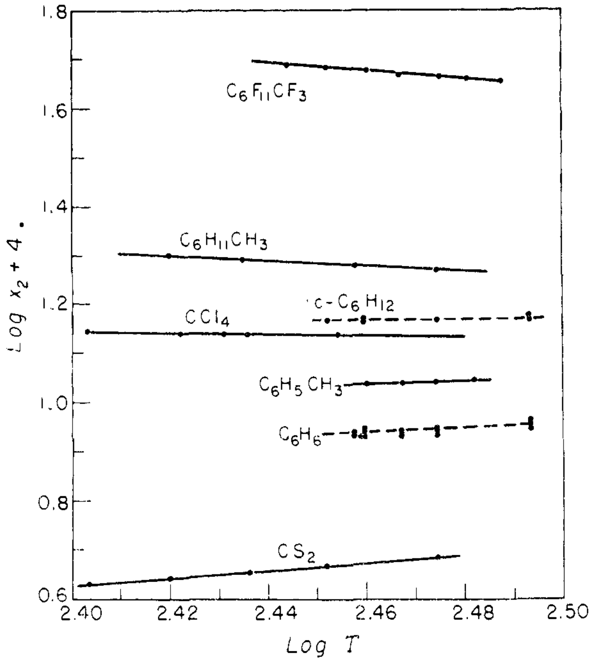

Fig. 1.—Solubility of argon.

Discussion.—The entropy of solution of argon increases rapidly in the solvents in Table II from top to bottom, but this is mainly the effect of increasing dilution. In the last column of the table we give the entropy of transferring argon at 1 atm. to solution at a dilution of $x_2 = 10^{-4}$, computed from the change in gas pressure required to reduce the solubility to $x_2 = 10^{-4}$. One sees that the values, except for $C_6F_{11}CF_3$, are close to 5 e.u. at equal mole fractions. This is not true if compared at equal molal concentrations. It is evident that the slopes of the curves in Fig. 1 are determined mainly by the degree of dilution necessary for equilibrium; the poorer the solvent, the larger the entropy of solution and the greater the temperature coefficient of solubility. There are also, however, additional contributions to the entropy of solution such as the one connected with the different partial molal volumes of the gas, to be reported in a forthcoming paper, and the properties of different gases, as we shall show by comparing the entropy of solution of argon, nitrogen and hydrogen.

TABLE I

SOLUBILITY OF ARGON AT 1 ATM. AND T°K. IN MOLE FRACTION $\times 10^{-4}$

T, °K.	10^4x_2	Run	T, °K.	10^4x_2	T, °K.	10^4x_2
$C_6H_5CH_3$			$C_6F_{11}\cdot CF_3$		$C_6H_{11}\cdot CH_3$	
288.23	10.882	a	278.09	48.709	262.90	19.888
288.22	10.875	b			272.53	19.433
			283.06	47.999	286.75	18.872
293.04	10.918	b	283.10	47.965	298.14	18.543
293.03	10.921	a				
			288.36	47.234	CS_2	
297.87	10.963	a			253.13	4.272
297.87	10.949	b	293.08	46.625	262.76	4.391
297.86	10.943	b	293.17	46.634	273.22	4.513
297.88	10.955	a	293.18	46.689	283.14	4.654
298.20	10.950	b	293.19	46.623	298.14	4.866
303.31	10.982	b	298.48	45.962	CCl_4	
303.31	10.995	a			252.98	13.976
			303.16	45.470	264.18	13.809
			307.86	44.978	269.83	13.736
					272.65	13.697
					284.29	13.669

TABLE II

MOLE FRACTION, x_2 AND ENTROPY OF SOLUTION OF ARGON FROM GAS AT 1 ATM. AND 25° (a) TO x_2, MEASURED; (b) TO $x_2 = 10^{-4}$

Solvent	δ_1	10^4x_2	$\bar{S}_2 - S_2{}^g$ (a)	(b)
$C_6F_{11}CF_3$	6.0	46.00	−1.50	6.1
$C_6H_{11}CH_3$	7.85	18.55	−0.9	4.8
c-C_6H_{12}	8.2	14.8[a]	0	~5
CCl_4	8.6	13.4	−0.5	4.7
$C_6H_5CH_3$	8.9	10.95	+0.4	5.15
C_6H_6	9.15	8.85[a]	~1	~4.8
CS_2	10.0	4.87	1.8	5.0

[a] A. Lannung.

Acknowledgment.—We are indebted to Dr. D. N. Glew for suggestions during the early stages, to Dr. J. E. Jolley for checking the calculations, and to the Atomic Energy Commission for the support of the program.

BERKELEY, CAL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Kinetics of the Pyrolysis of Ethyl Bromide[1]

BY ARTHUR EDWARD GOLDBERG AND FARRINGTON DANIELS

RECEIVED NOVEMBER 3, 1956

The kinetics of the reaction $C_2H_5Br(g) \rightarrow C_2H_4 + HBr$ has been investigated between 310 and 476°, by determining the HBr formed by chemical analysis. The effects of surface and added gases have been studied. The primary step gives C_2H_4 and HBr directly with an activation energy of about 52 kcal. mole^{-1}, but the hydrogen bromide reacts at the surface with ethyl bromide producing a steady state of bromine atoms which give a faster reaction. The over-all reaction is first order and is given by the expression $k = 6 \times 10^{11} e^{46,400/RT}$ sec.$^{-1}$ but it is not a simple unimolecular reaction. Rate equations and a mechanism are given.

