN E. VANCE

The electromotive forces of the cells

$$H_2 \mid Sr(OH)_2(m_1),\ SrCl_2(m_2) \mid AgCl \mid Ag$$

are given by the equation

$$E = E_0 - 0.05915 \log \gamma_H \gamma_{Cl} m_H m_{Cl} \tag{1}$$

Substituting the equilibrium constant for the dissociation of water

$$K_W = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_H m_{OH} \tag{2}$$

and rearranging, the equation

$$E - E_0 + 0.05915 \log \frac{m_2}{m_1} = -0.05915 \log K_W a_{H_2O} - 0.05915 \log \frac{\gamma_H \gamma_{Cl}}{\gamma_H \gamma_{OH}} \tag{3}$$

results. Knowing $E_0 = 0.22239$,[1] we can, by measuring the cell designated above with varying values of m_2 and a single suitable value of m_1, and by determining separately $\gamma_H \gamma_{Cl(m = 0)}$ in strontium chloride solutions of the same total ionic strength, make an extrapolation, plotting the left side of equation (3) against μ and obtain a value for K_W at zero ionic strength.

Subsequently K_γ may be calculated by rearranging equation (3)

$$\log K_\gamma = \log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log m_2/m_1}{0.05915} + \log K_W + \log \gamma_H \gamma_{Cl} \tag{3a}$$

Finally, values of $m_W = m_H = m_{OH}$, $\gamma_H \gamma_{OH}$, and $\gamma = \sqrt{\gamma_H \gamma_{OH}}$ may be obtained from equation (2) after values of a_{H_2O} are calculated from a suitable source.

This process or an essentially similar one has been used to determine K_W accurately and to find K_γ in several aqueous salt solutions of cesium,[1b] potassium, sodium,[2] lithium,[3] and barium chloride,[4] as well as of potassium and sodium bromide.[5]

Measurement of the Cells $H_2 \mid Sr(OH)_2(m_1),\ SrCl_2(m_2) \mid AgCl \mid Ag$.—The determinations were made in the customary manner in the usual type of

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[1] (a) Roberts, THIS JOURNAL, **52**, 3877 (1930); (b) Harned and Schupp, *ibid.*, **52**, 3892 (1930); (c) Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[2] Harned, *ibid.*, **47**, 930 (1925).

[3] Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and Copson, *ibid.*, **55**, 2206 (1933).

[4] Harned and Mason, *ibid.*, **54**, 3112 (1932).

[5] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).