

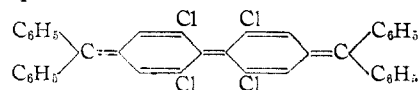
data on the rates of racemization of biphenyl compounds, shows that the potential barrier must be less than 20 kcal. This low value seems to us to rule out definitely the coplanar configuration of dianthrone as an explanation of state 2.

The betaine structure of dianthrone, having no uncoupled spins, is presumably one of several valence bond structures which must be considered in deriving the real resonance state of the molecule. *A priori*, it is possible that states 1 and 2 are two related resonance states, for instance one even and the other odd. This would account for the observed selection rules, but Professor R. S. Mulliken kindly informed us that in his opinion a separation of only 3.5 kcal. between two such resonance states is highly improbable; with this opinion we are entirely in accord. In view of the participation of betaine structure in the resonance of the molecule, the further existence of a tautomeric betaine structure of different nuclear configuration seems rather improbable. Furthermore, such a non-resonating tautomer would presumably have the properties of a zwitterion and yet the absorption spectrum was found to be virtually independent of the polarity of the solvent.

Mulliken<sup>15</sup> has pointed out that the energy separation of the lowest singlet and triplet levels in ethylenic molecules should decrease with increasing torsion of the double bond. This torsion is present in dianthrone because of steric hindrance between atoms in the 4,4'-positions and we favor,

(15) Mulliken and Roothaan, *Chem. Revs.*, **41**, 219 (1947).

therefore, an interpretation of state 2 (and state 3) as the diradical triplet state of the molecule, with the two halves at approximately 90° angle to each other, whereas the ground state (and state 4) is a singlet, with the double bond in a state of considerable torsion. This interpretation finds strong support in the studies of Mueller and Neuhoff<sup>16</sup> on the magnetic susceptibility of the compound



which was shown to exist partially in paramagnetic state and in some other observations cited by Bergmann.<sup>17</sup>

### Summary

The thermochromism of diphenylmethylenanthrone and dianisylmethylenanthrone has been shown to be due to a trivial cause, the broadening of a near-ultraviolet absorption region by changing distribution of molecules among vibrational states.

The thermochromism of dianthrone and dianthrone-2,2'-dicarboxylic acid is due to the existence of a distinct electronic level situated 3.5 kcal. above the ground state. By elimination of other possibilities it is concluded that this level is a triplet (diradical) state of the molecules.

(16) Mueller and Neuhoff, *Ber.*, **72**, 2063 (1939).

(17) Bergmann, "Isomerism and Isomerisation," Interscience Publishers, Inc., New York, N. Y., 1948.

CAMBRIDGE 38, MASSACHUSETTS

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

## Isotopic Exchange Reactions of Gaseous Ethyl Bromide with Bromine, Hydrogen Bromide and Deuterium Bromide<sup>1</sup>

BY JOHN B. PERI AND FARRINGTON DANIELS\*

The thermal decomposition of ethyl bromide into ethylene and hydrogen bromide at elevated temperature has been the object of extended investigations in this Laboratory. Selected in 1932<sup>1a</sup> as a "simple" gas phase reaction it has been used in successive researches<sup>2,3,4</sup> to test prevailing views in the kinetics of gas phase reactions, collision hypotheses, free radicals, chain mechanisms and wall effects.

Following the easiest procedure, commonly accepted in the 1930's, the course of the reaction

\* Harvard University Ph.D. 1914.

(1) More complete details of this investigation may be obtained from the Ph.D. thesis of John B. Peri, filed in the library of the University of Wisconsin in June, 1949.

(1a) E. T. Lessig, *J. Phys. Chem.*, **36**, 2335 (1932).

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

(3) P. Fugassi and F. Daniels, *ibid.*, **60**, 771 (1938).

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

in most of the experiments was followed by the measurement of total pressure as a function of time, and it was concluded that although the reaction was affected by the glass walls of the vessel and although chain mechanisms could not be ruled out, the main rate-determining step nevertheless was probably the unimolecular breaking of the C-Br bond.

Isotopic tracers have provided a new tool for exploring further into the mechanism of this reaction. Preliminary studies with inadequate amounts of radioactive bromine<sup>5</sup> seemed to show that at temperatures above 325°, bromine in hydrogen bromide exchanged places with the bromine in ethyl bromide, and that the reaction was faster than the decomposition of ethyl bromide, but that at temperatures below 225° only slight

(5) H. M. Hulbert, Ph.D. Thesis, University of Wisconsin, 1942.

exchange took place. Liberatore and Wiig reported exchange at elevated temperatures.<sup>6</sup>

A study of this reaction was taken up again in 1947 making use of the isotopic tracers available from the U. S. Atomic Energy Commission. The present communication records these results showing that bromine reacts with ethyl bromide at low temperatures to give dibromides, that in mixtures of ethyl bromide and hydrogen bromide the bromine exchange occurs as a wall-catalyzed reaction around 300°. The deuterium exchange is probably a chain reaction not affected by wall area. Possible mechanisms for these exchanges are discussed together with their bearing on the decomposition of ethyl bromide. The decomposition of ethyl bromide is now under further investigation using specific chemical analysis instead of total pressure for following the course of the reaction.

### Experimental Procedures

**C<sub>2</sub>H<sub>5</sub>Br.**—Ethyl bromide was synthesized or purchased from the Eastman Kodak Co. and then purified by washing with dilute carbonate solution, drying and distilling repeatedly from phosphorus pentoxide in a packed distilling column with a reflux ratio of 15 to 1, until there was no difference in refractive index between the initial and final fractions. Materials from different sources all gave the accepted boiling point, refractive index and density.<sup>7,8</sup>

Samples of 1 to 2.5 ml. were degassed by freezing, evacuating and melting five or six times until no discharge was obtained with a Tesla coil above the frozen sample. They were then sealed off under vacuum in small tubes which were later broken with magnetic hammers in all-glass apparatus.

Radioactive potassium bromide containing bromine 82 with a half life of 35.5 hours was obtained from Oak Ridge, Tennessee. The authors are pleased to acknowledge the valuable assistance provided in this way by the U. S. Atomic Energy Commission.