The decomposition of ethyl bromide $C_2H_5Br \rightarrow C_2H_4 + HBr$ at elevated temperatures was originally chosen as a first-order, gas-phase reaction, suitable for the study of chemical kinetics. As successive researches in this Laboratory[1-6] have brought forth new facts, and as these facts have been used to check the current theories, such as pressure effect on unimolecular gas reactions, free radical mechanisms and isotopic exchange reactions, it has become apparent that the kinetics of the reaction are quite complicated. This complexity of kinetics is frequently found to be characteristic of reactions when they have been studied thoroughly. The research reported here confirms the facts reported earlier, but shows that some of the earlier interpretations need revision in view of the additional new facts and the complicated mechanism which is now known to exist: namely, a simple homogeneous, molecular splitting into hydrogen bromide and ethylene followed by a faster, wall-catalyzed reaction to give the same products.

A reaction between ethyl bromide and its decomposition product, hydrogen bromide, produces a steady state of bromine atoms which results in a first-order, over-all reaction. It is believed that a high accuracy of rate measurement has been obtained through the electrometric titration of the hydrogen bromide formed.

Experimental Procedure

Earlier work had shown that although the amount of ethylene produced and the magnitude of the total pressure of the three gases involved do not necessarily give an accurate measure of the extent of the decomposition of ethyl bromide, the number of moles of hydrogen bromide produced is always stoichiometrically equivalent to the number of moles of ethyl bromide decomposed. Accordingly, in the present investigation the course of the reaction was followed by evacuating the partially reacted gaseous system through a liquid air trap to freeze out the solid products, and then titrating the hydrogen bromide formed. Alkali titration was used at first, but most of the data were obtained by potentiometric titration with silver nitrate. The hydrobromic acid formed by the decomposition reacts with silver ion but the undecomposed ethyl bromide does not.

A 300-ml. Pyrex reaction vessel was connected to a manometer, a vacuum line and a gas reservoir, which in turn was connected to a tube of liquid ethyl bromide and a tube for the admission of foreign gases. After definite time intervals, the gases were withdrawn from the reaction vessel with a vacuum pump through a liquid air trap. The products were then mixed with sodium hydroxide and titrated. Details of the apparatus and operation are given elsewhere.[1] The thermostat bath of potassium, lithium and sodium nitrates melting at 120° was regulated with electric heaters and a resistance thermometer regulator to 0.3°. The volume of the capillary connecting tube outside the bath was less than 0.1% of the reactor volume. Silicone grease on stopcocks permitted rapid filling and evacuation.

In carrying out a determination, the entire system was evacuated to 10^{-4} mm. Ethyl bromide was then vaporized to a predetermined pressure in the reservoir. By holding constant the pressure, volume and temperature of the reservoir and the volume and temperature of the reaction chamber, it was possible to introduce identical amounts of ethyl bromide into the reaction chamber. This condition was vital because several successive experiments with different degrees of decomposition were required to determine a single rate constant under a given set of conditions.

In some of the experiments a manometer was used to measure the total pressure and the partial pressure of added gas. All results were calculated with the formula log $n_0/(n_0 - x) = kt/2.30$ where k is the first-order specific rate constant and n_0 is the initial amount of material, x the amount decomposed in time t, both being expressed in titration volumes. The value of n_0 was determined by titrating the amount of hydrogen bromide produced after letting a charge of ethyl bromide stand for several hours at 430° to guarantee completion of the reaction.

Measurements at many different temperatures and initial pressures established the applicability of the ideal gas law at these pressures and temperatures and made possible a calculation of n_0 from the initial pressure and temperature for each reaction chamber used.

In the few experiments making use of pressure measurements with ethyl bromide alone, $n_0/(n_0 - x)$ was taken as approximately equal to $p_i/(2p_i - p_t)$ where p_i is the initial pressure and p_t is the pressure at time t. Where a foreign gas was added $n_0/(n_0 - x)$ was taken as $p_{C_2H_5Br}/(2p_{C_2H_5Br} - p_t + p_g)$ where $p_{C_2H_5Br}$ is the initial pressure of ethyl bromide, p_g is the pressure of the added gas and p_t is the total pressure at time t.

Ethyl bromide was used from three different commercial sources and all gave the same physical constants and kinetic behavior after purification with sulfuric acid, rinsing, drying and distillation with a long, packed column. The standard boiling temperatures were in the range 38.37–38.41° (the accepted value is 38.40°). The refractive index (n^{20}D) was 1.4239. The purified ethyl bromide, after being sealed in the system, was thoroughly degassed by repeated freezing in liquid air and thawing while under evacuation. It was then stored in the dark.

