The heat contents of *meso* and racemic 2,3-dibromobutane are practically the same[15] and both molecules have the "*trans*" configuration; hence it follows that

$$X_{CH_3-CH_3} + X_{H-H} - 2X_{CH_3-H} = 0 \qquad (a)$$

and from the results of Beach and Turkevich[3b] we have

$$X_{Br-Br} + X_{H-H} - 2X_{Br-H} > 2.5 \text{ kcal./mole)} \qquad (b)$$

while from the "*trans*" configuration of racemic 2,3-dibromobutane

$$X_{Br-Br} + X_{CH_3-CH_3} - 2X_{Br-CH_3} > 0 \qquad (c)$$

It is interesting to note that while additivity obtains for the X's involving methyl groups and hydrogen atoms, (a), it does not hold for the X's involving bromine atoms in substituted ethanes.

From equation (a) it follows that the three staggered configurations of *n*-butane have approximately the same energy, in agreement with the assumption of Pitzer.[16]

The authors would like to express their thanks to Dr. Saul Winstein of the Institute for the samples of the compounds used in this research, as well as for information regarding the properties and purity of the compounds.

Summary

From electron diffraction photographs it has been found that both racemic and *meso* 2,3-dibromobutane have "*trans*" configurations with respect to the bromine atoms, the bromine–bromine distance being 4.60 ± 0.03 Å. It has been shown further that a model for the structure of this pair of compounds, based on the known structure of isopropyl bromide, gives a theoretical scattering curve which is compatible with the photographs. Evidence for considerable torsional oscillation about the equilibrium "*trans*" configuration is presented.

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(15) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, This Journal, **60**, 2770 (1938).

(16) K. S. Pitzer, *J. Chem. Phys.*, **6**, 473 (1937).

Pasadena, Calif. Received September 6, 1939

[Contribution from the Coates Chemical Laboratory, Louisiana State University]

The Homogeneous Decomposition of Ethyl Chlorocarbonate

By A. R. Choppin, H. A. Frediani and G. F. Kirby, Jr.

Though a number of homogeneous decomposition reactions in the gas phase are reported in current literature, the number of such reactions which are not complicated as to order or mechanism is comparatively small. From a series of compounds which have been investigated in this Laboratory, ethyl chlorocarbonate was chosen for more complete study since it appeared to have the characteristics of a member of this somewhat select group. Ethyl chlorocarbonate was found to undergo homogeneous, unimolecular decomposition to ethyl chloride and carbon dioxide between 150 and 200°.

Experimental

The ethyl chlorocarbonate used in this series of experiments was obtained from the Eastman Kodak Company. The commercial product was purified as follows: 250 ml. of the substance was placed in a round-bottomed flask, fitted with a 90-cm. fractionating column and distilled. The first and last 100 ml. were discarded, the intermediate 50 ml. retained. This intermediate portion was refractionated. The first 20 ml. was discarded and the next 10 ml., having a boiling range of 0.01°, was used for study.

The thermostat employed had a capacity of five gallons (20 liters), was insulated with filter-cell set in a plaster of paris mold, and employed as a bath medium hydrogenated cottonseed oil circulated by means of a turbine stirrer. After a short period of use the oil darkened in color, cracking became less pronounced, and the bath was serviceable at temperatures as high as 250°.

Three specially wound resistance coils capable of a total heat input of 1200 watts constituted the permanent heater. In addition to this heating unit, two 250-watt hairpin type heaters were connected to the line through a 460-ohm rheostat to give a partial regulation of the heat input. These two sets of heaters were so adjusted as to maintain the bath within one degree of the desired temperature.

Exact temperature regulation was obtained by means of a 200-watt light bulb operated by the thermoregulator, which consisted of a Leeds and Northrup reflecting galvanometer connected to a platinum resistance thermometer through a Wheatstone bridge. The circuit was so arranged that light reflected from the galvanometer turned on the light heater at zero scale reading through a photoelectric cell. An unbalanced circuit through a resistance change in the platinum resistance thermometer caused the light to swing away from the cell a distance of 10 cm. for a change of less than 0.01°. The temperature of the bath was constant to 0.01°.