**Br\*.**—Radioactive bromine was prepared from KBr\* with the addition of a carrier by the action of phosphoric acid and a 50% excess of potassium bromate. The bromine was prepared in an all-glass apparatus, and collected and sealed off in capillary tubes—usually about  $3.5 \times 10^{-4}$  mole per tube. The experiments on mixtures of bromine and ethyl bromide were carried out in a 4-liter vessel attached to an all-glass assembly with the usual mercury vapor pumps for outgassing the vessel, McLeod gage, drying tubes, liquid air traps and gates broken with magnetic hammers. When the exchange with bromine had proceeded far enough, the magnetic gate was opened and the products were collected in a liquid air trap. The trap was allowed to warm up to -40° and dry hydrogen bromide was determined by absorption in standardized sodium hydroxide and the radioactivity which it contained was determined by the Geiger-Mueller counter. Known amounts of inactive ethyl bromide and other compounds were added as carriers to the products remaining in the cold trap and the whole was warmed up, purified and distilled into eight to ten different fractions each of which was measured for its radioactivity in a Geiger-Mueller counter which had a capacity of about 12 ml. of solution in the annular jacket. The experiments were usually planned to give a total of about a million disintegrations per minute.

**HBr\*.**—Most of the exchange experiments with hydrogen bromide and deuterium bromide were carried out in sealed-off glass tubes of 235 ml. immersed in an oil thermostat up

to 258°, and a sodium and potassium nitrate thermostat up to 306°. Four to six of these carefully prepared tubes were immersed in the thermostat for varying lengths of time after which they were removed and quickly chilled with an air blast and broken open for analysis. The radioactivity in the different fractions was then determined.

The hydrogen bromide containing radioactive bromine was prepared by mixing an excess of 48% hydrobromic acid with the radioactive potassium bromide solution. Exchange is very rapid and the hydrobromic acid was distilled out into a phosphorus pentoxide tube. The gaseous hydrogen bromide containing radioactive bromine was then purified by distilling back and forth through red phosphorus and phosphorus pentoxide between two cold traps to remove traces of bromine and water.

Several bulbs were filled at one time with measured amounts of ethyl bromide and hydrogen bromide using a manifold of stopcocks lubricated with high-vacuum, stopcock grease of silicone. The amount of hydrogen bromide was determined from the total activity present in the bulb and its initial molal activity. The bulbs were outgassed and filled to the desired partial pressures of ethyl bromide and hydrogen bromide, as calculated from the geometry of the apparatus, the stopcocks were closed and the contents of the bulbs were frozen out with liquid air in narrow tubes extending as tips below the bulbs. When the bulbs were thus temporarily freed from the decomposable gases they were sealed off from the manifold.

The bulbs were then set in the high-temperature thermostat for the desired length of time. After removal and condensation of the materials in the tips using liquid air the bulbs were opened and ethyl bromide carrier and 0.1 molar sodium carbonate were added immediately. All operations were carried out in weak artificial light. The ethyl bromide and the several sodium carbonate washings containing the bromine from the hydrogen bromide were then counted for radioactivity and the per cent. of total activity present in ethyl bromide and hydrogen bromide was calculated.

**DBr.**—The deuterium bromide was prepared from deuterium (over 99.5% pure) from the Stewart Oxygen Co. which had been purified further by passage through liquid air tubes. The principal impurity was probably hydrogen but the amount, which was less than 0.5%, was too small to be detected by the analytical method used in this work. Highly purified bromine was mixed with a slight excess of deuterium at approximately 400° for twelve hours or more. The reaction was complete and the deuterium bromide was frozen and separated from the excess of deuterium in a multiple trap, consisting of five loops of Pyrex tubing with the lower part of the loops dipping into liquid air. The deuterium bromide was dried and further purified by distillation in vacuum through a multiple trap, cooled with ethyl bromide slush at -120° and then frozen out with liquid air. It was degassed with repeated freezing, evacuating and melting.

The pressure of each gas was determined with the help of a mercury manometer acting through a glass diaphragm,<sup>9,10</sup> consisting of two glass bulbs fused together with a single diaphragm, one side of which was silvered to act as a reflecting surface for a beam of light.

The gases were then frozen out in a side tube while the bulb was sealed off. Each bulb contained a break-seal so that after allowing the reaction to proceed for a given period of time the bulb could be removed, chilled and sealed to fractionating apparatus. After evacuating the apparatus to 10<sup>-6</sup> mm. the seal was broken with a magnetic hammer.

In order to separate most of the hydrogen and deuterium bromide from ethyl bromide, the contents were distilled through a multiple trap immersed in a slush of ethyl bromide at -120°. Then hydrogen bromide and deuterium bromide passed on through and were condensed in

(6) L. C. Liberatore and E. O. Wiig, *J. Chem. Phys.*, **8**, 349 (1940).

(7) J. Timmermans and F. Martin, *ibid.*, **23**, 768 (1926).

(8) A. I. Vogel, *J. Chem. Soc.*, 636 (1943).

(9) Thomas Newton, *J. Chem. Phys.*, forthcoming publication.

(10) H. Mouquin and R. L. Garman, *Ind. Eng. Chem., Anal. Ed.*, **9**, 287 (1937).

a reduction bulb immersed in liquid air. The reduction bulb contained aluminum foil and a drop of mercury which reduced the hydrogen and deuterium bromides to hydrogen and deuterium so that the extent of the deuterium exchange with ethyl bromide could be determined. Usually five or six hours at 350° was sufficient for complete reduction, but occasionally the aluminum was passive and required long exposure with several cycles of rapid heating and cooling.

The H<sub>2</sub>, D<sub>2</sub> and HD mixtures were analyzed by means of thermal conductance.<sup>11</sup> In Fig. 1 the aluminum reduction tube is shown at the left, in which H<sub>2</sub>, HD and D<sub>2</sub> are prepared from their bromides. These gases are transferred

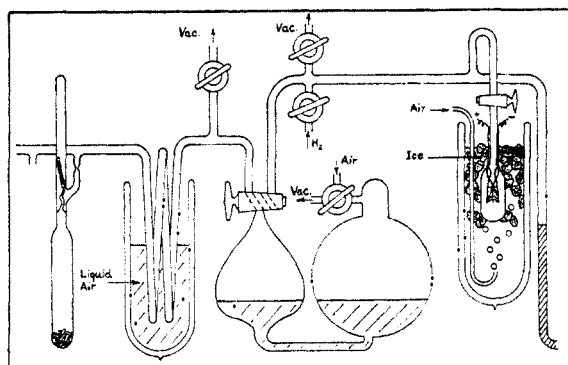


Fig. 1.—Apparatus for determining deuterium and hydrogen content in mixtures of bromides.

to the thermal conductance cell at the right through a magnetic-break seal, a multiple trap and a Toepler pump. This type of multiple trap was very useful in this investigation. Ten tubes or less were sealed to a manifold and their deuterium contents determined in quick succession. The thermal conductance cell, shown at the right, was constructed from a 15-watt General Electric appliance lamp. The base was removed from the bulb, the evacuation tip cracked off and a stopcock sealed on with sealing wax. The filament of the lamp was heated at a constant potential difference of exactly 22 volts and a current in the neighborhood of 100 milliamperes. The cell was thermostated and the terminals led to a Wheatstone bridge circuit. The difference in resistance of the filament with pure hydrogen and with pure deuterium was approximately  $55.0 \pm 0.2$  ohms.