Hydrogen bromide was obtained by warming slowly 48% aqueous hydrobromic acid and passing the vapors through P_2O_5 in a connecting tube. Further purification was accomplished by passing over copper, freezing, fractionally distilling and outgassing. The ethylene was purified by repeated distillation from Dry Ice to liquid air temperatures under a high vacuum.

Experimental Results

Influence of Surface.—It was well known that the first rate constants obtained in fresh clean Pyrex glass are abnormally high and that subsequent experiments give lower values until a reproducible value is obtained.[2-5] Two days' contact with decomposing ethyl bromide at 400° and 300 mm. pressure was sufficient to coat the surface with a black graphitic film and give reproducible results for several months. The film changed with time from a slightly dirty appearance to a smooth black coating. After five months of experiments, the coating could be flaked off and it was found to be less than 2 μ thick and to have a longitudinal resistance of 15,000 ohms when a 1 cm. wide strip was placed between electrodes 1 cm. apart. All experiments were conducted in flasks coated in this manner. If any oxygen is allowed to get into the reaction vessel, the carbonaceous surface is affected and the decomposition rates increase. Evacuation does not restore the normal value, but a fresh deposit of carbonaceous material from decomposing ethyl bromide does restore it.

Equilibrium Measurements.—The thermodynamic equilibrium of the dissociation of ethyl bromide has been a matter of concern to those who have studied the kinetics of this reaction. The final pressure is always less than twice the initial pressure, a fact which could be due to a reverse reaction[3] or to a polymerization of ethylene.[5] In this investigation a direct measurement was made of the extent of the dissociation of the ethyl bromide at equilibrium. Ethyl bromide was introduced at various pressures in the neighborhood of 300 mm. into a flask of measured volume at 430° and allowed to stand for several hours. The hydrogen

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[1] More complete details of this thesis may be obtained from the Ph.D. thesis of Arthur E. Goldberg, filed in the library of the University of Wisconsin in 1951.

[2] E. T. Lessig, *J. Phys. Chem.*, **36**, 2335 (1932).

[3] E. L. Vernon and F. Daniels, THIS JOURNAL, **55**, 922 (1933).

[4] P. Fugassi and F. Daniels, *ibid.*, **60**, 771 (1938).

[5] F. Daniels and P. L. Veltman, *J. Chem. Phys.*, **7**, 756 (1939).

[6] J. B. Peri and F. Daniels THIS JOURNAL, **72**, 424 (1950).

bromide produced was titrated with silver nitrate, and controls were run with HBr. The titrations agreed with the pressure measurements assuming the perfect gas laws. The average of seven experiments gave 97.0 ± 1.0% dissociation at 430° and initial pressure of 300 mm., and an extrapolation of directly determined equilibrium constants recently reported[7] gives 95%. There is adequate evidence that the dissociation of ethyl bromide is nearly complete and that it gives stoichiometric amounts of hydrogen bromide.

Rate of Decomposition.—It was established in preliminary measurements[8] using this method of chemical analysis that the decomposition of ethyl bromide follows the first-order equation to at least 70% completion of the reaction. Between 384 and 422° an activation energy of 47.5 ± 1.0 kcal. mole^{-1} was obtained.

Data of the present investigation at 390.1° at different initial pressures of ethyl bromide are given in Fig. 1, where it is clear that the rate mechanism is complicated. Although the lines are straight, indicating first order, the slopes increase with the initial pressure. In Fig. 2 the corresponding specific reaction rates are plotted against the initial pressure. Furthermore, the fact that the lines of Fig. 1 do not extrapolate to the origin shows that there is an induction period. Many experiments were carried out in studying this autocatalytic induction period. It is not easily detected at temperatures above 400° but at the lower temperatures and pressures it may extend over several hours.

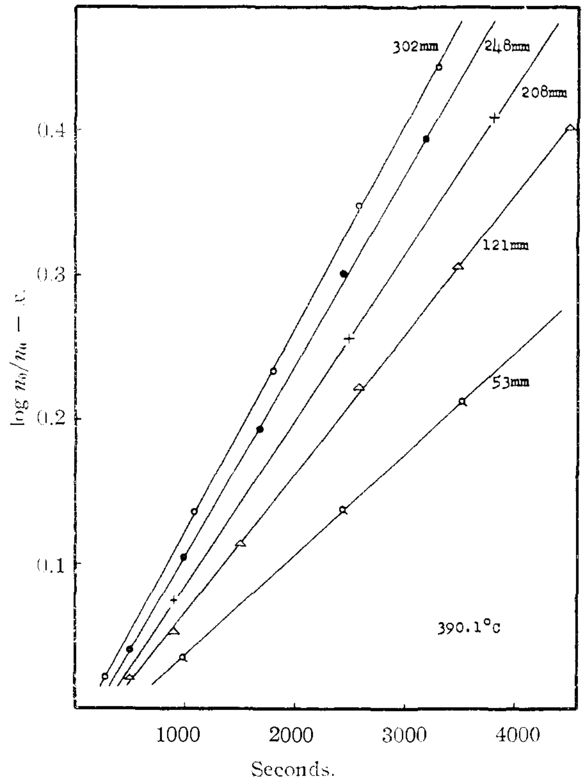

Fig. 1.—Decompositions at various initial pressures.

