using the solvents at a temperature just slightly below their respective boiling points, and were then extracted using the solvents at the boiling point. Furthermore, we used three solvents, ether, acetone and chloroform, where Cooper used only ether. These differences in experimental technique may account for the contradictory results.

Crowder, Stodola, Pangborn and Anderson[7] compared lipids obtained from four recently isolated strains of human tubercle bacilli with those from H-37. Qualitative results showed the same fatty acids in various strains; quantitative results showed great variation in lipid content. Total lipid content varied from 10.8 to 23.8%. Phosphatide content varied from 0.84 to 6.54%. Their results may explain our findings as being the usual variation observed in different lots of the same bacterium grown on the same medium; or the quantitative variations observed by them may be due to differences in proportions of rough and smooth forms in different lots of bacteria which would account for variations in lipoid content.

Sabin[8] in an extensive series of investigations has studied cellular reactions to the lipoids of the tubercle bacillus. This work shows that all of the lipoid fractions act as maturation factors for monocytes, epithelioid cells and giant cells resulting in the formation of tuberculous tissue. This effect was traced to peculiar fatty acids of high molecular weight isolated from the lipoids. It may be assumed therefore that the effect of the tubercle bacillus on the host can in some measure be attributed to the lipoid content of the bacteria.

Our results, showing a higher lipoid content of the virulent organism, suggest that virulence might be due to quantitative differences in lipoid content and/or mode of combination of lipoid in the cell. The variations in degree of virulence shown by the human H-37 tubercle bacillus again indicate that quantitative factors are concerned. If virulence depended entirely on qualitative factors, a clear-cut separation into virulent and avirulent organisms could be made. This is not possible in the case of the tubercle bacillus.

Summary

Marked differences in the lipoid contents of the dissociants of the human H-37 tubercle bacillus are shown by quantitative estimations of extractability with various solvents. The Rv form contains nearly twice as much lipoidal material which is more easily extractable by organic solvents. An analysis of media on which the two variants were cultivated showed differences in nitrogen utilization.

WINONA, MINN. RECEIVED JANUARY 31, 1938

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[7] J. A. Crowder, F. H. Stodola, M. C. Pangborn and R. J. Anderson, THIS JOURNAL, **58**, 636 (1936).

[8] Florence R. Sabin, Charles A. Doan and Claude E. Forkner, *J. Exptl. Med.*, **52**, Supplement No. 3, 1 (1930).

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

A Study of the Decomposition of Gaseous Ethyl Bromide

BY PAUL FUGASSI[1] AND FARRINGTON DANIELS

The decomposition of ethyl bromide has been studied previously in this Laboratory.[2,3] The present work was undertaken to determine whether theories of free radical chains are applicable to this reaction and to explore further the peculiar behavior of inert, foreign gases in decreasing the reaction rate. Particular attention was paid to the elimination of traces of oxygen and to the analysis of the products.

Experimental Procedure

The molten lead thermostat was the same as used before except that the two stage amplifier was replaced with a single stage amplifier using a 2A5 tube. All the measurements reported here were carried out at 395 ± 0.15°.

The ethyl bromide was prepared by Professor Timmermans in Brussels and obtained from the U. S. Bureau of Standards.

Static Experiments.—Measurements were made in all-glass apparatus. Two different techniques were employed for filling the reaction chambers which were 125-cc. Pyrex flasks provided with glass diaphragms for measuring pressures.

The filling apparatus for the first procedure is shown in Fig. 1,

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

[3] (a) Vernon and Daniels, THIS JOURNAL, **54**, 2563 (1932). (b) Vernon and Daniels, *ibid.*, **55**, 922 (1933).

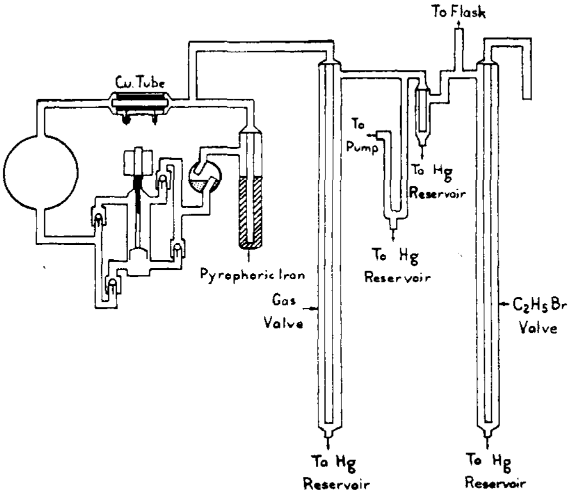

Fig. 1.

