a greater number of polar groups, rather than to the formation of zwitter ions, is not conclusively answered by the present results. Nevertheless, in a general way they are against it. The moment obtained for the ester of glycylglycine is only half again as great as that of the ester of glycine itself. On the other hand, in contrast to this, the data on the dielectric constant indicated that the electric moments of the peptides in aqueous solution were directly proportional to the number of glycine units in the molecule, as if due to the formation of zwitter ions. It is unfortunate that their great insolubility in non-polar solvents makes it impossible to measure the moments of the esters of the higher peptides.

V. Summary

Highly approximate values of the electric moments of amino acids and peptides have been obtained from measurements on solutions of the esters in benzene. An analysis of these results furnishes additional support for the zwitter ion hypothesis.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Kinetics of the Unimolecular Dissociation of Gaseous Ethyl Bromide[1]

BY ELVIN L. VERNON AND FARRINGTON DANIELS

A search for unimolecular reactions has been in progress in this Laboratory for several years. Another communication[2] describes the thermal decomposition of several organic compounds and, of these, the dissociation of ethyl bromide was selected as the reaction most promising from a theoretical standpoint. It has been subjected to further intensive study as described in this article.

In the first investigation[2] it was established, experimentally, that the reaction is

$$C_2H_5Br \rightleftharpoons C_2H_4 + HBr$$

and various ways of calculating the rate of dissociation were discussed. The course of the reaction was followed in both researches by measuring the pressure as a function of time, using glass diaphragms[3] and all-glass or all-quartz vessels, totally immersed in a lead bath. In the present investigation the measurements were carried to lower pressures for the purpose of testing recent theories of unimolecular reactions and an improved method

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[1] Further details of this investigation may be obtained from the Ph.D. thesis of Elvin L. Vernon filed in the Library of the University of Wisconsin in June, 1932.

[2] Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

[3] Daniels, THIS JOURNAL, **50**, 1115 (1928).

of calculation was used. The accuracy was increased by a thermostatic control, using a photoelectric cell, and by carefully testing for minute leaks before each determination.

Experimental Procedure

The thermostat consisted of an insulated iron box containing well-stirred, molten lead.[2] Considerable elasticity in the arrangement of heaters was necessary in order to insure fine temperature control over a wide range and to eliminate wasted heat in external resistances. Only a small amount of current passed through the intermittent heater, the main heating being produced by various series and parallel combinations of seven independent coils controlled by twelve switches. Each unit comprised 16 ohms in the form of a helix of No. 18 nichrome wire wound around the inside of the "transite" box and covered with "alundum" cement. With this arrangement, twenty-three different switch combinations were used to give graded inputs of energy ranging from 112 to 1300 watts with a minimum current (never exceeding 4.5 amp.) through any one heater.

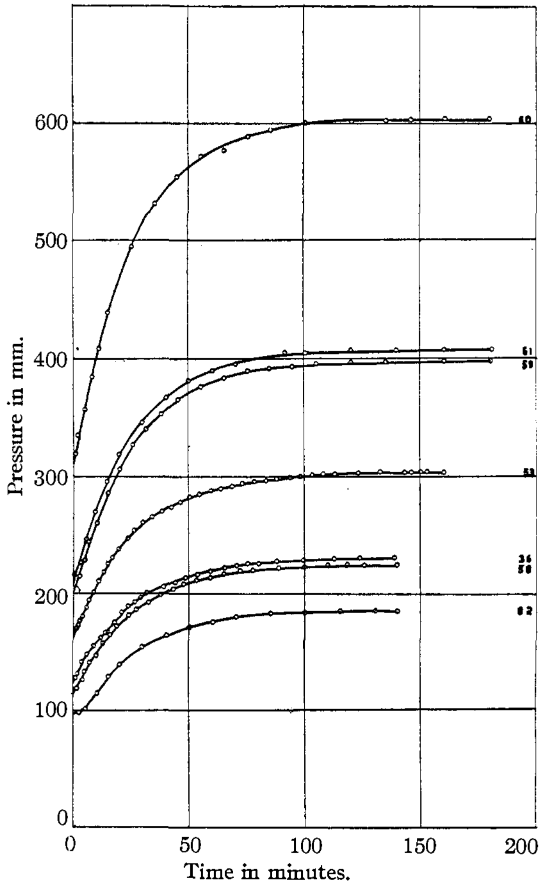

Fig. 1.—High pressure, 395°.