The best results were obtained when the total pressure was about 200 mm. There were minor complications such as the presence of enough nitrogen or oxygen in the tank hydrogen to give an "apparent deuterium" content of 3%, and an exchange of deuterium bromide with traces of ethyl bromide at the high temperature of reduction which amounted sometimes to as much as 3% hydrogen in the deuterium bromide blank. However the analytical errors were probably less than 5% except for mixtures containing very small percentages of either hydrogen or deuterium. The per cent. of hydrogen in the deuterium, caused by exchange between ethyl bromide and deuterium bromide is given by the expression  $(R_{D_2} - R_0)/(R_{D_2} - R_{H_2}) \times 100$  where  $R_0$  is the resistance of the filament with the sample and  $R_{D_2}$  and  $R_{H_2}$  are the resistances with pure tank deuterium and pure tank hydrogen, respectively.

Checks were made on the analysis of measured mixtures of hydrogen and deuterium from the reduced bromides as shown in Table I.

(11) A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, N. Y., 1939.

TABLE I

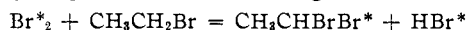
PER CENT. DEUTERIUM IN HYDROGEN-DEUTERIUM MIXTURES FROM THE BROMIDES

|                          |   |      |      |      |      |      |
|--------------------------|---|------|------|------|------|------|
| By pressure measurements | 0 | 16.8 | 35.0 | 51.3 | 66.9 | 84.6 |
| By thermal conductance   | 0 | 16.9 | 36.3 | 52.4 | 70.1 | 84.0 |

DBr\*.—Deuterium bromide containing radioactive bromine was prepared by precipitating finely divided silver bromide from a solution of potassium bromide, which contained radioactive bromine, and allowing it to stand in contact with deuterium bromide for approximately twelve hours at 400°.

### Ethyl Bromide Exchange with Bromine

The experiments on the exchange of bromine between radioactive bromine and ethyl bromide in the gaseous phase were not very satisfactory but they showed that there is practically no *direct* exchange at temperatures below 350°. Instead there is direct reaction to yield ethylidene bromide and hydrogen bromide according to the reaction



The ethylidene bromide and hydrogen bromide are both radioactive. Only a small fraction of the original ethyl bromide which remains unreacted is radioactive and this slight radioactivity of the ethyl bromide is due apparently to exchange of the radioactive bromine into the ethyl bromide from the hydrogen bromide produced by the reaction. The radioactive ethylidene bromide probably exchanges bromine, also, with ethyl bromide and hydrogen bromide.

The kinetics of this reaction was not studied thoroughly enough to justify further comments.

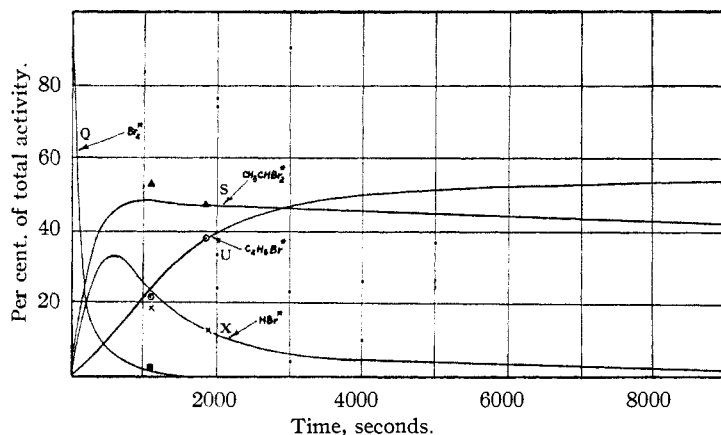


Fig. 2.—Bromination and exchange reactions at 230°.

On the basis of the few data obtained the pattern of distribution of radioactive bromine during the course of reaction at 230° is indicated by the graphs shown in Fig. 2. At this temperature the decomposition of ethyl bromide is negligible. At higher temperatures in the range 340 to 400° the ethyl bromide decomposes into ethylene and hydrogen bromide, and ethylidene bromide decom-

TABLE II  
INFLUENCE OF SURFACE ON RATE OF BROMINE EXCHANGE

| Cleaning agent         | Addition   | Per cent. activity              |      | $k', \text{sec.}^{-1} \times 10^6$ |
|------------------------|--|---------------------------------|------|------------------------------------|
|                        |  | $\text{C}_2\text{H}_5\text{Br}$ | HBr  |                                    |
| 1 Fuming nitric acid   | None   | 1.4                             | 98.6 | 3.9                                |
| 2 Fuming nitric acid   | 1.03 g. pyrex glass wool                           | 57.9                            | 22.3 | 510                                |
| 3 Chromic acid         | None   | 0.64                            | 99.3 | 1.9                                |
| 4 Chromic acid         | 0.97 g. pyrex glass wool                           | 47.9                            | 37.9 | 310                                |
| 5 Chromic acid         | Coating of Drifilm                                 | 0.59                            | 99.4 | 1.8                                |
| 6 Fuming nitric acid   | Coating of Drifilm                                 | 0.96                            | 99.0 | 3.1                                |
| 7 Chromic acid         | Coating of Drifilm                                 | 6.8                             | 93.2 | 4.2                                |
| 8 Chromic acid         | Coating of Drifilm + 470 cm. <sup>2</sup> of glass | 38.5                            | 61.5 | 30                                 |
| 9 Chromic acid         | Coating of Drifilm + 940 cm. <sup>2</sup> of glass | 68.4                            | 31.6 | 74                                 |
| 10 Freshly fused glass | None   | 2.7                             | 97.3 | 1.6                                |
| 11 Hydrofluoric acid   | None   | 7.6                             | 92.4 | 4.7                                |
| 12 Hot 1 N NaOH        | None   | 13.7                            | 86.3 | 9.6                                |

poses to give vinyl bromide and hydrogen bromide.<sup>12</sup>

The bromination of ethyl bromide at the lower temperature to give the dibromide is a straightforward gaseous reaction which has been reported but which deserves more careful kinetic study.