It consists of the gas purification system and an arrangement of mercury valves and cut-offs to permit the addition of measured quantities of ethyl bromide and foreign gases to the reaction flask. The purifying train at the left consists of a glass reciprocating pump, a 2-liter storage chamber, a pyrophoric iron chamber, a hot copper tube and a drying tube. The pump had a piston displacement of 20 cc. per oscillation and was operated at about 40 oscillations per minute by means of an external solenoid and circuit interrupter. Once the apparatus was filled, the pump was operated continuously to eliminate all traces of oxygen desorbed from the walls.

Pyrophoric iron was prepared *in situ* by the method of Finzel.[4] It was chosen because of its efficiency in removing oxygen at room temperatures. The "hot-copper" tube, made of quartz, was surrounded by an electrical heating coil which in turn was enclosed in a Pyrex envelope as shown. The electrical leads were brought through the envelope with tungsten seals. The copper was prepared in the usual manner by reduction of C. P. copper oxide with hydrogen.

The efficiency of oxygen removal was tested by the time taken for a beam of ultraviolet light to cause the fluorescence of acetone to change from green to blue.[5] Calibrating against known quantities of air it was found that two nitrogen samples (from tanks) contained 0.16 and 0.50% oxygen. After twelve hours of treatment with the pyrophoric iron the oxygen content of similar samples was reduced to 0.02 and 0.04% and after twenty-four hours it was reduced to less than 0.003%.

The volume of the system between the last cut-off and the reaction flask was kept as small as possible. No rubber connections or stopcocks were employed. The gases and ethyl bromide came in contact only with glass, mercury and the necessary purification agents.

The entire system was always evacuated with a mercury diffusion pump for several hours before filling. The flask and connecting tubes were thoroughly flamed during the evacuation. The mercury valves were rinsed three or four times with the ethyl bromide or with the stored gas. The flask was then surrounded with a water thermostat at 30.00° and the zero point of the diaphragm measured. Ethyl bromide vapor was admitted cautiously through the mercury valve at the right and the dry, oxygen-free gas was admitted through the valve adjoining the purification system. The pressure of ethyl bromide and foreign gas admitted was determined by means of the diaphragm and manometer, and the flask was quickly sealed off. Pressure readings before and after sealing showed that any decomposition of ethyl bromide from sealing was negligible. A small trap surrounded by ice and salt was interposed between the reaction chamber and the rest of the apparatus to avoid possible distillation of mercury vapor from the valves. In some cases a tube 10 cm. long, packed with gold foil was also interposed, but no difference was observed in the decomposition rate.

The flask was immersed in the molten lead thermostat and the pressures measured at definite time intervals.

In the second procedure the reaction flask was kept immersed in the thermostat of molten lead and ethyl bromide and other vapors, such as bromine, were introduced by breaking small bulblets of the liquid with glass enclosed iron hammers operated with solenoids. Except where noted, the reaction flask was cleaned thoroughly before each experiment with fuming nitric acid. It was heated and outgassed with a mercury diffusion pump. Special precautions were necessary in this procedure also to eliminate traces of oxygen. The ethyl bromide or bromine was deoxygenated in an all-glass apparatus provided with two reservoirs and a series of small bulbs. The liquid first was frozen in one reservoir, evacuated with the mercury pump, heated and distilled into the other reservoir. After five or six repetitions of this process the vacuum line was sealed off and a magnetically operated glass valve permitted the distillation of a definite amount of liquid into a capillary buret. From here it was distilled into one of the bulbs and the bulb was sealed off. Several bulbs were prepared at one filling.

Flow Experiments.—The flow experiments were designed primarily to obtain reaction products for analysis but sufficient data were taken so that rate constants could be calculated. The reaction chamber of Pyrex tubing was immersed in the lead bath. A storage bulb for ethyl bromide was sealed at one end and a condensing tube at the other. Two chambers were used; one of 4-mm. tubing with a volume of 20 cc. and the other of 12-mm. tubing with a volume of 120 cc. Three tubes were attached to the condensing tube—one leading to the mercury pump, one to the Sprengel pump and one to a tube in which the reaction product could be condensed and sealed off.