The temperature was determined and maintained constant with a platinum resistance thermometer and precision bridge. A photoelectric cell was set behind a narrow slit at the zero point of the galvanometer. A beam of light from a 500-watt projection lamp was reflected from the mirror of the galvanometer and passed back and forth across the cell as the temperature of the bath rose and fell. It controlled the intermittent heater through a two-stage amplifier (71A and 01A tubes) and a sensitive relay which operated a special switch. This switch was designed to offset the time lag in the controlling apparatus by closing the heating circuit only on alternate excitations. It was arranged with a spring contact pressing against a brass tilting arm which was snapped back and forth with each pull of the relay armature. Careful balancing with springs and a counterpoise was necessary. One side of the tilting arm had an insert of hard rubber which interrupted the heating circuit. As the thermostat heated up and the galvanometer beam reached the zero point the armature of the relay snapped the arm over to the non-conducting side and turned off the heating current. As it swung past the cell, the armature was released but the contact point still remained on the insulated side of the arm. As the bath cooled the galvanometer beam swung back to the photoelectric cell, thereby pulling the armature and snapping the switch to the conducting side and starting the intermittent heater. When it passed beyond the cell, on the opposite side, the armature was released but the switch was still on the conducting arm. The current remained on until the galvanometer beam swung across the photoelectric cell the third (and fifth, seventh, etc.) time. Temperature plotted against time gave a curve similar to a sine wave but after the control was in operation for half an hour the total fluctuation was less than 0.3°. The large cooling effect produced by placing a cold body in the bath was nearly eliminated by introducing the object at a time when the heating current had just been turned off.

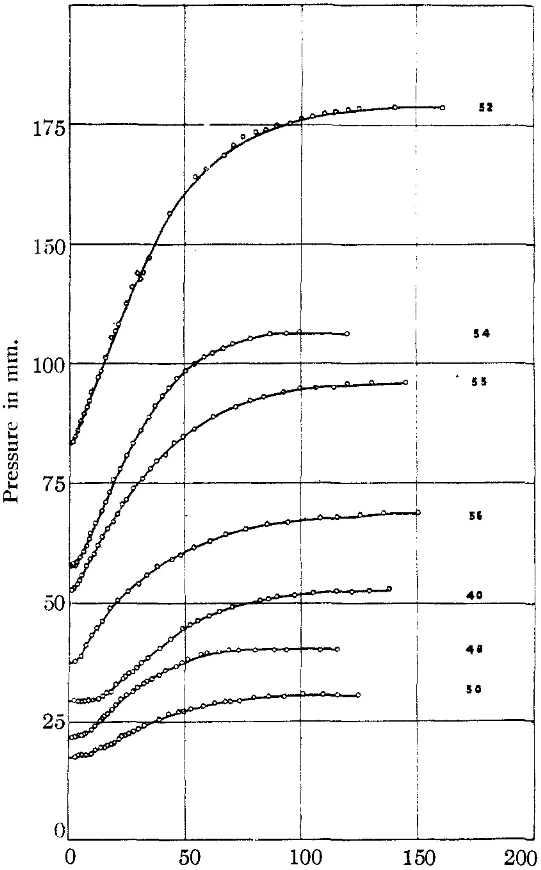

Fig. 2.—Low pressure, 395°.

The flasks and tubes were thoroughly cleaned and rendered free from carbon by heating to redness when filled with oxygen or by boiling with fuming nitric acid and rinsing with distilled water. After cleaning and testing for leaks the 250-cc. Pyrex flask was lowered into position in the lead bath and the zero point of the diaphragm was taken. It was then raised into the cavity above the bath and the side arm was drawn down. The liquid ethyl bromide was previously sealed off under vacuum in a small bulb provided with a capillary tube. A short T-tube with rubber connections was so arranged that the flask could be evacuated while the capillary from the bulb extended well into the side arm of the flask. A wad of asbestos fibers in the connection to the vacuum line filtered out any particles that might be swept into the flask. The flask and newly made connections were tested for leaks with the Tesla coil and when the vacuum was satisfactory the vacuum line was closed off and the tip of the capillary broken. The liquid vaporized at once, the side arm was sealed off and the vessel lowered immediately into position in the lead bath. Pressure readings were then taken. At the end of an experiment the vessel was removed, a rubber tube was placed over the sealed-off tip of the side arm and connected to the vacuum pump. Thus when the flask was opened there was no sudden inward pressure to break the sensitive diaphragm.

The zero point changed with temperature in a specific manner for each diaphragm. In a typical case a zero point of 39 mm. was obtained (*i. e.*, the manometer side of the diaphragm required 39 mm. more air pressure than the vessel side in order to make electrical contact) at 395°. At 300° the zero point was 52 and when reimmersed in the lead bath at 395° the zero point returned to 39 mm., within one and a half minutes. A newly made diaphragm usually showed a slow drift for the first hour in the thermostat but then remained constant for the rest of its life. When the flask was sealed off with 83 mm. of air and immersed in the bath, about five minutes was required to reach a constant pressure with thermal equilibrium in both vessel and lead bath. The first minute and a half was further complicated with changes in the zero point.