#### Exchange of Bromine between Hydrogen Bromide and Ethyl Bromide

**Surface Effects.**—It was soon found that the exchange of bromine between hydrogen bromide and ethyl bromide is wall-catalyzed at these temperatures, the rate depending on the nature and area of the surface as shown in Table II. The specific rate of exchange is given in terms of the apparent constant  $k'$  which is discussed in the next section. Determinations 1–6 were made in sealed-off vessels of about 235-ml. capacity after standing at 200° for one hour. The concentration of ethyl bromide was  $6.6 \times 10^{-3}$  mole per liter and the concentration of hydrogen bromide was  $5.5 \times 10^{-4}$ . Determinations 7–12 were made at 200° after standing five hours and the concentration of ethyl bromide was  $6.9 \times 10^{-3}$  and that of hydrogen bromide  $5.3 \times 10^{-4}$  mole per liter. When glass tubes or glass wool were added they were subjected to the same treatment as the walls. Except in the case of experiment 10 all surfaces were rinsed six times with distilled water and always heated and evacuated before filling with the gases.

The freshly fused glass gave the slowest reaction as indicated in experiment 10. After sealing to the supply lines the surface of the glass vessel was fused all over and reblown with air which had been passed through a drying tube so that the inner surface did not come in contact with moisture at any time. This surface was the least active.

A surface cleaned with fuming nitric was about twice as active as one cleaned with standard cleaning solution of potassium dichromate in sulfuric acid. Cleaning with sodium hydroxide too,

gave a slightly greater activity, but hydrofluoric acid etching did not increase further the rate of exchange. Noticeable amounts of a brownish organic film were visible in the glass vessels which had been cleaned with fuming nitric acid or sodium hydroxide, although a film of reaction product is always formed as indicated by the fact that the glass surface is no longer wetted by water.

The coating of the glass with Drifilm did not have an appreciable effect. This material, manufactured by the General Electric Co., is a methyl silicon fluoride which supposedly reacts with the glass to yield a surface covered with methyl groups. Possibly at the high temperatures the material is partially desorbed, but either the active centers of the glass are not covered over or the material itself is nearly as effective as the glass surface.

The influence of increased surface produced by adding glass tubes with fire-polished ends, is clearly shown in experiments 7, 8 and 9 in which the ratio of surface area to volume was, respectively, 1, 3.3 and 6.2. The increasing rate of exchange is shown in Fig. 3.

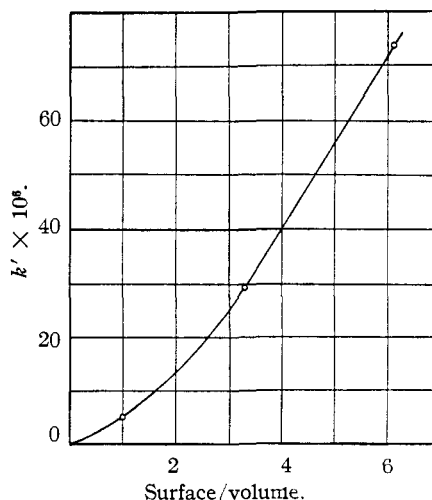


Fig. 3.—Effect of surface/volume ratio on rate of exchange of bromine.

(12) P. T. Bennett and A. Maccoll, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 527–537 (1941).

The addition of Pyrex glass wool in experiments 2 and 4 increased the rate of exchange by 100 to 200 even though the ratio of surface to volume was only of the order of 6. In calculating the apparent constants for experiments 2 and 4 it was assumed that the radioactive bromine unaccounted for in the sum of the two percentages was present in the ethyl bromide which was adsorbed on the walls of the glass wool. The distribution of the glass wool throughout the vessel, thus decreasing the time of diffusion of the gas to a glass surface, may be responsible for the acceleration. Again the broken ends of the fibers may have been a factor. It will be shown later in Table IV that freshly fractured glass is particularly active.

In all experiments except those in Table II the glass vessels were always cleaned with hot dichromate-sulfuric acid and rinsed six times with water, thus removing any organic material and leaving a standard surface of moderate catalytic activity.

**Kinetics of the Reaction.**—An isotopic exchange reaction will yield an apparent first order rate constant  $k'$  when the concentration of the reactants remains fixed during the course of the reaction,<sup>13</sup> as calculated from the formula

$$k' = \frac{1}{t} \ln \frac{1}{1-f} \quad (1)$$

where  $f$  is the fraction of total tagged atoms present in a reactant at time  $t$ , divided by the fraction present at equilibrium. This apparent constant  $k'$  is independent of the mechanism, the surface effects or the true order of the reaction as long as these remain unchanged.

The experiments of Table III were designed to test the applicability of this formula. In all cases the volume of the vessels was about 235 ml., and the concentration of ethyl bromide was  $6.6 \times 10^{-3}$  mole per liter. The concentration of hydro-

gen bromide was  $5.8 \times 10^{-4}$  at  $240^\circ$ , and  $3.8 \times 10^{-4}$  at  $220$  and  $260^\circ$ . It will be seen that the values of  $k'$  are reasonably constant. A graph of  $\log 1/(1-f)$  at  $240^\circ$  plotted against time gave a fairly satisfactory straight line with scattered points.

In another experiment with freshly fused glass walls like those of experiment 10 in Table II only 4.7% of the radioactive bromine was found in the ethyl bromide thus giving the smaller apparent constant of  $3.7 \times 10^{-6}$ . This experiment shows again that the glass walls are catalytic for this bromine exchange.

Although the exchange reaction gives an apparent first order rate constant, as calculated by equation (1), the true order of the reaction can be determined by changing the concentrations of the reactants and observing the resulting changes in the apparent rate constant  $k'$ . In the reaction



where  $Br^*$  is the radioactive bromine, the constant  $R$  for the rate of exchange of bromine is given by the expression

$$R = k c_{C_2H_5Br}^m c_{HBr}^n \quad (2)$$

where  $m$  and  $n$  are numbers which can be determined by experiment and  $k$  is the true specific reaction rate. The apparent reaction rate constant  $k'$  is related<sup>15</sup> to the true rate constant  $k$  by the expressions

$$k = k' \frac{c_{C_2H_5Br} c_{HBr}}{c_{C_2H_5Br}^m c_{HBr}^n (c_{C_2H_5Br} + c_{HBr})} \quad (3)$$

and

$$k = k' \frac{c_{C_2H_5Br}^{1-m} c_{HBr}^{1-n}}{(c_{C_2H_5Br} + c_{HBr})} \quad (4)$$

In the experiments summarized in Table IV the concentrations of ethyl bromide and hydrogen bromide were varied to determine the order of the reaction. It is seen that the apparent rate constant  $k'$  is nearly proportional to the variation in ethyl bromide concentration and inversely proportional to the hydrogen bromide concentration. Accordingly the reaction is actually first order with respect to ethyl bromide and independent of hydrogen bromide over the nearly tenfold range of hydrogen bromide concentration. The true rate constants are given in the last column as calculated from equation (4). It is expected that at sufficiently low concentrations of hydrogen bromide the true rate of exchange will no longer be independent of the concentration of the hydrogen bromide but it was impractical to go below the concentrations listed.