In starting an experiment the apparatus was evacuated for several hours with a mercury vapor pump, the ethyl bromide in the storage bulb being alternately liquefied, distilled and solidified, to eliminate traces of air. Then the evacuation system was sealed off, the condensation tube was surrounded by liquid air and the ethyl bromide vapor was allowed to stream through the furnace and collect in the condensation chamber.

The rate of flow was controlled by varying the vapor pressure of ethyl bromide and by sealing in sections of

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(4) Finzel, THIS JOURNAL, **52**, 142 (1930).

(5) (a) Damon and Daniels, *ibid.*, **55**, 2363 (1933); (b) Damon, *Ind. Eng. Chem., Anal. Ed.*, **7**, 133 (1935); (c) Fugassi, THIS JOURNAL, **59**, 2092 (1937).

0.5-mm. capillary between the reaction chamber and the condensation chamber. By-passes were sealed around the capillary during the preliminary evacuation, after which they were sealed off. The vapor pressure was fixed by surrounding the storage bulb of ethyl bromide with a constant-temperature bath. A constant-temperature mixture of bromobenzene (or other material) was prepared by adding dry ice and stirring until a thick mush of solid and liquid was obtained. Such baths would maintain the temperature constant to within 0.2° over two-hour periods. After the flow of vapor through the furnace had continued for two to four hours, both tubes were immersed in liquid air and the condensation tube was sealed off from the reaction chamber. The condensed products were surrounded by an acetone–dry ice mixture and the gases pumped off with a Sprengel pump and stored over mercury. A soda-lime tube removed the small amounts of hydrogen bromide that were pumped off. After several hours of pumping the remaining liquid was assumed to be ethyl bromide. It was sealed off and weighed in order to determine the quantity of undecomposed ethyl bromide vapor that passed through the reaction chamber.

Analysis of Products.—Analyses were made with a small Orsat type of apparatus using a 15-cc. buret and a slow combustion chamber with a platinum spiral. Olefinic compounds were determined by absorption in 1% fuming sulfuric acid. Mercury was used as the confining liquid in all operations, except that in the static experiments the gases were displaced with carbon dioxide-free water. In the static experiments designed for analysis of products the initial pressure of ethyl bromide was 345 mm. and the heating period less than twenty-five minutes. The temperature in all the experiments was 395°.

In order to determine the composition of the small amount of products other than ethylene and hydrobromic acid, vapor pressure measurements were made at low temperatures. A 2-cc. cell was attached with capillary tubing to a manometer provided with a small trap at the bottom to prevent the introduction of any gases from the levelling bulb. After three "passes" through fuming sulfuric acid to remove ethylene, and after treatment with potassium hydroxide solution, the gases were liquefied in the small cell with liquid air, and sealed off. The cell then was surrounded by different freezing baths and the pressure measured when the manometer liquid was brought to a definite position on the scale by means of the levelling bulb. Identical results were obtained when the equilibrium was approached from higher temperatures and from lower temperatures.

Calculations.—The rate constants of the static experiments were determined by plotting log $(2p_i - p)$ against time for the first fourth or more of the decomposition. This is the method IV, discussed previously.[3b] The initial pressure, p_i, was determined by extrapolation to zero time. The pressure of any added gas was included in the diaphragm correction.

In the flow experiments the constants were calculated by the equation of Benton.[6]

Experimental Results

The results of a series of static experiments are given in Table I and Fig. 2.

TABLE I

SPECIFIC DECOMPOSITION RATES OF ETHYL BROMIDE (395°)

Initial pressure C_2H_5Br, mm.	$k \times 10^4$, sec.$^{-1}$	Initial pressure C_2H_5Br, mm.	$k \times 10^4$, sec.$^{-1}$
130.3	4.08	57.8	2.95*
125.6	4.15	56.2	3.18
103.8	4.14	48.4	2.79
84.3	3.84	47.7	2.91
70.1	3.66	46.5	2.22
65.4	3.63	43.1	1.78
61.4	3.44	29.5	1.16

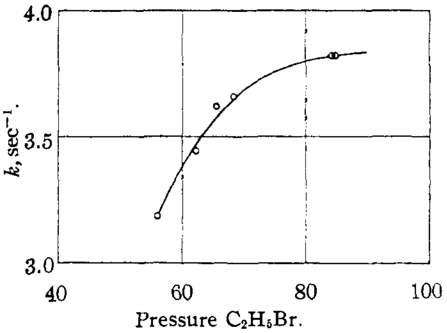

Fig. 2.