It was found[2] that impurities seriously affected the rate of dissociation and so the final measurements, including all those reported here, were made with ethyl bromide purified in the laboratory of Professor Timmermans[4] at Brussels.

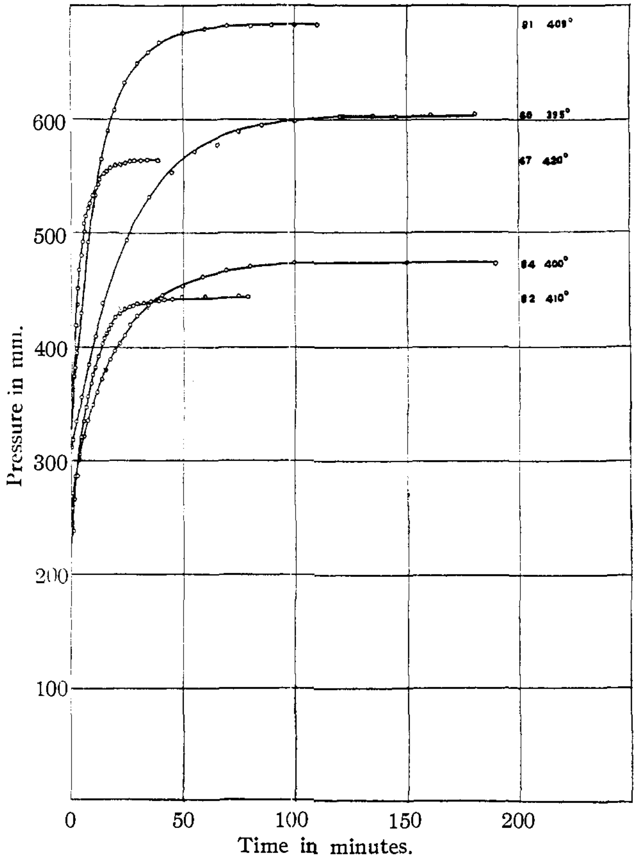

Fig. 3.—High pressure, 395°, 400°, 405°, 410°, 420°.

Tests

It was necessary to exclude every trace of air because oxygen greatly accelerates the decomposition. In one case 10 mm. of air nearly doubled the rate and in another

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(4) Timmermans and Martin, *J. chim. phys.*, **23**, 768 (1926). A few purified organic liquids from Professor Timmermans' laboratory may be obtained through the U. S. Bureau of Standards.

case 2 mm. of air had no additional effect on the final pressure but increased the rate markedly. Parallel experiments at 395° with an empty Pyrex flask and with the same vessel containing a considerable quantity of powdered Pyrex glass gave unimolecular constants of 5.90×10^{-4} and 5.88×10^{-4}, respectively. The close agreement shows that the large excess of glass surface does not affect the reaction rate. The reverse reaction, the combination of ethylene and hydrobromic acid, had apparently become homogeneous, also, at this temperature, for in both cases the constants (calculated as shown later) are approximately 3×10^{-7} sec.$^{-1}$.

It was necessary to have the reaction vessels scrupulously cleaned as already described. If a vessel is allowed to stand in the thermostat for several hours after the reaction is finished, a film of carbon can be seen on the vessel walls. Presumably this film is caused by the decomposition of ethylene into carbon and hydrogen. In all the experiments recorded here the reaction vessel was thoroughly cleaned at the beginning of an experiment and this effect did not start until after the reaction was practically complete. In slow reactions at low temperatures, however, this secondary reaction was sometimes appreciable, but the final pressure was not required in the calculations. When a vessel was not cleaned and a film of carbon from a previous experiment was present, a sudden rise of perhaps 10 mm. in ten minutes was noted after the pressure had nearly reached a stationary value and the curve was nearly flat. Adsorption of gas by the original carbon film and dissociation of one molecule of ethylene into two molecules of hydrogen and solid carbon were probably involved.

Experimental Results

The experimental data are shown in Figs. 1–3 and in Table I.