The reaction was followed by a static method in an all-glass system. Reaction vessels were constructed of

Pyrex glass, and the pressure was balanced through a diaphragm actuating platinum contacts, as described by Daniels.[1] Small bulbs containing the reactant were introduced through a side-arm and broken at the proper time by a glass enclosed, solenoid-operated hammer. A mercury relay was actuated by the completion of the diaphragm circuit. This relay was in turn connected to a power relay, the arm of which was placed opposite the tip of an automatic valve sealed into the outside system. Completion of the relay circuit by an unbalanced condition of the diaphragm resulting from a pressure increase inside the reaction vessel caused the arm of the power relay to tap the valve at a rate of about 300 times per minute, admitting air into the outside system. In this way automatic pressure regulation was secured by practically continuous balancing of the outside pressure with the pressure inside the reaction vessel. The changes in pressure were followed by means of a mercury manometer which fell smoothly during the course of a reaction. For experiments in which the initial pressure was 100 mm. or greater, a vertical mercury manometer reading to 0.5 mm. was used. In those experiments in which the initial pressure was below this value, a Fisher vacuum gage and a calibrated inclined mercury manometer were sealed into the line. Each of these gave pressure readings directly to an accuracy of 0.05 mm. of mercury.

The diaphragms employed in the system were flexed to a constant zero point before use. This required about half an hour of automatic flexing with a slightly reduced pressure inside the reaction vessel and the vacuum pump working only on the outside system.

Before use cells were boiled with cleaning solution, rinsed with fuming nitric acid and finally with distilled water. There was no opportunity for contact with stopcock grease, mercury or other foreign materials and no dead space correction was necessary.

To test the homogeneity of the reaction runs were made at the same temperature and approximately the same pressure with the unpacked vessel and with a vessel having an increased surface. The increase in surface was obtained by packing the vessel with ground glass, quartz or with glass wool.

A bulb of ethyl chlorocarbonate was chosen to give approximately the desired pressure and sealed into the side arm of the reaction cell. The vessel was evacuated to a pressure of 0.001 mm. of mercury, rinsed with nitrogen, and this process repeated several times. Pressures on each side of the diaphragm were equalized by drawing gas from the cell through a small side tube which was sealed off immediately preceding a run. After the final evacuation and sealing of the cell, the bulb of reactant was broken by the solenoid operated hammer and the bath quickly raised by means of a hydraulic jack to immerse the vessel. The initial pressure was taken as one-half the final constant pressure eventually reached and this value was checked against the value calculated from the weight of the sample and the volume of the cell, which was determined with distilled water.

The final products were analyzed for ethyl chloride gravimetrically and for carbon dioxide by means of a Fisher apparatus. In order to obtain large amounts of material for analysis, a special type of vessel was used. A sealed bulb containing from 0.1 to 0.5 g. of ethyl chlorocarbonate was introduced into the vessel, after which the vessel was rinsed with nitrogen and sealed. The bulb was broken by shaking and the vessel submerged in the thermostat. At the end of the time required for complete decomposition it was removed from the thermostat, packed in dry ice–acetone, and the ethyl chloride collected as a liquid. Silver nitrate was used to precipitate the chloride and the carbon dioxide was absorbed in 40% potassium hydroxide. The analysis of carbon dioxide was accurate within 2% and the more accurate gravimetric determination of chloride checked the theoretical within 0.5%.

No chemical evidence of products other than ethyl chloride and carbon dioxide has been obtained. No test for chlorine could be obtained upon allowing the decomposition products to come in contact with a potassium iodide–starch solution. Spectroscopic work being done on the compound at present should give a more positive answer as to the possibility of the presence of small amounts of substances other than those determined chemically. Typical examples of the data taken from chemical analyses of the products are shown in Table I.

TABLE I

Sample, g.	Carbon dioxide, cc. Found	Calcd.	Silver chloride, g. Found	Calcd.
0.3125	62.9	64.9	0.4031	0.4105
.4311	90.1	89.4	.5648	.5663
.2104	44.2	43.6	.2761	.2763
.1071	22.0	22.2	.1423	.1409

Experimental Results

Since the only products of the reaction found by the analytical methods employed thus far are carbon dioxide and ethyl chloride, the equation for the reaction is

$$C_2H_5OCOCl = CO_2 + C_2H_5Cl$$

Since the decomposition of one mole of reactant results in an increase of one mole in the total number of moles of gases present, the pressure increase upon decomposition may be taken as directly proportional to the change in concentration of the reactant. Thus the concentration of undecomposed ethyl chlorocarbonate is given by the equation

$$p = 2P_1 - P_t$$

where P_1 is the initial pressure, P_t the pressure at any time t and p the partial pressure of undecomposed ethyl chlorocarbonate. The apparent simplicity of the reaction does not seem to be general for the chlorocarbonates.[2]

The curves obtained by plotting pressure against time are the typical log curves of a first order reaction. The number of these curves which have been plotted over the normal pres-

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(1) Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, p. 59.