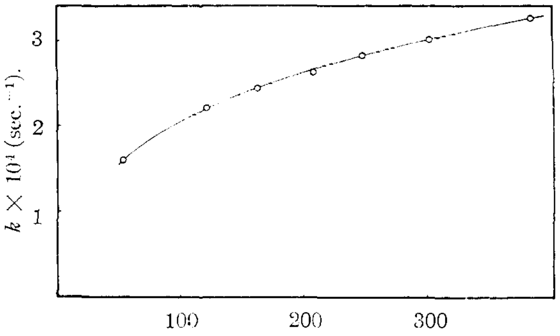

Fig. 2.—Variation of k with ethyl bromide pressure.

The influence of temperature extending from 309.7 to 476.5° at pressures of 200 to 300 mm. is summarized in Fig. 3. The data at the highest temperature ($t_{1/2}$ = 38 sec.) and at the lowest temperature over a 45-hour period with a correction for the induction period are not very reliable. An activation energy of 46.4 ± 0.5 kcal. mole^{-1} is indicated. The logarithm of the frequency factor is 11.8 ± 0.2. The results are in good agreement with the earlier results of Daniels and Veltman obtained with pressure measurements as indicated in Fig. 3. All the experiments were carried out in Pyrex vessels of about 300 ml. which had been thoroughly coated with a carbonaceous film from the decomposition of previous charges of ethyl bromide. The still earlier results of Vernon and Daniels do not agree because in that investigation each experiment was carried out in a freshly cleaned glass flask.

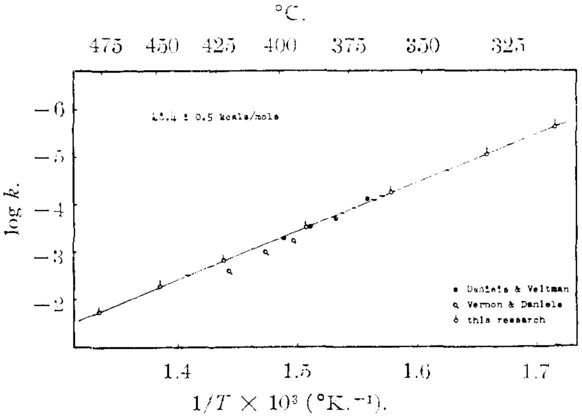

Fig. 3 —Activation energy.

Influence of Added Gases.—The falling off of the specific rate constant k at the low pressures shown in Fig. 2 might, at first sight, be taken to support the collision theory of unimolecular reactions, but it was noted early[3] that this is not the case because the addition of an inert gas does not bring the low pressure rate constant up to the high pressure value. Experiments in the present investigation at 421.8° gave k = 0.00153 at 300 mm. and only 0.00102 sec.$^{-1}$ at 120 mm. Nitrogen, helium and hydrogen in successive experiments were added to 120 mm. of ethyl bromide to bring the to-

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(7) M. R. Lane, J. W. Linnett and H. G. Dawson, *Proc. Roy. Soc.* (*London*), **216A**, 361 (1953).

(8) A. E. Goldberg, M.S. Thesis, University of Wisconsin Library, 1951.

tal pressure to 300 mm., but in all cases, the value of *k* remained the same as for the 120 mm. pressure of ethyl bromide alone.

The pronounced induction period called for further study. The addition of hydrogen bromide accelerated the decomposition of ethyl bromide markedly and eliminated the induction period. The addition of the other reaction product, ethylene, inhibited the decomposition rate markedly, and extended the autocatalytic period.

Effects of HBr and C_2H_4.—To facilitate the study of added hydrogen bromide and ethylene, the next experiments were carried out with manometric measurements instead of chemical measurements. The two methods were carefully checked and agreed within 7% out to 50% completion. In the later stages of the reaction, the total pressure is not a fair indication of the extent of the reactions. Experiments also proved that the volume of the manometer and the vapor of mercury at room temperature caused no errors.

The influence of added hydrogen bromide on the decomposition rate was studied in four series of experiments with HBr pressures of 14, 29, 66 and 150 mm. In all experiments the initial pressure of ethyl bromide was 300 mm. and the temperature was 390.1°. The normal decomposition with no extra hydrogen bromide showed the pronounced induction period, after which the curve straightens and remains linear to 50% decomposition. The addition of hydrogen bromide considerably reduced the induction period and at the highest pressure eliminated it entirely.

Good straight lines were obtained when $\log n_0/(n_0 - x)$ was plotted against time.

Further experiments with added hydrogen bromide are summarized in Table I.

TABLE I

VARIATION OF *k* WITH PRESSURE OF ETHYL BROMIDE AT 390.1° IN THE PRESENCE OF 66 MM. OF HYDROGEN BROMIDE

Initial pressure C_2H_5Br	300	219	149	120	83
$k \times 10^4$, sec.$^{-1}$	6.6	6.5	6.3	6.2	5.9

In the absence of the added hydrogen bromide, the constants *k* would have decreased markedly as indicated by the changing slopes shown in Fig. 1.