The activation energy is calculated as  $31.5 \pm 1.0$  kcal. per mole from Fig. 4 in which the logarithms of the average true specific rate constants are plotted against the reciprocals of the absolute temperatures. In addition to the values listed in Tables III and IV data are taken from preliminary work, not recorded here, in which a 4-liter flask was used with a correction for the different ratio of surface to volume.

TABLE III

APPARENT FIRST ORDER CONSTANTS CALCULATED FOR RATE OF BROMINE EXCHANGE FROM HBr

| Temp.,<br>°C. | Time,<br>sec. $\times 10^{-3}$ | Per cent. total activity<br>In $C_2H_5Br$ | Per cent. total activity<br>In $HBr$ | Apparent<br>constant<br>$k' \times 10^3$ |
|---------------|--------------------------------|---|--------------------------------------|--|
| 220           | 14.4                           | 22.0                                      | 78.0                                 | 1.9                                      |
| 220           | 28.8                           | 40.1                                      | 59.9                                 | 1.9                                      |
| 220           | 43.2                           | 67.6                                      | 32.4                                 | 2.9                                      |
|               |                                |   | Average                              | 2.2                                      |
| 240           | 1.8                            | 9   | 91                                   | 6.0                                      |
| 240           | 3.6                            | 14  | 86                                   | 4.5                                      |
| 240           | 7.2                            | 35  | 65                                   | 6.7                                      |
| 240           | 10.8                           | 41  | 58                                   | 5.5                                      |
| 240           | 18.0                           | 55  | 45                                   | 5.1                                      |
|               |                                |   | Average                              | 5.5                                      |
| 260           | 1.8                            | 33  | 67                                   | 24                                       |
| 260           | 3.6                            | 65  | 35                                   | 33                                       |
| 260           | 5.4                            | 69  | 31                                   | 24                                       |
|               |                                |   | Average                              | 27                                       |

(13) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

TABLE IV  
 APPARENT AND TRUE RATE CONSTANTS FOR EXCHANGE OF BROMINE

| Temp.,<br>°C.    | Time,<br>sec. $\times 10^3$ | $^{13}\text{C}_2\text{H}_5\text{Br}$<br>moles/liter<br>$\times 10^2$ | $^{13}\text{HBr}^*$<br>moles/liter $\times 10^3$ | $\% \text{ Br}^*$<br>In $\text{C}_2\text{H}_5\text{Br}$ | $\% \text{ Br}^*$<br>In HBr | $k'$                 | $k$                  |
|------------------|-----------------------------|--|--|---|-----------------------------|----------------------|----------------------|
| 180              | 3.6                         | 8.0  | 0.093  | 3   | 97                          | $7.7 \times 10^{-6}$ | $5.8 \times 10^{-8}$ |
| 180              | 3.6                         | 8.0  | .033   | 6   | 94                          | $1.6 \times 10^{-5}$ | $6.6 \times 10^{-8}$ |
| 180              | 3.6                         | 8.0  | .013   | 21  | 79                          | $6.5 \times 10^{-5}$ | $1.1 \times 10^{-7}$ |
| 180              | 3.6                         | 8.0  | .0033  | 45  | 55                          | $1.6 \times 10^{-4}$ | $7.0 \times 10^{-8}$ |
| 200              | 10.8                        | 8.0  | .28  | 10  | 90                          | $9.6 \times 10^{-6}$ | $3.3 \times 10^{-7}$ |
| 200              | 10.8                        | 8.0  | .28  | 13  | 87                          | $1.4 \times 10^{-5}$ | $4.7 \times 10^{-7}$ |
| 200 <sup>a</sup> | 10.8                        | 8.0  | .28  | 81  | 19                          | $1.7 \times 10^{-4}$ | $5.8 \times 10^{-6}$ |
| 200 <sup>b</sup> | 10.8                        | 8.0  | .28  | 11  | 89                          | $1.2 \times 10^{-5}$ | $3.9 \times 10^{-7}$ |
| 200 <sup>c</sup> | 10.8                        | 8.0  | .28  | 19  | 81                          | $2.0 \times 10^{-5}$ | $6.9 \times 10^{-7}$ |
| 254              | 3.6                         | 4.6  | .23  | 60  | 40                          | $2.8 \times 10^{-4}$ | $1.3 \times 10^{-5}$ |
| 254              | 3.6                         | 10   | .46  | 60  | 40                          | $2.8 \times 10^{-4}$ | $1.2 \times 10^{-5}$ |
| 254              | 3.6                         | 4.6  | .46  | 39  | 41                          | $1.5 \times 10^{-4}$ | $1.4 \times 10^{-5}$ |
| 254              | 3.6                         | 2.0  | .46  | 17  | 83                          | $6.8 \times 10^{-5}$ | $1.3 \times 10^{-5}$ |
| Average          |                             |  |  |   |                             |                      | $1.3 \times 10^{-5}$ |
| 243              | 1.8                         | 16   | 2.0  | 4.5   | 95.5                        | $2.9 \times 10^{-5}$ | $3.1 \times 10^{-5}$ |
| 243              | 1.8                         | 16   | 1.0  | 9   | 91                          | $5.6 \times 10^{-5}$ | $3.1 \times 10^{-6}$ |
| 243              | 1.8                         | 16   | 0.40   | 18  | 82                          | $1.1 \times 10^{-4}$ | $2.8 \times 10^{-6}$ |
| 243              | 1.8                         | 16   | 0.18   | 36  | 64                          | $2.5 \times 10^{-4}$ | $2.8 \times 10^{-6}$ |
| Average          |                             |  |  |   |                             |                      | $3.0 \times 10^{-6}$ |

<sup>a</sup> Surface/volume ratio doubled by addition of broken 6 mm. Pyrex tubing. <sup>b</sup> 2.5 mm. air added. <sup>c</sup> 150 mm. air added.

The points give a fairly satisfactory straight line in spite of the fact that the reaction involves at least one wall step. The rather high activation energy seems to suggest that the rate-determining step is chemical in nature rather than physical adsorption.