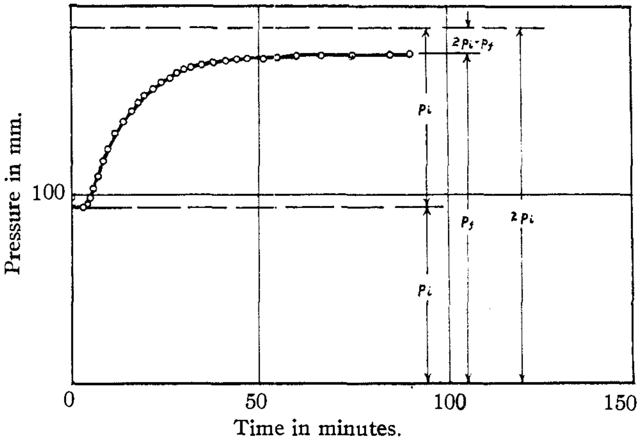
TABLE I

PRESSURE-TIME DATA INTERPOLATED FROM LARGE GRAPHS

Expt.	0	5	10	15	20	40	50	100	15
				Temperature 395° at minutes					
62	98	100	115	127	138	164	171	184	185
53	162	185	207	224	239	271	281	300	303
61	212	237	269	294	317	367	380	405	408
60	309	360	400	421	469	542	562	597	602
50	17.5	17.5	18.2	19.4	20.6	25.4	27.2	30.2	
40	24.1	24.1	24.2	25.2	27.0	35.6	39.5	46.8	
55	52	55.0	59.5	63.8	67.5	80.4	84.7	94.7	
52	83	86.8	93.3	99.6	105.9	127.6	135	156	
				Temperature 405°					
80	94.1	100	125	142	155	172	174		
73	234.3	293	347	381	404	445	452	458	
81	364	438	521	581	609	664	674	683	
86	18–18.5		19.8	21.6	23.5	27.5	27.8		
74	40	49.7	57.2	62.8	67.7	75.2	76.7		
87	67.1	77.5	90.3	100.4	108.6	118.8	119.9		
				Temperature 420°					
66	12.5–13	14.2	17.9	19.3	20.0	20.1			
68	34	41.7	51.7	55.4	56.9	57.6			
63	57.5	72.5	87.3	93.1	96.8	98.8			
64	89	116.7	140.3	156.0	162.7	168.1			

Calculations

The following terms are used in the calculations: p_i = initial pressure, p_f = final pressure, p_t = pressure at any time, t, in minutes, a = initial concentration of ethyl bromide proportional to p_i, and $x = p_t - p_i$ = amount of ethyl bromide decomposed in time t. $p_f - p_t$ would give the partial pressure of ethyl bromide at any time if the reverse reaction was negligible and the final pressure was exactly twice the initial pressure.



$2p_i - p_f = p_{EtBr}$. $p_f - p_i = p_{HBr} = p_{C_2H_4}$.

Fig. 4.—Pressure relations at equilibrium.

From Fig. 4 it is evident that at equilibrium $2p_i - p_f = p_{C_2H_5Br}$ and $p_f - p_i = p_{HBr} = p_{C_2H_4}$. k_1 = rate constant for the reaction $C_2H_5Br \longrightarrow C_2H_4 + HBr$, k_2 = rate constant for the reverse reaction $C_2H_4 + HBr \longrightarrow C_2H_5Br$. K = equilibrium constant $= \frac{k_1}{k_2} = \frac{p_{C_2H_4}\, p_{HBr}}{p_{C_2H_5Br}} = \frac{(p_f - p_i)^2}{2p_i - p_f}$.

When log $(p_f - p_t)$ was plotted against t, it was shown[2] that excellent straight lines are obtained out to nearly 90% dissociation. Some of the data of the present investigation are plotted in this way in the dotted lines of Fig. 5. Ordinarily these straight lines would be taken as proof that the reaction is of the first order and that k_1 is equal to the slope of the line multiplied by 2.303. As shown before[2] the rate constants calculated in this manner are too high by about 20% and they show an abnormal dependence on pressure because they do not allow for the reverse reaction.

Allowing for the reverse reaction, which is bimolecular, the differential equation is

$$dx/dt = k_1(a - x) - k_2x^2 = k_1(a - x) - \frac{k_1}{Kx^2} \qquad (1)$$

and integrating and evaluating the integration constant by setting $x = 0$ when $t = 0$

$$k_1 = \frac{2.303}{t\sqrt{\frac{4a}{K}+1}} \log \frac{\left(\frac{2x}{K}+1+\sqrt{\frac{4a}{K}+1}\right)\left(-1+\sqrt{\frac{4a}{K}+1}\right)}{\left(-\frac{2x}{K}-1+\sqrt{\frac{4a}{K}+1}\right)\left(1+\sqrt{\frac{4a}{K}+1}\right)} \qquad (2)$$

K can be calculated from the initial and final pressures as shown and theoretically this method should be entirely satisfactory. Practically, however, the use of K is uncertain at low pressures and the accuracy is low because slight errors in finding p_i by extrapolation prevent exact calculation of K. Equation (2) is extremely sensitive to slight variations in p_i.