The activation energy of this hydrogen bromide accelerated reaction was obtained from the data of Table II. Plotted on a log *k* *vs.* $1/T$ graph these data give a good straight line with an activation energy of 43 ± 3 kcal. for the reaction catalyzed by HBr.

TABLE II

VARIATION OF *k* WITH TEMPERATURE FOR THE DECOMPOSITION OF ETHYL BROMIDE AT 300 MM. IN THE PRESENCE OF HYDROGEN BROMIDE AT 66 MM. PRESSURE

Temp., °C.	324.7	340.5	364.4	390.1
$k \times 10^5$	1.9	4.5	20	66

The effects of added ethylene (from 25 to 149 mm.) on the decomposition of ethyl bromide at 300 mm. and 390.1° were determined in a series of experiments. The specific rate constants as determined from the slopes of the straight portions of the curves decrease considerably with increased ethylene pressure, but all curves extrapolate to the same slope at zero time showing that the primary process is unaffected by the additions. Evidence will be presented later which proves that this primary process is kinetically of the first order. The specific rate constant of this process will be designated by k_0, and it is distinguished from the specific rate constant *k* which is determined from the linear portion of the curve, after the induction period is over.

The effects of added *n*-hexane on the decomposition of ethyl bromide at 300 mm. and 390.1° are shown in Fig. 4. The progress of the normal decomposition is represented by A. B and D show the effects of 5.5 and 49 mm. of *n*-hexane, respectively. C shows the effect of 149 mm. of ethylene for comparison. It is clear that the limiting slope is the same in all cases and, for the higher pressure of *n*-hexane, slow decomposition is maintained for a considerable time before there is any evidence of acceleration.

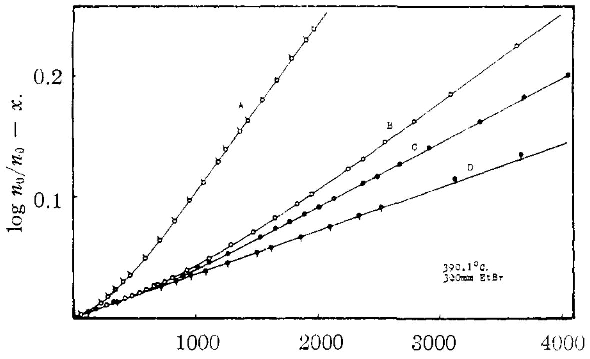

Fig. 4.—Effect of added *n*-hexane.

In Fig. 5 the effect of delaying the addition of extra reaction products to the decomposing bromide is shown. All experiments started with 300 mm. of ethyl bromide. C represents the normal decompo-

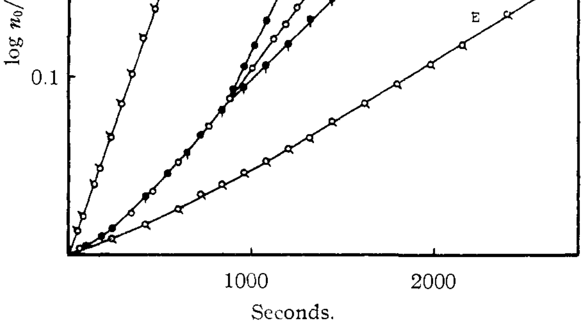

Fig. 5.—Delayed additions.

sition of ethyl bromide. In A 66 mm. of hydrogen bromide was added and in E 100 mm. of ethylene was added at the start. In B the 66 mm. of hydrogen bromide was added 870 seconds later, after the induction period; and in D the 100 mm. of ethylene was added also after 870 seconds. The inhibiting effect of ethylene and the accelerating effect of HBr are greater if these gases are added at the beginning of the reaction.

The addition of *n*-hexane was far more effective than ethylene in retarding the reaction, but the extrapolated slope at the beginning of the reaction, which is a measure of k_0, is the same in all experiments.

The addition of 50 mm. of carbon dioxide to 300 mm. of ethyl bromide did not affect the decomposition rate.

Surface Effects.—Increasing the ratio of surface to volume, S/V, by placing Pyrex glass tubes in the flask increased the rate of decomposition as indicated in Table III.

TABLE III

INFLUENCE OF SURFACE AREA ON DECOMPOSITION RATE

S/V (cm.$^{-1}$)	0.7	1.9	5.9	8.4
$k \times 10^4$	3.01	3.68	..	6.5
k_0	0.6	0.9	1.5	2.2
$k_0{}^a$	..	0.7	..	1.0

[a] In presence of 49 mm. of hexane.

Both the initial reaction rate during the induction period and the final steady-state rate are increased somewhat by increasing the surface. The effect is much less marked, however, in the presence of hexane, which inhibits the reaction and prolongs the induction period, due in part at least to preferential adsorption on the surface.