The last two determinations were made with extra gold foil to trap any possible mercury vapor. The determination marked by an asterisk (*) was made by the second procedure in which mercury valves were not present. These three experiments give values consistent with the others and show that mercury vapor from the valves at room temperature was not a factor in the decomposition rate. The rate constants are uniformly lower by 20 or 30% than the results of Lessig[2] and of Vernon and Daniels[3] for the same initial pressures of ethyl bromide. The difference is due possibly in part to the extra precautions taken in the present work for the complete removal of oxygen and in part to the fact that smaller reaction chambers were used here. It was shown before that oxygen in small amounts exhibits a marked catalytic effect.

It is seen in Table I and Fig. 2 that the specific rate constant starts to fall off at initial pressures of about 100 mm. in agreement with earlier findings[3] and with the predictions of current theories of unimolecular reaction rates.

In Table II are shown the results of experiments on the influence of inert foreign gases. The initial

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(6) Benton, THIS JOURNAL, 53, 2984 (1931).

pressure of ethyl bromide was kept in the range from 60 to 70 mm. where present theories of unimolecular reactions demand that the specific rate constant should be increased by the higher pressure, approaching its normal high-pressure value.

TABLE II

EFFECT OF HYDROGEN AND NITROGEN ON THE DECOMPOSITION RATE OF C_2H_5Br

Pressure C_2H_5Br, mm.	Pressure added gas, mm.	$k \times 10^4$, sec.$^{-1}$	k/k_0
	Hydrogen		
63.7	10.4	3.47	0.99
64.7	32.7	3.50	.98
67.6	48.3	3.96	1.09
70.2	66.0	3.80	1.03
64.3	70.9	3.54	1.00
60.6	234.6	2.53	0.74
68.7	362.0	1.77	.48
	Nitrogen		
64.3	13.5	3.58	1.01
68.2	39.1	3.99	1.09
65.2	58.9	3.58	1.00
66.3	114.3	3.57	0.99
70.5	118.2	3.06	.83
68.4	210.9	2.81	.77
65.9	258.3	2.58	.77

The last column gives the ratio of the measured rate constant to the rate constant in the absence of any added gas as interpolated from a large-size graph similar to that of Fig. 2. These values of k/k_0 are plotted against the pressure of the added gas in Fig. 3. It will be noted that the value of k/k_0 passes through a maximum and then decreases. Considerable accuracy in the measurements is necessary to establish this maximum—in less accurate measurements it would be missed. The fact that the points for both nitrogen and hydrogen hit this smooth curve shows that there is nothing chemically specific in the action, even if a chemical action could be imagined.

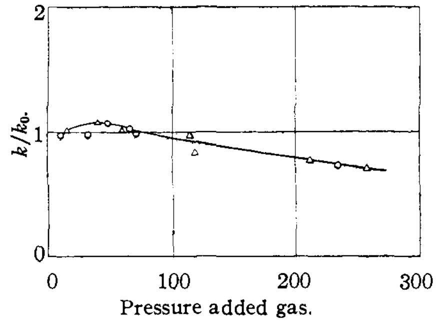

Fig. 3.—○, Hydrogen; △, nitrogen.

Experiments with other added gases are shown in Fig. 4, but significant constants are not reported since the decomposition rate does not follow the first order relation. When carbon dioxide is added there is a slight decrease in decomposition rate.

When bromine is added there is a marked increase in the rate of pressure rise as noted before.[2]

A photochemical experiment was attempted to study still further the action of bromine (atoms). In a cell surrounded by boiling mercury (300°) a bromine bulb was broken to give 7.6 mm. and then a second bulb of ethyl bromide was broken to give a total pressure of 31 mm. Within six minutes the bromine color had faded appreciably and even after darkening the cell with tin foil the bromine disappeared in about thirty minutes. The pressure rose about 4 mm. in all. Apparently bromine undergoes direct chemical reaction with ethyl bromide at this temperature, thus complicating the situation.

Mercury vapor markedly retarded the rate of pressure increase and at the end of any experiment with mercury present, it was found that chilling the flask at one point produced a flocculent, white precipitate at that point. The effect of mercury cannot be stoichiometrical for even if all the 2.5 mm. of mercury reacted to form mercury bromide the resulting pressure should be considerably greater than that observed in Fig. 4.