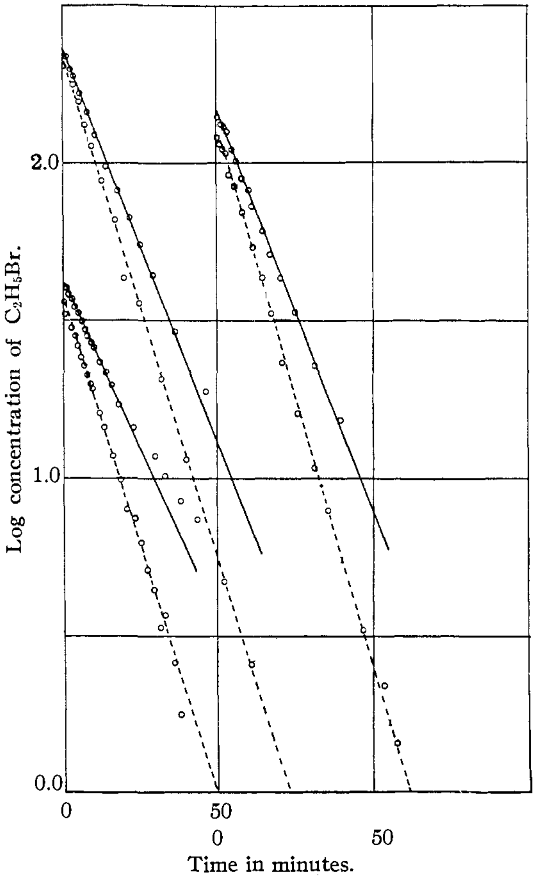


Fig. 5.—Graphs showing first order reaction: full line, log $(2p_i - p_t)$; broken line, log $(p_f - p_t)$.

A more accurate method was devised in which the slope

$$dp/dt = \frac{d(p_t - p_i)}{dt} = dx/dt$$

of the pressure–time curves (Figs. 1–3) was measured graphically at several different times and the true values of k_1 and k_2 solved by least squares in the equation

$$\frac{1}{a-x}\frac{dx}{dt} = k_1 - k_2\frac{x^2}{a-x} \qquad (3)$$

This method is quite satisfactory except at high temperatures or very low pressures where the curve becomes too flat to permit an accurate determination of dp/dt. It gives also a check on the accuracy of the extrapolated value of p_i since the reverse reaction rate k_2 is very sensitive to slight changes in the initial pressure while k_1 is comparatively insensitive under the conditions of these experiments. When the value of the initial pressure is taken too low k_2 becomes negative and since a negative value is physically absurd, a lower limit to the extrapolated value is thus obtained.

A fourth method for calculating k_1 consists in measuring the slope of the straight portion of the graph in which log $(2p_i - p_t)$ is plotted against t. This method is based on the assumption that the reverse reaction is negligible at first and that the reaction starts as if it were going to a final pressure equal to twice the initial pressure. Toward the end of the dissociation a large error is produced by assuming that the final pressure is twice the initial pressure. This method does not involve the use of p_f. In Fig. 5 it is seen that the steeper lines log $(p_f - p_t)$ fit the experimental points excellently well but in spite of this fact the less steep lines log $(2p_i - p_t)$ are more nearly correct even though the points deviate greatly from a straight line in the latter half of the reaction. This fourth method is less accurate than the third, based on the differential method, but it can be used in cases where equation (3) cannot be used, and it is much simpler.

A comparison of the results obtained with the four different methods is shown in Table II for three different experiments to which all the methods could be easily applied.

TABLE II

COMPARISON OF FOUR DIFFERENT METHODS OF CALCULATING k

$k \times 10^4$ sec.$^{-1}$ (395°)

			I	II	III	IV
Expt	p_i	p_f	$\ln(p_f - p_t)$ vs. t	Eq. (2)	Eq. (3)	$\ln(2p_i - p_t)$ vs. t
53	162	303.3	6.75	4.3	5.82	5.70
52	83	153.2	6.18	4.0	5.33	5.29
55	52	95.8	5.08	4.2	4.68	4.73

The close agreement between the independent methods 3 and 4 gives confidence in their validity.

In Table III are given the results of three groups of experiments at different temperatures over a fairly wide pressure range calculated by

TABLE III

CALCULATIONS OF k

395°. $k_\infty = 5.92 \times 10^{-4}$				405°. $k_\infty = 11.1 \times 10^{-4}$				420°. $k_\infty = 25.0 \times 10^{-4}$			
Expt.	p_i mm.	$k \times 10^4$	k/k_∞	Expt.	p_i mm.	$k \times 10^4$	k/k_∞	Expt.	p_i mm.	$k \times 10^4$	k/k_∞
60	309	5.98	1.010	81	364	11.19	1.011	67	308	25.0	1.000
61	212	5.88	0.994	73	234.3	11.23	1.014	64	89	20.8	0.833
59	203	5.90	.996	72	139	10.85	0.980	70	63	17.2	.690
53	162	5.70	.962	80	94.1	11.02	.995	63	57.5	16.0	.640
36	123	5.60	.946	87	67.1	9.02	.815	69	45	13.8	.552
58	116	5.82	.984	83	41.7	7.15	.646	68	34	12.5	.500
62	98	5.66	.956	74	40	6.98	.631	63	23	10.3	.413
52	83	5.29	.893	76	21.7	3.88	.350		24	11.7	.467
54	57.5	4.87	.822			3.67	.422	66	12.5	10.8	.433
55	52	4.73	.799	86	18	3.04	.274		13	11.7	.467
56	37.4	4.20	.710		18.5	3.00	.361			400°	
40	24.1	3.50	.592					84	247	7.67	
48	21.7	3.28	.554							410°	
50	17.5	2.76	.465					82	242	15.3	