#### Exchange of Deuterium between Deuterium Bromide and Ethyl Bromide

The exchange of deuterium from deuterium bromide to ethyl bromide was found to proceed at a conveniently measurable rate in the temperature range from 250 to 320°. The data were not easily reproducible and it was not possible to determine the order of the reaction with assurance. The reaction is certainly complex and it involves a wall effect. The fact that a separate reaction vessel was required for every single determination brought out the "worst" in the reaction and contributed to variations which might have been less noticeable if the same vessel had been used for a whole series of data.

The question as to whether all of the five hydrogen atoms are exchangeable was settled by mixing 8 millimoles of  $\text{C}_2\text{H}_5\text{Br}$  and 8 millimoles of DBr in a 235-ml. Pyrex vessel for one hundred hours at 300°. Reduction of the hydrogen and deuterium bromides and analysis by thermal conductance showed that after the correction of 2% for the blank obtained at zero time, 83.5% of the deuterium in the original deuterium bromide had been replaced by hydrogen. The calculated value after complete exchange with all five hydrogens is 83.3%.

The ratio of surface in sq. cm. to volume in cu.

cm. was about equal to 1. When the 235-ml. vessel was packed with short lengths of Pyrex tubing with fire-polished ends so as to give a surface to volume ratio of about 9, the rate of the reaction expressed, as the apparent rate constant  $k'$ , practically doubled. This catalytic effect of the walls is much less noticeable than in the case of the exchange of bromine from the hydrogen bromide. The rather discordant data are summarized in Table V.

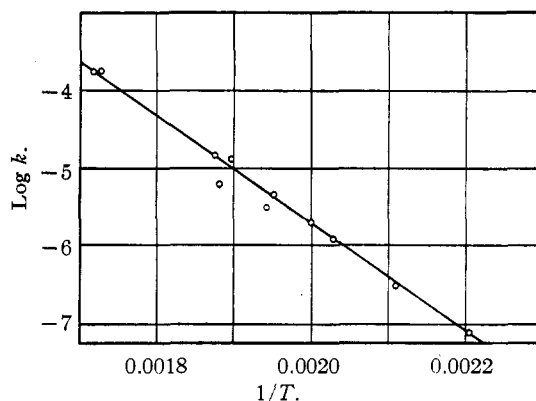


Fig. 4.—The activation energy for bromine exchange between hydrobromic acid and ethyl bromide.

At both temperatures the last four determinations were made in glass vessels that had been treated with hydrofluoric acid and rinsed four times with water in addition to the standard treatment with dichromate cleaning solution.

In the next to the last column the constants  $k_{1,1}$  are calculated from the apparent constants  $k'$  by

TABLE V  
EXCHANGE OF DEUTERIUM BETWEEN DBr AND C<sub>2</sub>H<sub>5</sub>Br

| Time,<br>hours   | C <sub>2</sub> H <sub>5</sub> Br<br>moles/<br>l. × 10 <sup>3</sup> | CDBr<br>moles/<br>l. × 10 <sup>3</sup> | % HBr in<br>DBr + HBr |                                  | k'<br>sec. <sup>-1</sup><br>× 10 <sup>4</sup> | k <sub>1,1</sub><br>sec. <sup>-1</sup><br>× 10 <sup>10</sup> | k <sub>0,1</sub><br>sec. <sup>-1</sup><br>× 10 <sup>4</sup> |
|------------------|--|--|-----------------------|----------------------------------|---|--|---|
|                  |  |  | Found                 | Calcd.<br>for<br>equil.<br>(5 H) |   |  |   |
| Temperature 258° |  |  |                       |                                  |   |  |   |
| 0                | 8.0  | 2.2                                    | 3.0                   | 95                               | ...   | ..   | ..  |
| 12.25            | 8.0  | 2.5                                    | 12                    | 94                               | 3.1   | 3.6  | 2.9   |
| 12.25            | 2.4  | 2.9                                    | 63                    | 98                               | 23.0  | 9.8  | 22.5  |
| 12.0             | 4.1  | 3.7                                    | 12                    | 85                               | 3.6   | 7.4  | 3.1   |
| 12.0             | 8.1  | 3.9                                    | 29                    | 91                               | 8.9   | 10.0   | 8.1   |
| 12.0             | 12.0   | 3.8                                    | 34                    | 95                               | 10  | 7.8  | 9.4   |
| 12.0             | 16.0   | 3.9                                    | 5                     | 95                               | 1.3   | 0.8  | 1.2   |
| 12.0             | 20.0   | 3.7                                    | 10                    | 96                               | 2.5   | 1.2  | 2.4   |
| 12.0             | 24.0   | 3.7                                    | 17                    | 97                               | 4.5   | 1.8  | 4.4   |
| 12.0             | 4.0  | 3.6                                    | 27                    | 85                               | 8.9   | 19.0   | 7.5   |
| 12.0             | 8.1  | 3.7                                    | 43                    | 92                               | 15.0  | 17.0   | 14.0  |
| 12.0             | 16.0   | 3.4                                    | 22                    | 96                               | 6.0   | 3.6  | 5.8   |
| 12.0             | 24.0   | 3.4                                    | 45                    | 97                               | 14.0  | 5.7  | 13.0  |
| 7.75             | 8.0  | 2.8                                    | ..                    | ..                               | 5.4   | 6.3  | 4.7   |
| Average          |  |  |                       |                                  | 8.2   | 7.2  | 7.6   |
| Temperature 306° |  |  |                       |                                  |   |  |   |
| 6.0              | 8.1  | 5.0                                    | 84                    | 89                               | ...   | ..   | ..  |
| 12.0             | 8.1  | 5.0                                    | 85                    | 89                               | ...   | ..   | ..  |
| 1.0              | 8.0  | 3.8                                    | 32                    | 91                               | 120   | ..   | ..  |
| 1.0              | 8.0  | 11.5                                   | 66                    | 78                               | 500   | 1.4  | 3.9   |
| 1.0              | 8.1  | 3.8                                    | 56                    | 91                               | 260   | 2.9  | 2.4   |
| 1.0              | 8.1  | 7.2                                    | 43                    | 85                               | 200   | 2.1  | 1.7   |
| 1.0              | 8.1  | 1.2                                    | 35                    | 77                               | 170   | 1.6  | 0.8   |
| 1.0              | 8.1  | 2.1                                    | 55                    | 96                               | 240   | 2.8  | 2.3   |
| 1.0              | 24.0   | 3.9                                    | ..                    | ..                               | 460   | 1.9  | 4.5   |
| Average 230      |  |  |                       |                                  | 1.7   | 2.0  |   |

the method described in the preceding section, assuming that the true rate of exchange is proportional to the first power of the ethyl bromide concentration and the deuterium bromide. The constants have been multiplied by 5 (for the 5 hydrogen atoms of ethyl bromide) in order to permit a direct comparison with the bromide exchange. The constants  $k_{0,1}$  are calculated on the assumption that the rate is not affected by the concentration of the ethyl bromide. Although the data at 258° are not consistent enough to determine which calculation gives the best constants, the data at 306° indicate that the rate is proportional to the first power of the ethyl bromide and the first power of the deuterium bromide,  $k_{1,1}$ . The calculated activation energies are 42 kcal. for  $k'$ ; 40 for  $k_{1,1}$ ; 41.5 for  $k_{0,1}$ . The activation energy for the exchange calculated on the basis of a zero order dependence on DBr  $k_{1,0}$  is 51 kcal. This value can safely be discarded, inasmuch as the rate of exchange seems to be proportional to the DBr concentration.