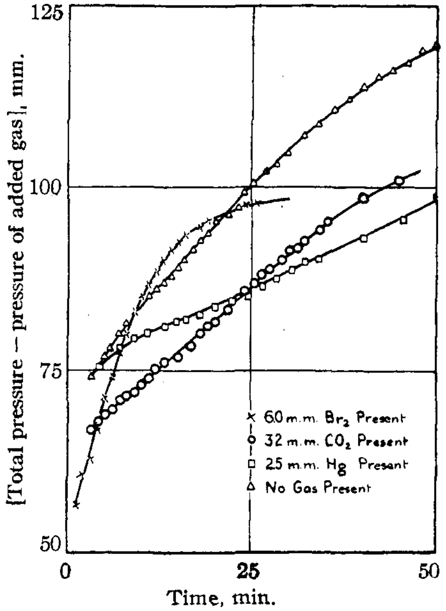

Fig. 4.

Packed Flasks.—Experiments with packed flasks are summarized in Table III. The flask was filled with short pieces of 4-mm. Pyrex tubing and the second procedure was used in filling the chamber.

TABLE III

EFFECT OF PACKING ON THE SPECIFIC DECOMPOSITION RATE

Init. press. C_2H_5Br, mm.	92.1	14.2	58.0	64.6
$k \times 10^4$, sec.$^{-1}$	8.79	1.66	7.89	5.99

The first three results were obtained consecutively without removing the flask. When the flask was removed a reddish-brown deposit was found near the top. Such a deposit was not found in the static experiments in which a cleaned flask was used for each experiment. The last experiment in the table was made after the flask and packing had been thoroughly cleaned. It is seen that the decomposition rate constant as measured by the pressure increase is nearly twice as large in the packed flasks.

Flow Experiments.—The results of the flow experiments are summarized in Table IV.

TABLE IV

DECOMPOSITION OF THE ETHYL BROMIDE BY THE FLOW METHOD

Initial pressure C_2H_5Br mm.	Contact time, sec.	Decomposition, %	$k \times 10^4$, sec.$^{-1}$
32.9	37	1.0	2.8
32.9	220	4.3	2.0
32.9	240	3.7	1.6
32.9	350	4.2	1.2
22.3	3030	20.0	0.8
22.3	3920	24.3	.7

These constants are less reliable than those obtained by the static method but the rate constant decreases with increasing time of contact. The reaction proceeds faster during its initial stages. The determinations with the longer contact time check with the measurements by the static method.

Analysis of Products.—After removal of the olefinic compounds and hydrobromic acid a small residue of hydrocarbons was obtained, the composition of which was determined with the help of vapor pressure data ("I. C. T.") and measurements on the decrease in pressure produced by decreasing the temperature in various ranges. The experimental vapor pressures are consistent with standard data if it is assumed that the residual gas has the following percentage composition: hydrogen, 42.7; ethane, 35.9; propane, 14.5; and butane, 6.8. The maximum percentage of methane that could have been present is about 2 and so methane has been neglected. As a check on this composition it can be calculated that such a mixture on combustion would give a contraction in volume 1.55 times as great as the contraction produced by absorbing the resulting carbon dioxide in sodium hydroxide.

Neglecting the smaller amounts of propane and butane the analysis of all the products except hydrobromic acid is given in Table V.

TABLE V

ANALYSES OF GASES

Type of expt.	C_2H_4, %	C_2H_6, %	H_2, %	$\Delta V_{\text{comb.}}/V_{CO_2}$
Static	98.6	1.0	0.4	1.53
Static	98.7	1.0	.3	1.47
Static	98.7	1.1	.2	1.45
Flow	92.1	6.3	1.6	1.46
Flow	93.1	5.7	1.2	1.54
Flow	93.7	5.1	1.2	1.47

This table shows that the products other than ethylene increase when the reaction is carried out in a flow system with its larger ratio of surface to volume. The values of $\Delta V_{\text{comb.}}/V_{CO_2}$ are considered to be in agreement among themselves and with the value calculated from vapor pressure analysis. It is believed that the percentage composition of the residual gas is roughly the same for all the experiments.

Discussion

Historical.—Nef[7] in 1901 found by a flow method that ethyl bromide at high temperatures decomposes into ethylene and hydrobromic acid. He postulated an intermediate step with the formation of ethylidene free radicals which then rearranged to give ethylene

$$C_2H_5Br \longrightarrow CH_3CH{=} + HBr$$
$$CH_3CH{=} \longrightarrow C_2H_4$$

Vernon and Daniels[3] assumed a direct unimolecular decomposition

$$C_2H_5Br \rightleftharpoons C_2H_4 + HBr$$

partly complicated by the reverse reaction, namely, the addition of hydrobromic acid to ethylene. Corrections for this reverse reaction gave rate constants in good agreement with those obtained under conditions which did not involve the reverse reaction. They obtained an activation energy of 55,000 cal. for the decomposition of ethyl bromide. Quantum calculations[8] for the

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(7) Nef, *Ann.*, **318**, 1 (1901).