method IV or method III. The specific reaction rate k refers to k_1, the corrected forward reaction expressed in sec.$^{-1}$, and k_∞ refers to the average of the high pressure values of k, where k is independent of the pressure.

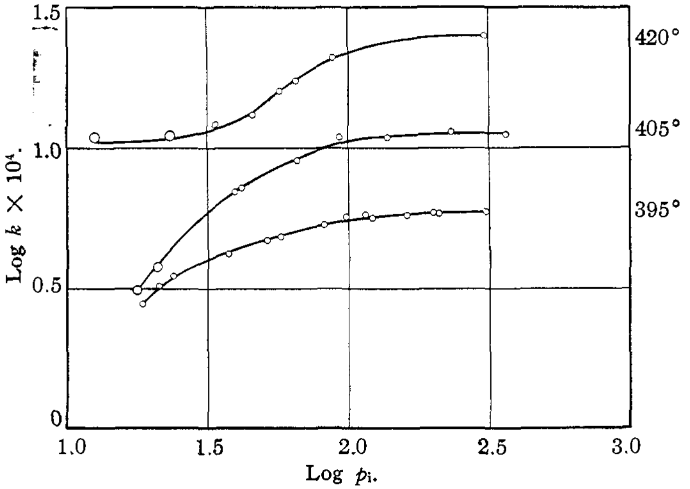


Fig. 6.—Influence of pressure on specific rate,. k.

In Fig. 6 log ($k \times 10^4$) is plotted against log p_i. For higher pressures the rate is independent of pressure. No falling off is observed down to initial pressures in the neighborhood of 125 mm. At 90 mm. and below, the decrease in k is noticeable. With this decrease there is also a tendency for the reaction to follow the second order equation rather than the first order. In Fig. 7 the reciprocal of the concentration of ethyl bromide ($1/(2p_i - p_t)$) is plotted against time for the first third of the reaction in the case of a few experiments in which p_i is about 35 mm. Under these conditions where the reaction is not complicated by the reverse reaction and where the pressure is well below the first order region the straight lines show that the second-order formula is being followed.

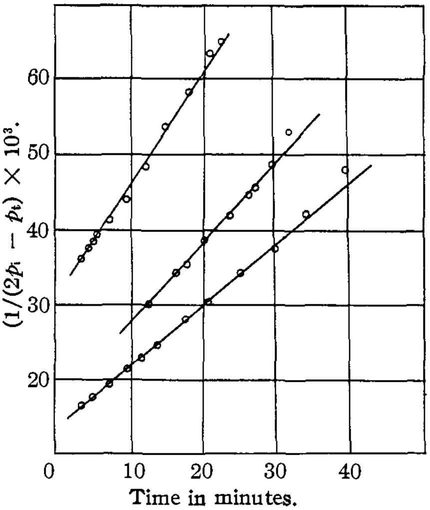


Fig. 7.—Graphs at low pressure (35 mm.) showing second order reaction: reciprocal of concentration *vs.* time.

The influence of temperature on the normal dissociation rate at high pressures is shown in curve I of Fig. 8 where log $k_\infty \times 10^4$ is plotted against $1/T$. The slope of this straight line, obtained by the method of least squares, gives a heat of activation E of 54,800 calories per mole.

From this value is calculated the value of s in the equation

$$k_\infty = se^{-E/RT} \qquad (4)$$

as shown in Table IV.

These facts are summarized by the equation

$$k_\infty = 3.85 \times 10^{14} e^{-54,800/RT} \qquad (5)$$

or

$$\ln k_\infty = 33.58 - 54,800/RT \qquad (6)$$

Curve II in Fig. 8 represents the data at low pressures (p_i = 35 mm.) and the slope of this line gives a heat of activation of 43,000 calories per mole for the low pressure or second order region.