In the following section it will be shown that traces of bromine and air accelerate the deuterium exchange markedly and that mercury inhibits it greatly. These facts support the view that a chain mechanism is involved, and the fact that the

rate is not greatly affected by the ratio of surface to volume suggests that the chains start on the walls and are stopped by the walls. Independence of reaction rate on the surface area of the walls does not always and necessarily prove that the reaction is homogeneous.<sup>14,15</sup> The dependence of the rate of exchange on traces of impurities and on variations in adsorbed water may account for some of the erratic data.

#### Exchange between DBr\* and C<sub>2</sub>H<sub>5</sub>Br

In the last two sections it has been shown that the rate of exchange, activation energy, effect of concentration and surface area are different for deuterium and bromine in a mixture of ethyl bromide and hydrogen bromide. This difference can be made much more impressive by comparing the two exchanges under identical conditions of temperature, concentrations, surfaces and traces of impurities. Accordingly, measurements of exchange were made of both deuterium and radioactive bromine when DBr\* was added to ethyl bromide. The data are summarized in Table VI where

$$f_{\text{Br}} = \frac{\% \text{ Br}^* \text{ in C}_2\text{H}_5\text{Br after reaction}}{\% \text{ Br}^* \text{ in C}_2\text{H}_5\text{Br after complete exchange}}$$

$$f_{\text{D}} = \frac{\% \text{ HBr found in DBr + HBr after reaction}}{\% \text{ HBr in DBr + HBr after complete exchange}}$$

Experiments 2 and 4 show clearly the great difference between the effect of packing on the bromine exchange and its effect on the deuterium exchange. Increasing the surface to volume ratio ninefold has a very large effect on the bromine exchange but it does not increase the deuterium exchange. The apparent slight decrease with deuterium is not significant in view of the erratic results always obtained. These facts have already been established in the preceding sections but in the experiments described here, where the exchanges were studied simultaneously in the same bulb with the same molecules and the same packing, the result is doubly convincing.

In experiments 3 and 4 one microliter of mercury was placed in each bulb before evacuation, and additional glass packing was introduced in #4 giving a ninefold increase in the surface to volume ratio. It had been hoped that these experiments which combined an increased surface with a gas phase inhibitor would show if a chain reaction was started at the walls and extended out into the gas phase. If the chains started and ended at the walls, packing would not increase the over-all rate of reaction, but if the chains were stopped in the gas phase by an inhibitor the increased surface should give a faster rate of reaction. The experiments were inconclusive, however, because the mercury inhibited the deuterium exchange so strongly that no exchange could be detected in the

(14) R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, N. J., 1942, Chapter VII.

(15) N. Semenov, "Chemical Kinetics and Chain Reactions," Oxford University Press, Oxford, 1935.

TABLE VI  
 EXCHANGE EXPERIMENTS WITH DBr\* AND C<sub>2</sub>H<sub>5</sub>Br

| Expt. number     | Time, hours       | $c_{C_2H_5Br}$ moles/l. $\times 10^2$ | $c_{DBr^*}$ moles/l. $\times 10^2$ | Moles/l. of added elements $\times 10^2$ | $f_{Br}$ | $d$  | $k'_{Br}$ sec. <sup>-1</sup> $\times 10^6$ | $k'_D$ sec. <sup>-1</sup> $\times 10^6$ |
|------------------|-------------------|---------------------------------------|------------------------------------|--|----------|------|--|---|
| Temperature 258° |                   |                                       |                                    |  |          |      |  |   |
| 1                | 7.75              | 8.0                                   | 2.8                                | .....                                    | 0.45     | 0.14 | 22   | 5.4                                     |
| 2                | 7.75 <sup>a</sup> | 8.0                                   | 3.6                                | .....                                    | 1.0      | .09  | Very large                                 | 3.8                                     |
| 3                | 7.75              | 8.0                                   | 2.5                                | Hg 0.37                                  | 0.60     | .00  | 33   | Very small                              |
| 4                | 7.75 <sup>a</sup> | 8.0                                   | 3.0                                | Hg 0.37                                  | .94      | .02  | (100)                                      | (0.74)                                  |
| 5                | 7.75              | 8.0                                   | 3.1                                | Air 0.78                                 | .33      | .51  | 15   | 26                                      |
| 6                | 7.75              | 8.0                                   | 3.1                                | Br <sub>2</sub> 0.26                     | .60      | .55  | 33   | 29                                      |
| Temperature 306° |                   |                                       |                                    |  |          |      |  |   |
| 7                | 1.0               | 2.4                                   | 3.9                                | .....                                    | .99      | .81  | 1300                                       | 460                                     |
| 8                | 1.0               | 2.0                                   | 2.1                                | .....                                    | .51      | .03  | 200  | (9)                                     |
| 9                | 1.0               | 2.0                                   | 1.3                                | .....                                    | .70      | .05  | 330  | (15)                                    |
| 10               | 0.0               | 8.0                                   | 3.9                                | .....                                    | .00      | .03  | Blank                                      | Blank                                   |

<sup>a</sup> The vessels were packed with Pyrex tubing giving a surface to volume ratio of approximately 9.

unpacked bulb and there was only 2% exchange in the packed bulb. Although these data are in the right direction, the exchange is probably too small to be experimentally significant. It is clear that mercury vapor does not affect the bromine exchange and that it affects greatly the deuterium exchange. The strong inhibition by mercury was not due to a stoichiometric reaction. DBr did not react with mercury vapor even after prolonged heating at 400°. Microscopic examination of the bulb in experiments 3 and 4 showed the surface of the glass to be covered with tiny globules of mercury and about 10% as much of small white crystals, even though the DBr concentration was 8 times that of the mercury. On freezing in liquid air a mercury mirror was formed. The reaction with mercury involved less than 1% of the deuterium bromide and ethyl bromide present, and yet the exchange reaction was completely stopped. These facts constitute strong evidence for the existence of a chain reaction.