(8) Unpublished.

addition of hydrobromic acid to ethylene combined with the known heat of the dissociation gave a calculated value very close to 55,000 cal. The direct unimolecular decomposition into ethylene and hydrobromic acid then seems quite plausible. Possible longitudinal vibrations of bromine and hydrogen atoms on adjoining carbon atoms are involved, bringing the two atoms H and Br into close proximity so that the hydrobromic acid molecule may split off. As already explained the decreasing value of the rate constant at low pressures is in agreement with the concept of a direct unimolecular decomposition.

Semenoff[9] pointed out that some of the curves of Vernon and Daniels showed an induction period and suggested that a chain mechanism is involved. The increasing importance of free radical chains as advocated by F. O. Rice[10] also made advisable a reëxamination of the decomposition as a possible free-radical chain reaction.

Quantum calculations[11] have indicated that the decomposition of ethylene chloride takes place by a free-radical chain mechanism but that the energies of activation for the unimolecular decomposition and the chain mechanism are so nearly the same for ethylene bromide and iodide that both mechanisms probably occur simultaneously.

Effect of Added Gases.—The reduction in rate constant produced by hydrogen and nitrogen is not explained easily. If hydrogen adds to ethylene, a decrease in pressure would be expected. However an extrapolation of Pease's data[12] shows that the reaction at 395° is much too slow to be detected in these experiments. The equilibrium is favorable for the reactions and conceivably there may be a catalytic effect. However, the behavior of nitrogen is roughly the same as that of hydrogen, and certainly with nitrogen there can be no reaction with ethylene. The action of hydrogen and nitrogen suggests some type of complex reaction involving intermediate steps.

The effect of a trace of mercury in decreasing the rate constant and the effect of a trace of oxygen[3] in increasing it, also demand a complex reaction. The quantities were too small to account for the observed pressure change on the basis of any stoichiometrical reaction with ethyl bromide or its decomposition products.

Reaction Products.—The discovery of small but definite amounts of hydrogen, ethane and propane shows again that the reaction cannot be entirely the simple unimolecular decomposition into ethylene and hydrobromic acid. It is true that these materials might be expected to come from a polymerization and decomposition of the product ethylene. Pease[13] reported traces of methane, hydrogen and ethane in the polymerization–decomposition of ethylene but he also showed that the reaction is a complex chain reaction which is ended on the walls of the reaction chambers. This reaction should then be less in the flow experiments (narrow cylinder) than in the static experiments (large flask). In the experiments described here just the opposite effect was found; the flow experiments gave the higher yield of saturated hydrocarbons.

Primary Steps.—The primary steps in the decomposition of ethyl bromide might be written as any of the following

$$C_2H_5Br \longrightarrow C_2H_4Br + H \qquad (1)$$
$$C_2H_5Br \longrightarrow CH_3 + CH_2Br \qquad (2)$$
$$C_2H_5Br \longrightarrow C_2H_4 + HBr \qquad (3)$$
$$C_2H_5Br \longrightarrow C_2H_5 + Br \qquad (4)$$

The first reaction involves the breaking of a carbon–hydrogen bond which requires the absorption of nearly 100,000 cal. The energy of activation for this endothermic reaction must be at least as great as this and perhaps greater, and since the experimental facts show that only 55,000 cal. is required for the decomposition of ethyl bromide, it follows that reaction (1) is not possible. Likewise reaction (2) can be ruled out on the assumption that 77,000 cal. is required to break a carbon–carbon bond because the energy of activation would have to be at least as great as this. There is some uncertainty regarding the heat required to rupture the carbon–carbon bond and if the value should be revised down to 55,000 or less reaction (2) could not then be ruled out on the basis of thermochemical calculations. It might still be ruled out, of course, if calculations of the activation energy should give a high value. Reaction (3) is possible, the energy required for it being of the order of 55,000 cal. Another mechanism might be written, splitting out ethylidene or ethylene free radicals but the existence of these particular free radicals has not been demonstrated.