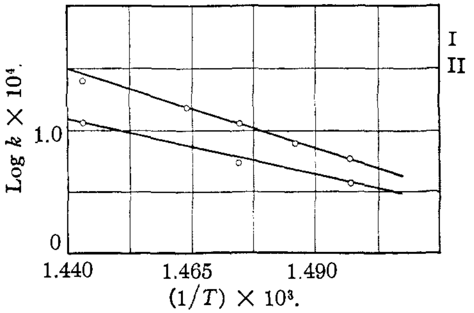


Fig. 8.—Influence of temperature on specific rate: log k *vs.* $1/T$; I, high pressure; II, low pressure (35 mm).

TABLE IV

CALCULATION OF s

$T°$	668	673	678	683	693
$s \times 10^{-14}$	3.86	3.67	3.93	4.07	3.71

Theoretical Discussion

The values of E and s just given are of the same magnitude as those obtained for the other fifteen unimolecular reactions already known.[5] The value of E/RT for a given value of k falls in line with the approximately constant value found in many of the unimolecular reactions.

The theoretical treatment of unimolecular reactions and the falling off of the rate constant k at low pressures has been fully covered elsewhere.[6] Collision theories offer the best explanation of unimolecular reactions. The collision theories known as Theory I,[7,8] Theory II[8] and Theory III[9] have been widely discussed and it is worth while to test them with the data of the present investigation.

According to Theory I the chance of an activated molecule decomposing does not depend on the excess of energy over the critical energy ϵ_0 and it does not depend on the location of the energy within the molecule. The specific decomposition rate at any pressure is given by equation (7)

$$k = \frac{k_\infty}{1 + (\beta_1/p_i)} \qquad (7)$$

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(5) (a) Ramsperger, *Chem. Rev.*, **10**, 27 (1932). (b) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, Chap. X.

(6) Reference 5b, Chapters V and X.

(7) Hinshelwood, *Proc. Roy. Soc.* (London), **A113**, 230 (1927).

(8) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

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

or

$$\log \frac{k}{k_\infty} = \log p_i - \log (p_i + \beta_1) \tag{8}$$

where β_1 depends on collision frequency and the complexity of the molecule.[10] These equations may be tested by plotting $\log k/k_\infty$ against $\log p$ as shown in Fig. 9 for the data at 395°. The theoretical curve calculated from equation (8) is shown by the curved line. The agreement between the two is not such as to support Theory I but a definite conclusion is not possible because considerable leeway is allowable in shifting the calculated curve.

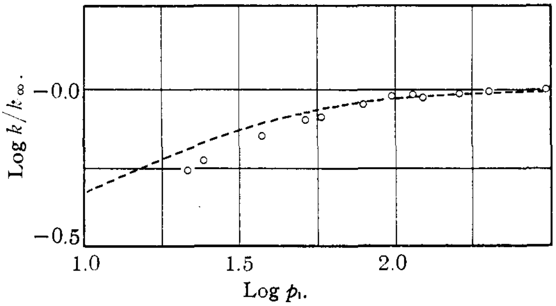

Fig. 9.—Test of equation (8).

In calculating this curve the best value of β_1 was found to be about 45 mm. ϵ_0 was calculated from the equation

$$\frac{\mathrm{d} \ln k_\infty}{\mathrm{d}T} = \frac{\epsilon_0 - \frac{n-2}{2}kT}{kT^2} = \frac{U_1}{kT^2} \tag{9}$$

If the molecular diameter is taken as 6×10^{-8} cm. and β_1 is taken as 45, n, the number of degrees of freedom, has a value of 21.[10] If the diameter is taken as 5.5×10^{-8} cm. the best value of n is 22. U_1 is the energy of activation per molecule calculated by the simple formula of Arrhenius. k is the gas constant per molecule.

Another test seems to show that Theory I is not adequate. Writing equation (7) in the form

$$\frac{1}{k} = \frac{1}{k_\infty} + \frac{\beta_1}{k_\infty}\frac{1}{p_i} \tag{10}$$

it is seen that when $1/k$ is plotted against $1/p_i$ a straight line should be obtained with a slope of β_1/k_∞ and an intercept of $1/k_\infty$. In Fig. 10 the points represent the experimental data at 395° and the line represents the theoretical straight line obtained from the above value of β_1. If a value of β_1 is calculated from the slope of a line passing among the experimental points there is even less agreement with Theory I than that indicated in Fig. 9.

In Theory II it is assumed that the energy of activation must be localized in a particular degree of freedom, n, before the molecule will disrupt and the

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[10] β_1 is used as defined by Rice and Ramsperger, THIS JOURNAL, **49**, 1621, equation (5) (1927).

chance of this localization increases as the energy ϵ increases beyond the critical value ϵ_0. Theory III is quite similar except that energy is assumed to be localized in a particular bond (2 degrees of freedom). The relative merits of Theories I, and II and III as applied to a specific reaction may be judged by comparing the energy of activation at high pressures (in the first order region) with that at low pressures (in the second order region),[11] both being calculated by the simple formula of Arrhenius. As already stated there is a large difference in these quantities. The difference is evident also from an inspection of the slopes of the lines in Figs. 6 and 8. This difference shows that Theory I is not satisfactory for explaining the facts of the present investigation but that Theories II and III are in better agreement with them. The numerical value is such as to favor Theory III slightly, but the allowable variations in the factors preclude a definite decision between the two.