Bromine as an Intermediate.—Fugassi[4] found that the decomposition rate is accelerated by the addition of bromine. Visual inspection of ethyl bromide decomposing at 450° in the present investigation failed to show any bromine color, but less than 10 mm. would not be detected by this means. In a flow method, however, the exit gases did turn starch–iodide paper blue, indicating the presence of a trace of bromine. Hydrogen bromide under the same conditions failed to give a test for bromine. The addition of oxygen produced substantial amounts of bromine in both ethyl bromide and hydrogen bromide.

Comparison with Flow Method.—Blades and Murphy[9] of this Laboratory studied the decomposition of ethyl bromide in a stream of toluene following work by Szwarc[10] on organic bromides. They used a gas stream containing about $^1/_2$ mm. of C_2H_5Br in 20 mm. of toluene and followed the extent of the reaction at various flow rates by analysis of the hydrogen bromide formed. They found no dibenzyl, thus confirming a preliminary experiment communicated by Szwarc, and concluded that the ethyl bromide does not react by the mechanism

$$C_2H_5Br \longrightarrow C_2H_5 + Br$$

nor by any gas phase mechanism giving free radicals or bromine but must decompose alternatively by the reaction

$$C_2H_5Br \longrightarrow C_2H_4 + HBr$$

They obtained first-order rate constants between 527 and 626° and an activation energy of 52.3 kcal. mole^{-1}. Their results are plotted in Fig. 6 together with the high pressure results of this investigation for k and k_0.

The values of k_0, for the initial rate during the induction period are seen to agree with the values of the rate constants of Blades and Murphy, in an excess of toluene giving an activation energy of 52 kcal. mole^{-1}.

Discussion

We are now in a position to better understand the decomposition of ethyl bromide and to explain the data presented earlier.

Green, Harden, Maccoll and Thomas[11] found that whereas some organic halides may break a C–Br bond to give free radicals and bromine atoms, any subsequent reaction with bromine atoms is inhibited by an excess of cyclohexane and then the reaction proceeds by the unimolecular splitting-out of HBr. They obtained an activation energy of 53.9 for the decomposition of ethyl bromide in cyclohexane, in good agreement with Blades and Murphy and with the results of the present investigation.

The normal decomposition of ethyl bromide consists of at least two distinct processes. The first of these is the molecular splitting of ethyl bromide directly into ethylene and hydrogen bromide by a unimolecular mechanism in a homogeneous, first-order gas reaction. This is the reaction measured by Blades and Murphy and by Green, Harden, Maccoll and Thomas and found in the present research during the early induction period before an accumulation of decomposition products, or when sufficient ethylene or hexane is added.

As this first reaction continues the hydrogen bromide concentration increases and as previously shown this material leads to a faster over-all decomposition rate, resulting in an autocatalytic induction period. The fact that the over-all decomposition exhibits first order behavior, even after this induction period, is attributed to the additional inhibiting effect of the product ethylene—a "buffering" effect with both accelerator and inhibitor present. The first-order characteristics of this reaction, *i.e.*, the apparent dependence of the rate of reaction on the pressure of ethyl bromide alone, suggests a steady-state concentration of an intermediate which causes the accelerated reaction.

This intermediate might be bromine atoms. In the earlier work[4] it was assumed that bromine atoms were formed by an initial breakdown into ethyl free radicals, but this mechanism has been disproved by Blades and Murphy. Moreover, the activation energy for the over-all reaction 46.4 ± 0.5 kcal. mole^{-1} is not sufficient to break the carbon–bromine bond which is about 67 kcal. mole^{-1}.[11a,12] At the time of the earlier work,[4] the

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[9] A. Blades and G. W. Murphy, THIS JOURNAL, **74**, 6219 (1952).

[10] M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

[11] J. H. S. Green, G. D. Harden, A. Maccoll and P. J. Thomas, *ibid.*, **21**, 178 (1953).

[11a] Reference 7 gives 67.2.

[12] A. S. Carson, E. M. Carson and B. Wilmshurst, *Nature*, **170**, 320 (1952), give 66.5.

C–Br bond was supposed to have a value of around 53 kcal. mole^{-1}.

Accordingly, another source of bromine must be found. According to evidence already cited a small amount of bromine is found in the decomposing ethyl bromide and it does not come from the hydrogen bromide. The source of the bromine lies in the reaction

$$C_2H_5Br + HBr \longrightarrow C_2H_6 + Br_2$$

The equilibrium constant for this reaction may be calculated thermodynamically using the data of Lane, Linnett and Dawson[7] and other published data. Thus

$$\log K_p = \log \frac{p_{C_2H_6}p_{Br_2}}{p_{C_2H_5Br}p_{HBr}} = -\frac{2430}{T} - 0.5$$

This equation shows that for equal pressures of HBr and C_2H_5Br in the temperature and pressure ranges of these experiments the reaction proceeds sufficiently far (about 1% at 400°) to give bromine molecules and atoms which can give rise to an accelerated over-all reaction. There is experimental evidence for the presence of small amounts of C_2H_6.[4] The kinetics of a similar reaction between C_2H_5I and HI has been studied by Ogg[13] who found it to be a bimolecular reaction with an activation energy of 29.8 kcal. mole^{-1}.