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

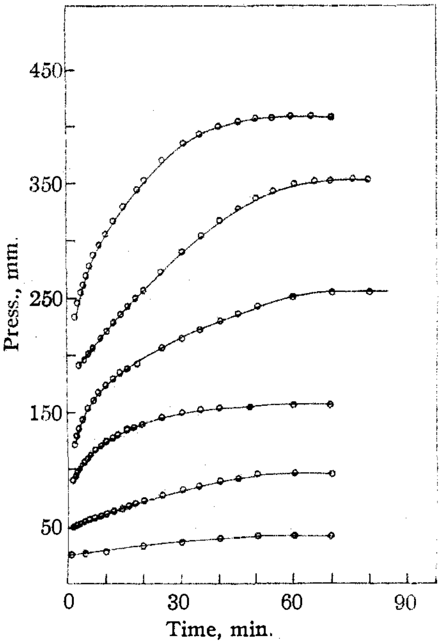

Fig. 1.—Typical ethyl chlorocarbonate decomposition curves: pressure *vs.* time at 175°.

sure range gives ample evidence of the smooth and regular rate of decomposition (Figs. 1 and 2).

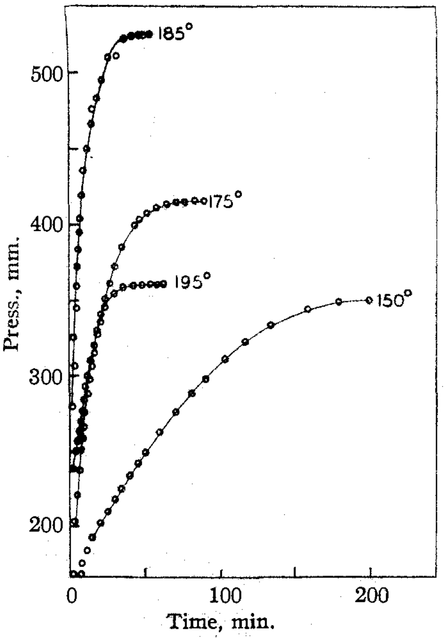

Fig. 2.—High pressure curves.

The specific reaction rate was determined from the slopes of the lines in Fig. 3. In these curves the log of $2P_1 - P_t$ has been plotted against time. The slope in each case was determined by the method of least squares and this value was

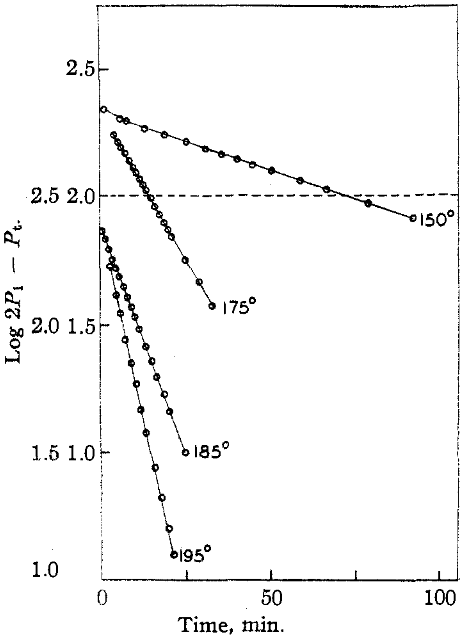

Fig. 3.—Plot of log of concentration against time.

Table II

P_1, mm.	k, min.	k/k_0
Temperature 150°; k_0 = 0.00780		
325	0.00769	0.986
177[a]	.00787	1.009
125	.00481	0.617
115	.00749	.960
105	.00472	.605
Temperature 175°; k_0 = 0.0451		
246[a]	0.0449	0.995
212	.0446	0.998
177	.0459	1.017
176[a]	.0406	0.899
152[a]	.0348	.771
131	.0366	.811
126[a]	.0338	.759
102	.0301	.677
85	.0278	.612
45	.0263	.583
37	.0204	.450
24	.0127	.286
18	.0156	.377
Temperature 185°; k_0 = 0.0899		
260[a]	0.0894	0.994
176	.0904	1.005
158	.0691	0.768
76.5	.0600	.667
Temperature 195°; k_0 = 0.1815		
179	0.183	1.008
175	.180	0.991
151	.138	.760
85	.114	.628
20	.102	.562

[a] Vessel packed.

multiplied by 2.303 according to the conventional first order rate equation

$$-\log c = kt/2.303 + C$$

The values of the specific rate constant k determined by this method have been reported in Table II. The value of k_0 in this table was taken as the average value of the velocity constants of the high pressure runs.