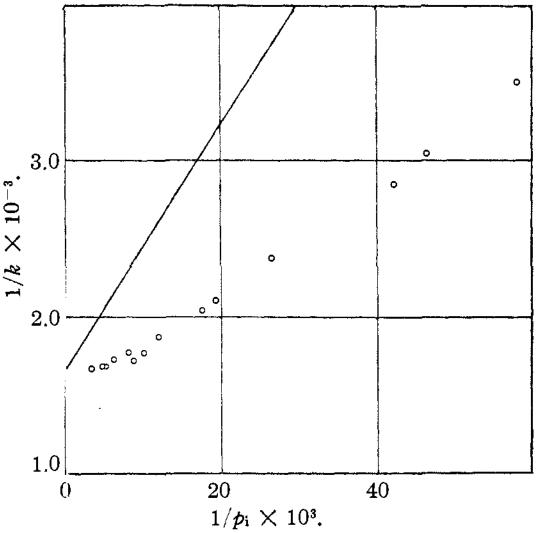

Fig. 10.—Test of equation (10).

A change in the kinetics of a reaction cannot affect the true thermodynamic equilibrium constant but it is interesting to consider possibilities with reference to an apparent equilibrium constant, calculated from partial pressures.

The present investigation offers an unusual opportunity for studying a reversible dissociation in which the bimolecular and unimolecular reactions proceed simultaneously. The classical equilibrium constant K is ordinarily written as

$$K = \frac{k_1}{k_2} = \frac{p_{\mathrm{HBr}}p_{\mathrm{C_2H_4}}}{p_{\mathrm{C_2H_5Br}}} \qquad (11)$$

It is shown in this investigation that k_1 decreases at low pressures. If k_2 changes in such a manner as to compensate this change in k_1 the value of K will remain constant; but if k_2 remains constant, K will decrease at low pressures. In such a case the numerical value of the ratio of the partial pressures at the right would have to decrease also at low pressures to preserve the relation indicated by equation (11).

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(11) Ramsperger, *Chem. Rev.*, **10**, 35 (1932).

Summary

1. The dissociation of gaseous ethyl bromide into ethylene and hydrobromic acid has been determined between 395 and 420° and at pressures ranging from 12 mm. to 360 mm. It is a unimolecular reaction suitable for the study of kinetics.

2. Ethyl bromide was sealed off in glass vessels totally immersed in a lead thermostat controlled by a photoelectric cell. The pressure was followed through a glass diaphragm.

3. The influence of traces of air was studied.

4. The unimolecular dissociation is accompanied by a bimolecular recombination. Four different methods for calculating the specific decomposition rate k are discussed.

5. The specific rate k starts to decrease at pressures below 100 mm. and at lower pressures the reaction tends to follow the second order equation.

6. The data above 100 mm. pressure are well expressed by the formula, $k = 3.85 \times 10^{14} e^{-54,800/RT}$.

7. The data are used to test collision theories of unimolecular reactions. They do not agree well with the predictions of Theory I. The temperature coefficients at high and low pressures suggest a better agreement with Theory III or II.

8. A relay switch is described which operates only on alternate excitations.

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The Effect of an Electric Field on the Flame Temperature of Combustible Gas Mixtures[1]

BY BERNARD LEWIS[2] AND C. D. KREUTZ[3]

The effect of an electric field on the flames of a number of combustible gases has been reported on by several investigators.[4] It was found that the electric field exerted a marked influence, increasing or decreasing the speed of propagation of the flame (depending on experimental conditions), seriously deforming and weakening the appearance of the flame, and under suitable conditions eventually extinguishing it completely.

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(4) Malinowski, *J. chim. phys.*, **21**, 469 (1924); Malinowski and Lawrow, *Z. physik*, **59**, 690 (1930); Bernackyj and Retaniw, *Ukr. Physik Abhand.*, vol. II, no. 1, p. 9 (1928); F. Haber, *Sitzb. Preuss Akad. Wiss.*, **11**, 162 (1929); Thornton, *Phil. Mag.*, **9**, 260 (1930); Guénault and Wheeler, *J. Chem. Soc.*, **195** (1931); Lewis, THIS JOURNAL, **53**, 1304 (1931); Muendel, Thesis, Carnegie Institute of Technology, 1931; Malinowski and Lawrow, *Phys. Z. Sowjetunion*, **2**, 52 (1932).