This reaction between ethyl bromide and hydrogen bromide probably takes place on the walls where the heterogeneous reaction would have a lower activation energy than in the gas phase. Peri and Daniels[6] showed that the exchange of radioactive bromine between hydrogen bromide and ethyl bromide is wall-catalyzed in the range 180–310° with an activation energy of about 31 kcal. mole^{-1}. Thus there is support for the reaction of the adsorbed reactants.

Any mechanism proposed for the over-all decomposition must explain (1) the surface dependence, (2) the autocatalytic induction period, (3) the first-order behavior and (4) the influence of the decomposition products on the reaction rates. The accelerated reaction, which follows the homogeneous splitting into ethylene and hydrogen bromide, must be attributed to a process other than the rupture of the C–Br bond in ethyl bromide. On the basis of experiments[14] with ethyl bromide mixed with acetaldehyde a long chain mechanism is rejected.

The following mechanisms seem to offer a satisfactory explanation for the decomposition of ethyl bromide. The first step in the decomposition is the unimolecular gas phase reaction.

$$C_2H_5Br \xrightarrow{k_a} C_2H_4 + HBr \qquad \text{(a)}$$

After some HBr accumulates the following wall-catalyzed reaction takes place

$$C_2H_5Br_{wall} + HBr_{wall} \xrightarrow{k_b} C_2H_6 + Br_2 \text{ (slow)} \qquad \text{(b)}$$

The bromine dissociates into atoms

$$M + Br_2 \underset{k_c'}{\overset{k_c}{\rightleftarrows}} 2Br + M \qquad \text{(c)}$$

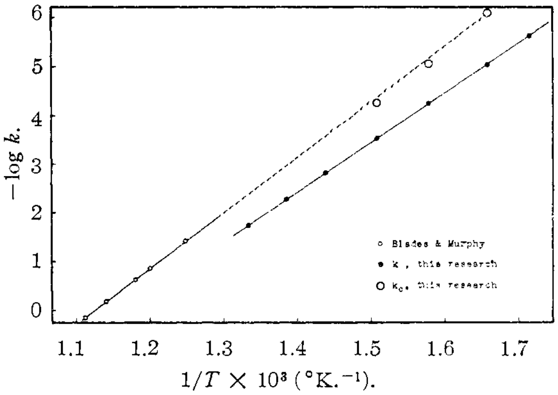

Fig. 6.—Comparison of flow and static experiments.

The bromine atoms then lead to an accelerated decomposition by the relatively slow endothermic step

$$Br + C_2H_5Br \xrightarrow{k_d} C_2H_4Br + HBr \qquad \text{(d)}$$

which is followed by the rapid decomposition

$$C_2H_4Br \xrightarrow{k_e} C_2H_4 + Br \qquad \text{(e)}$$

and the main over-all products C_2H_4 and HBr are thus obtained. Furthermore

$$\left.\begin{array}{ll} Br + C_2H_4 \xrightarrow{k_f} C_2H_3 + HBr & \text{(f)} \\ Br + C_2H_6 \xrightarrow{k_g} C_2H_5 + HBr & \text{(g)} \end{array}\right\} \text{relatively slow}$$

There are secondary reactions such as

$$\left.\begin{array}{l} C_2H_3 + \text{wall} \longrightarrow C_{wall} + CH_3 \\ CH_3 + C_2H_5 \longrightarrow C_3H_8 \\ C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \end{array}\right\} \text{rapid}$$

which give products which have been found in the decomposition of ethyl bromide.[4]

Step a describes the homogeneous reaction, observed at the beginning of the reaction with the rate constant k_0. It is also the reaction which in the presence of toluene, ethylene or hexane proceeds without the competition of other reactions.

The accelerated decomposition following the induction period is explained by steps b through g involving bromine.

The inhibition caused by the addition of ethylene is explained by reaction (f) as is also the inhibition by any other bromine atom acceptor such as hexane. The competition with ethyl bromide and HBr for catalytic surfaces is also a factor in the inhibition by less volatile materials. This competition is supported by the experimental facts that HBr and C_2H_4 added at the beginning of an experiment where the surfaces are relatively free give a greater effect than if they are added later.

The large acceleration produced by oxygen is explained by the reaction

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

which has been studied in the range 490–635°.[15] This reaction increases the supply of bromine and bromine atoms which increase the rate of the over-all reaction. If air is once admitted to a reaction vessel which is coated with carbonaceous material, the oxygen adheres to this coating and it is very

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[13] R. A. Ogg, THIS JOURNAL, **56**, 526 (1934).

[14] J. Roof and F. Daniels, *ibid.*, **62**, 2914 (1940).

[15] Z. Szabo and E. Kiss, *J. Chem. Soc.*, 803 (1949).

difficult to restore the vessel to a condition which will give normal decomposition rates.