The increase in the high pressure decomposition rate with temperature is shown in Fig. 4. The energy of activation calculated from the simple Arrhenius equation using this straight line is 29,410 cal. per mole. From this value are calculated the values of the frequency factor s in the expression $k = se^{-E/RT}$ as recorded in Table III.

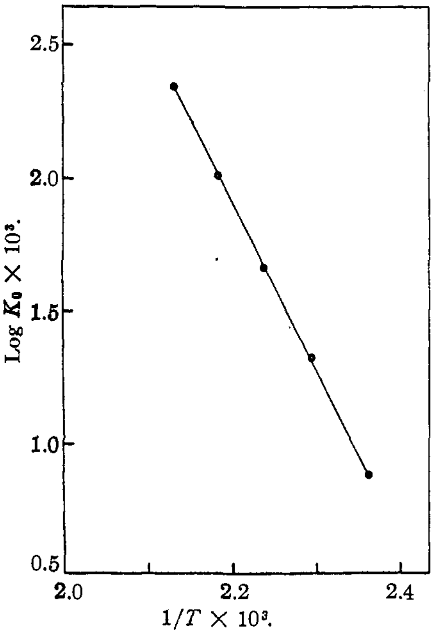

Fig. 4.

TABLE III

T, °K.	423	448	468	478
$s \times 10^{-10}$	5.943	5.254	5.225	5.403

The rate of reaction, then, may be obtained from the equation

$$k = 5.5 \times 10^{10} e^{-29,410/RT}$$

The magnitude of s, while smaller than similar values obtained in most unimolecular reactions,[3] has been calculated over the active temperature range and an average value taken as suggested by Rice and Gershinowitz.[4]

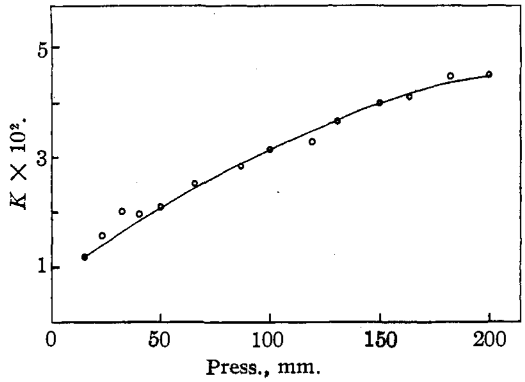

Fig. 5.—Variation of k with initial pressure.

Brearly, Kistiakowsky and Stauffer[5] observed that in experiments with t-butyl chloride much more reproducible results were obtained with coated walls. A similar effect has been reported by Daniels[6] in the decomposition of ethyl bromide. In view of the negligible influence of packing on the decomposition of ethyl chlorocarbonate, no appreciable surface catalysis was expected. However, pressure measurements of decomposition in clean vessels were observed to fluctuate slightly, with this effect disappearing and the pressure increasing smoothly after about two runs with the same vessel.

The exact effect of pressure[7] on the specific rate constant of unimolecular reactions is still

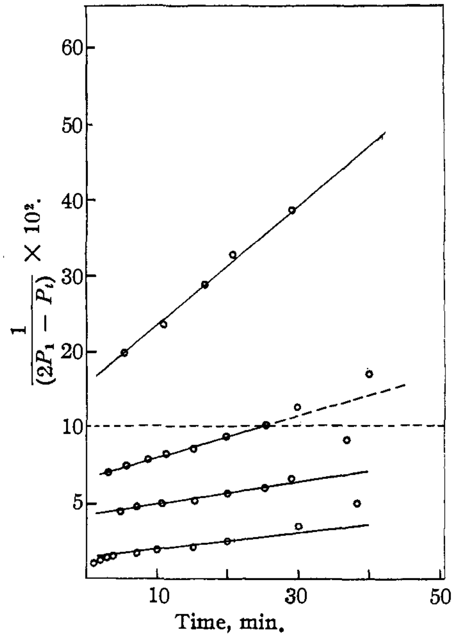

Fig. 6.—Low pressure approach to a second order rate.

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[3] Kistiakowsky, *Chem. Rev.*, **17**, 47 (1935).

[4] Rice and Gershinowitz, *J. Chem. Phys.*, **3**, 479, 490 (1935).

[5] Brearly, Kistiakowsky and Stauffer, THIS JOURNAL, **58**, 43 (1936).

[6] Daniels and Veltman, *J. Chem. Phys.*, **7**, 756 (1939).