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[9] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, 114 Fifth Ave., New York, N. Y., 1935, p. 450.

[10] Summarized in "The Aliphatic Free Radicals," by F. O. and K. K. Rice, The Johns Hopkins University Press, Baltimore, Md., 1935.

[11] Sherman and Sun, THIS JOURNAL, **56**, 1096 (1934).

[12] Pease, *ibid.*, **54**, 1876 (1932).

[13] Pease, *ibid.*, **52**, 1158 (1930).

Reaction (4) is possible and in fact quite likely. The breaking of a carbon–bromine bond involves the expenditure of about 58,000 cal., only slightly more than 55,000 cal., observed for the reaction. The difference of 3000 cal. comes within the limit of uncertainty of the experimental values. Independent photochemical data and spectral evidence also suggest that alkyl halides dissociate into the halide atom and the free radical[10] (pp. 28–29).

Mechanisms.—Many different chain propagating mechanisms were set up, but most of them were ruled out on the basis of the products formed, or on the basis of the energy requirements for the primary step. The following steps consecutive to the primary decomposition into C_2H_5 and Br are, however, worthy of consideration

$$\begin{array}{lll}
\text{I.} & C_2H_5Br \longrightarrow C_2H_5 + Br & (A) \\
 & C_2H_5 + Br \longrightarrow C_2H_5Br & (B) \\
 & Br + C_2H_5Br \longrightarrow HBr + C_2H_4Br & (C) \\
 & C_2H_4Br \longrightarrow C_2H_4 + Br & (D) \\
 & Br + C_2H_5Br \longrightarrow HBr + C_2H_4Br, \text{ etc.} & (C') \\
 & Br + Br + \text{wall} \longrightarrow Br_2 & (E) \\
 & C_2H_5 + \text{wall} \longrightarrow C_2H_5 \text{ (wall)} & (F) \\
 & 2C_2H_5 \text{ (wall)} \longrightarrow C_2H_4 + C_2H_6 & (G) \\
\text{II.} & C_2H_5 \longrightarrow C_2H_4 + H & (K) \\
 & H + C_2H_5Br \longrightarrow HBr + C_2H_5 & (L) \\
 & C_2H_5 \longrightarrow C_2H_4 + H, \text{ etc.} & (M)
\end{array}$$

The chain mechanism II can be ruled out on the basis of experiments on the direct addition of hydrogen atoms from an electrical discharge tube.[14] The products of this reaction were methane 65%, ethane 23%, ethylene 10%, and acetylene 2%. These products are widely different from the products found in the thermal decomposition of ethyl bromide. Furthermore the heat of step (K) is about 92,000 cal. and the reaction is impossible because the activation energy must be equal to this or greater—and only 55,000 cal. is available.

Side reactions accompanying some of these excluded chains were considered, to ascertain whether they might give the principal products ethylene and hydrobromic acid. The experimental fact that the addition of hydrogen affects the decomposition rate no more than the addition of nitrogen is sufficient to eliminate side reactions involving molecular hydrogen. Methane, ethane and propane do not decompose rapidly at 395°. Of the possible bromination products methyl bromide would not decompose appreciably, while propyl bromide and ethylene bromide would be decomposed completely at this temperature.

Mechanism I seems to be about the only chain mechanism which is in accord with the facts. It can be shown that it is possible to obtain a first order over-all reaction with it, in which the over-all reaction is proportional to the concentration of ethyl bromide, and that most of the facts concerned with the added gases and the surface effects can be explained. The chain is stopped eventually by the formation of bromine which then disappears by reaction with ethylene or with ethyl bromide. However, two objections may be raised to mechanism I. In the first place it is difficult to account for the large temperature effect which is known to exist, corresponding to an activation energy of 55,000 cal. The activation energy of the primary step (A) is not involved in the over-all reaction which gives a steady state of bromine atoms and leads to a first-order reaction. The other steps (C) and (D), which are involved in the chain, possess activation energies much less than the observed 55,000 cal. In the second place a free radical is very reactive and as a general rule will find it easier to react than to decompose. It is estimated that step (D) requires an activation energy of about 13,000 cal.,[15] whereas the activation energy for reaction of free radicals is much less.