According to the reactions as written (steps a through g) the rate of disappearance of C_2H_5Br will be given by the expression

$$\frac{-d(C_2H_5Br)}{dt} = k_a(C_2H_5Br) + k_b(C_2H_5Br_{wall})(HBr_{wall}) + k_d\,(C_2H_5Br)(Br) \quad (1)$$

When $d(Br_2)/dt = 0$

$$k_b\,(C_2H_5Br_{wall})(HBr_{wall}) + k_c'\,(Br)^2(M) = k_c\,(Br_2)(M) \quad (2)$$

When $d(Br)/dt = 0$

$$2k_c\,(Br_2)(M) + k_e\,(C_2H_4Br) = 2k_c'\,(Br)^2(M) + k_d\,(Br)(C_2H_5Br) + k_f\,(Br)(C_2H_4) + k_g\,(Br)(C_2H_6) \quad (3)$$

When $d(C_2H_4Br)/dt = 0$

$$k_d\,(Br)(C_2H_5Br) = k_e\,(C_2H_4Br) \quad (4)$$

Adding twice (2), (3) and (4) together

$$2k_b\,(C_2H_5Br_{wall})(HBr_{wall}) = k_f\,(Br)(C_2H_4) + k_g\,(Br)(C_2H_6)$$

and

$$(Br) = \frac{2k_b\,(C_2H_5Br_{wall})(HBr_{wall})}{k_f\,(C_2H_4) + k_g\,(C_2H_6)} \quad (5)$$

Substituting this value of (Br) into (1) it is seen that

$$-\frac{d(C_2H_5Br)}{dt} = k_a\,(C_2H_5Br) + k_b\,(C_2H_5Br_{wall})(HBr_{wall}) + \frac{2k_b\,(C_2H_5Br_{wall})(HBr_{wall})\,k_d\,(C_2H_5Br)}{k_f\,(C_2H_4) + k_g\,(C_2H_6)} \quad (6)$$

It appears that the concentration of HBr on the wall is directly proportional to the concentration in the gas phase, but at high pressures of C_2H_5Br, $(C_2H_5Br_{wall})$ is constant independent of the concentration of C_2H_5Br. The rate of the reaction $C_2H_5Br_{wall} + HBr_{wall}$ is slow and it does not remove much C_2H_5Br directly. The concentration of C_2H_6 is small compared to the concentration of C_2H_4.[4] Equation 6 may then be rewritten

$$\frac{-d(C_2H_5Br)}{dt} = k_a\,(C_2H_5Br) + \text{constant}\,\frac{(HBr)}{(C_2H_4)}\,(C_2H_5Br) \quad (7)$$

The ratio of (HBr) to (C_2H_4) is constant because these two products are kept stoichiometrically equal as they increase during the course of the reaction. Equation 7 is the equation of a first-order reaction, and it accounts for the fact that this complex reaction still gives good experimentally determined first-order rate constants for the overall reaction.

The kinetics of the decomposition of ethyl bromide and the various factors which affect the rate as reported in earlier work appear now to be fairly well understood. The formation of a halogen by a reaction between the alkyl halide and the hydrogen halide produced by the reaction to give a steady-state concentration of an accelerating intermediate compound may well be a factor in the kinetics of other alkyl halides.

Acknowledgment.—The authors are glad to acknowledge assistance in part of the work from summer fellowships made possible by an E. I. du Pont de Nemours Company grant-in-aid for fundamental research.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

Chemical Equilibria in the Gaseous System Bromine–Bromine Trifluoride–Bromine Monofluoride[1]

BY ROBERT K. STEUNENBERG, RICHARD C. VOGEL AND JACK FISCHER

RECEIVED OCTOBER 24, 1956

Equilibrium constants were determined for the gas-phase reaction $BrF_3 + Br_2 \rightleftarrows 3BrF$. The extent of the reaction was derived from manometric measurements at constant volume and the absorption spectra of the mixtures. Equilibrium constants obtained at different temperatures were used to calculate the standard free energy and enthalpy of formation of bromine trifluoride.

The first chemical evidence for the existence of bromine monofluoride was reported by Ruff and Menzel,[2] who recovered a highly volatile fraction from the distillation of a mixture of bromine and bromine pentafluoride. Further studies, made by Ruff and Braida,[3] indicated that the monofluoride is formed by the reactions of bromine with fluorine, bromine trifluoride and bromine pentafluoride. Pure bromine monofluoride was not isolated due to its dissociation, which was said to be nearly complete at 50°.[3]

A phase investigation in this Laboratory of the condensed system bromine–bromine trifluoride showed only the two pure components in the solid phases.[4] Liquid–vapor equilibrium measurements, however, strongly implied the formation of an intermediate species of high volatility.[5]

Brodersen and Schumacher[6] have calculated the dissociation energy of bromine monofluoride from the limit of the band spectrum, which they obtained from a mixture of bromine and fluorine. The microwave spectrum of a similar mixture has contributed further evidence for the existence of this compound.[7]

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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(3) O. Ruff and A. Braida, *ibid.*, **214**, 81 (1933).

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(5) J. Fischer, J. Bingle and R. C. Vogel, *ibid.*, **78**, 902 (1956).

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