[7] Kassel, *J. Chem. Phys.*, **32**, 1065 (1928); "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, N. Y., 1932, Chapters V and VI.

controversial. Recent statements by Pease[8] and Daniels[9] have shown that some investigators are far from satisfied with the present theories of quasi-unimolecular mechanisms. Reactions which throw light on this situation are still of great value, and the present series of experiments seems to have definite possibilities in this connection. The effect of pressure on rate has been studied at several temperatures, and more closely at 175°. The observed effects are shown graphically in Fig. 5 in which k is plotted against P_1. The fall off in rate has been found to begin appreciably above the expected value of about 40 mm.

The low pressure approach to a second order rate is demonstrated in Fig. 6. The reciprocal of reactant pressure has been plotted against time for several runs having initial pressures lower than 100 mm.

The effect of foreign materials has been investigated quite thoroughly. An account of this effect will be published in the next paper of the present series.

Summary

1. Ethyl chlorocarbonate has been found to decompose homogeneously and by a unimolecular mechanism between 150 and 195° and over a pressure range from 10 to 700 mm. of mercury.

2. The specific reaction rate may be obtained from the equation

$$k = 5.5 \times 10^{-10}\, e^{-29{,}410/RT}$$

3. A slight effect has been observed in the comparison of runs in coated and uncoated vessels.

4. It has been found that at low pressures the rate constant falls appreciably and that the reaction approaches a second order rate.

BATON ROUGE, LA. RECEIVED AUGUST 3, 1939

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(8) Pease, *J. Chem. Phys.*, **7**, 749 (1939).

(9) Ref. 1, pp. 71, 72; ref. 5, p. 100.

[FROM THE DEPARTMENT OF PHYSIOLOGY AND BIOCHEMISTRY IN THE MEDICAL COLLEGE AND THE DEPARTMENT OF DAIRY INDUSTRY IN THE NEW YORK STATE COLLEGE OF AGRICULTURE, CORNELL UNIVERSITY]

Molecular Weight and Association of the Enzyme Urease

BY DAVID B. HAND

Introduction

The osmotic pressure of crystalline urease solutions corresponds to an average particle weight of 700,000(1) but the diffusion rate, when measured by activity, establishes the presence of active particles of 17,000 or less. Although much is known about the particle weights of proteins in general, there is yet no knowledge of the size of the smallest units which can exist with unaltered specific properties. In the case of the protein urease, it is possible to prove that smaller particles than those predominating in the solution possess enzyme activity.

Osmotic Pressure Measurements

An apparatus has been designed for measuring the osmotic pressure in a 1.0 ml. sample of solution. Even with these small volumes the expense and difficulty of obtaining the urease were considerable. The apparatus, which has proved convenient, is shown in Fig. 1. The collodion sack is mounted on the outer portion of a universal glass joint, thus making the filling of the sack very simple. Mineral oil is used as a manometer fluid and can be added through the side arm after the apparatus is set up. Equilibrium is reached rapidly since only 0.5 ml. of outer solution are needed. The details of the method are essentially those described by other workers.[2,3,4] Figure 2 gives the measurements of osmotic pressure which were made at *p*H 7.0 in 0.01 *M* citrate buffer and at *p*H 6.3 in 0.001 *M* phosphate. It is impossible to work nearer the isoelectric point of 5.0[5] or to increase the buffer concentration because of the lower solubility of urease under these conditions.[6] It was found that osmotic pressures were high in 0.001 *M* buffer due to unequal distribution of ions, but that this effect was repressed in 0.01 *M* buffer (see Fig. 3).

Mineral oil above both the inner and the outer solutions was allowed to rise in capillary tubes so that a value for osmotic pressure was obtained directly from the difference in the height of the oil in the two capillary tubes. The capillary tube for the outer solution is not illustrated in Fig. 1. The density of the oil was 0.842. In a typical experiment 32 lots of jack bean meal of 100 g. each were extracted with a total volume of 16 liters of 31.6% acetone by the method of Sumner and the urease allowed to crystallize. After centrifuging, washing and recrystallizing, the urease was dissolved in 4.0 ml. of water at 0°.

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(1) Paper read before the American Chemical Society, New York City, April, 1935.

(2) Adair, *Proc. Roy. Soc.* (London), **A109**, 292 (1925); **A120**, 573 (1928); **A126**, 16 (1929).

(3) Krogh and Nakazawa, *Biochem. Z.*, **188**, 241 (1927).

(4) Weber and Stöver, *ibid.*, **259**, 269 (1933).

(5) Sumner and Hand, THIS JOURNAL, **51**, 1255 (1929).

(6) When the concentration of citrate is increased, the urease crystallizes in octahedra which are better defined and larger than those obtained with 32% acetone.