Under some conditions however step (A) may be made the rate-determining step and then the over-all reaction will have an activation energy at least as large as that required to break the carbon–bromine bond. Accordingly, mechanism III is proposed as follows

$$\begin{array}{lll}
\text{III.} & C_2H_5Br \longrightarrow C_2H_5 + Br & (a) \\
 & C_2H_5 + Br \longrightarrow C_2H_5Br & (b) \\
 & Br + C_2H_5Br \longrightarrow C_2H_4Br + HBr & (c) \\
 & C_2H_4Br + C_2H_5 \longrightarrow C_2H_5Br + C_2H_4 & (d) \\
 & Br + Br + \text{wall} \longrightarrow Br_2 & (e) \\
 & C_2H_5 + \text{wall} \longrightarrow C_2H_5 \text{ (wall)} & (f) \\
 & 2C_2H_5 \text{ (wall)} \longrightarrow C_2H_4 + C_2H_6 & (g) \\
 & 2C_2H_5 \text{ (wall)} \longrightarrow 2C_2H_4 + H_2 & (h) \\
 & 2C_2H_5 \text{ (wall)} \longrightarrow C_4H_{10} & (i)
\end{array}$$

It will be observed that these reaction steps are the same as those postulated for the chain reaction, I, with one important exception. The chain propagating steps (C) and (D) are dropped out and substituted by a single reaction (d) between the two free radicals, C_2H_4Br and C_2H_5. Although the concentrations of free radicals are

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[14] Chadwell and Titani, THIS JOURNAL, **55**, 1363 (1933).

[15] Sherman, Quimby and Sutherland, *J. Chem. Phys.*, **4**, 727 (1936).

very low, the reactions (c) and (d) nevertheless may be rapid because the energies of activation for reactions with free radicals are very small.

According to this scheme without the chain, the slow, rate-determining step is the primary dissociation of ethyl bromide into ethyl radicals and bromine atoms, according to (a) or (A). All the steps which follow are too fast to be measurable. Any changes in them will lead to small changes in the over-all observed rate, whereas the same changes might lead to large effects in a chain mechanism involving a steady state as in mechanism I. It is to be noted that none of the changes in the rate constant described in these experiments amount to more than 50%.

Final decision between mechanisms I and III must await more exact information concerning the relative rates of (D) and (d), but (d) now seems to be the faster, thus favoring mechanism III.

The various effects described in the experiments can be explained on the basis of mechanism III. When the ratio of surface to volume is increased, as with packed flasks or in the flow experiments, reactions (f) and (g) are favored and more saturated products such as ethane and hydrogen result.

The addition of an inert foreign gas such as nitrogen or hydrogen to ethyl bromide at low pressures increases the number of collisions and tends to increase the specific decomposition rate up to its normal high pressure value. However, the inert gas may *decrease* the reaction rate possibly by keeping the fragments Br and C_2H_5 closer together; or by providing molecules for third body collisions, thus dissipating energy as kinetic energy and increasing the chance of recombination. In either case the reverse reaction (b) or (B) is favored and the net result is a slower over-all decomposition rate. These two opposing effects produce a maximum shown in Fig. 3.

The accelerating effect of bromine is due to the increased concentration of bromine atoms from thermal dissociation, and an increase in reaction (c) or (C).

The catalytic effect of oxygen may be caused by the oxidation of ethyl radicals.

Although mechanism III for the thermal decomposition of ethyl bromide cannot be considered to be proved, it is nevertheless offered as a plausible one for at least part of the reaction. Added confidence follows from the fact that under several normal and abnormal conditions the results have been explained. It is significant that small variations in the decomposition, produced by surface changes and added gases, can be explained on the basis of free radicals without resorting to the assumption of a chain mechanism. A direct unimolecular decomposition into ethylene and hydrobromic acid may be occurring, but probably it is not the only means of decomposition. The effect of surfaces and added gases can be accounted for on the basis of a primary decomposition into ethyl free radicals and bromine atoms.

Further work on this problem is now in progress, particularly with reference to the activation energy, the time-lag and the behavior of the decomposition product, ethylene. The authors are glad to acknowledge financial support given for this investigation by the Wisconsin Alumni Research Foundation.

Summary

1. The rate of decomposition of ethyl bromide and the nature of the decomposition products have been determined at 395° in an all-glass apparatus with special precautions to eliminate traces of oxygen. Both static and flow methods were used.

2. The decomposition is of the first order and the constants agree with those of earlier work. The influence of increased surface and of hydrogen, nitrogen, bromine, and mercury have been determined.

3. The results have been explained in part on the basis of a primary decomposition into ethyl free radicals and bromine atoms, without involving a chain reaction.

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