Air and bromine in trace amounts caused accelerations of about fivefold in the rate of exchange of deuterium, an effect which is perhaps significant in spite of the erratic character of this chain reaction. They do not affect the bromine exchange and thus lend weight to the hypothesis that the bromine exchange is not a chain reaction — or at least they cannot involve the same chain carriers as the deuterium exchange.

Experiments 7, 8 and 9 were used to study the influence of concentration on the rates of exchange. They have been discussed previously.

### Mechanisms of the Exchange Reactions

Any mechanism proposed to account for the exchange of bromine from hydrogen bromide to ethyl bromide must explain the wall-dependence which has been established, and the rough proportionality which exists between the rate and the surface area. These facts would seem to limit the possible mechanisms to three classifications: (a) chains starting at the wall and ending in the

gas; (b) non-chain reactions that start at the wall; and (c) reactions occurring entirely on the wall. The absence of large inhibition effects may be taken as an argument against a chain mechanism.

The deuterium exchange, on the other hand, probably does involve a chain mechanism as indicated by the irreproducibility of the exchange rates and the marked effect of traces of mercury vapor and other substances. The fact that the exchange rate is not increased by increasing the surface indicates that if, as seems likely, the chains are initiated at the walls, they must be stopped also by the walls. Chains involving hydrogen atoms can be excluded on the basis of the large energy requirements of such processes. Further evidence against hydrogen chain mechanisms is supported by Chadwell and Titani<sup>16</sup> who showed that the introduction of hydrogen atoms into ethyl bromide gave products which were completely different from those normally observed.

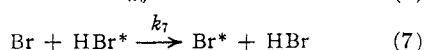
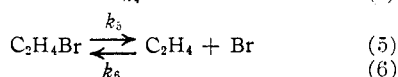
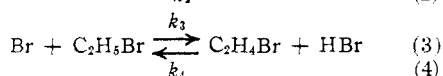
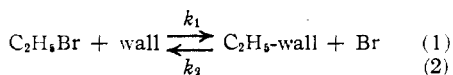
Many different mechanisms were postulated to explain the observed facts.<sup>17</sup> Many of these were discarded because they do not agree with all the experimental facts. The mechanism which seems to best fit all the facts will now be summarized.

It is assumed that (a) ethyl bromide is dissociated at the wall with an activation energy of  $31.5 \pm 1$  kcal. per mole giving free bromine atoms and ethyl radicals which remain attached to the wall until removed by reaction with other bromine atoms; (b) the concentration of ethyl radicals at the wall is proportional to the concentration of ethyl bromide in the gas phase; (c) the bromine atom concentration is determined primarily by the "equilibrium" between ethyl bromide and the ethyl radicals attached to the wall, and the free bromine atoms.

(16) H. M. Chadwell and T. Titani, *THIS JOURNAL*, **55**, 1363 (1933).

(17) Details of these mechanisms are given in Chapter V of the Ph.D. thesis of John B. Peri, filed in the Library of the University of Wisconsin in 1949.





Bromine exchange is given by (1), (7) and (2). Deuterium exchange occurs by (3) and (4) which constitute a chain. Mercury removes  $\text{C}_2\text{H}_4\text{Br}$  free radicals in the gas phase. Bromine accelerates by increasing the Br atom concentration. Oxygen creates additional radicals.

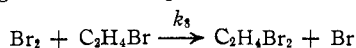
Setting up differential equations involving the concentration of  $\text{C}_2\text{H}_4\text{Br}$  radicals at the steady state and making simplifying assumptions and estimates of activation energies and frequency factors it can be shown that the rate of exchange of deuterium from deuterium bromide into ethyl bromide is given by the expression

$$\frac{dc_D}{dt} = \frac{k_1 k_3 k_4}{k_2 k_5} \times \frac{c_{\text{C}_2\text{H}_5\text{Br}}}{c_{\text{C}_2\text{H}_5\text{-wall}}} \times c_{\text{C}_2\text{H}_4\text{Br}} c_{\text{DBr}}$$

and that the over-all activation energy is of the order of 36 to 40 kcal. per mole. Assuming that  $c_{\text{C}_2\text{H}_4\text{Br}}/c_{\text{C}_2\text{H}_5\text{-wall}}$  remains constant the reaction is then first order with respect to  $\text{C}_2\text{H}_5\text{Br}$  and first order also with respect to deuterium bromide. These estimates are in essential agreement with the experimental determinations of the order of the reaction and the activation energy.

The fact that "Drifilm," which is supposed to cover the walls with methyl groups does not affect the rate of the exchange can be explained on the assumption that on the active spots the methyl groups are removed with bromine atoms and replaced by ethyl groups from the ethyl bromide leaving the surfaces essentially the same under both conditions.

The bromination of ethyl bromide to give the dibromide fits nicely into this general mechanism by adding one more step



### The Thermal Decomposition of Ethyl Bromide

This investigation has shown the importance of the walls of the containing vessel on the exchange reactions and suggests the desirability of re-examining the earlier work on the decomposition of ethyl bromide.<sup>1-4</sup> Wall effects were noted and studied before, but they were then considered of secondary importance. The fact that a large increase in surface area increased the rate of decomposition only slightly can be explained on the assumption that chains are broken at the walls as well as started at the walls.

The carbonaceous deposit from decomposing ethyl bromide rendered the walls much less active and gave more reproducible results, but they did

not necessarily render the walls completely inactive. Moreover, the activation energies were found to be the same with a coated wall as with a fresh wall, even though the latter was thought to give a wall-catalyzed effect. The preferred mechanism proposed by Daniels and Veltman<sup>4</sup> can be changed very slightly by making the primary dissociation step, into  $\text{C}_2\text{H}_5$  radicals and Br atoms, wall-catalyzed. The thermal decomposition of ethyl bromide then follows exactly the scheme of reactions (1) to (6) just given for the exchange reactions. Whereas step (5), the dissociation of  $\text{C}_2\text{H}_4\text{Br}$ , is unimportant at the low temperatures of the exchange reactions and there is no appreciable accumulation of ethylene; step (5) is important in the decomposition of ethyl bromide at the higher temperatures and, in fact, leads to a production of ethylene which except for secondary reactions is nearly equal to the production of hydrogen bromide. The chain breaking steps in either exchange or decomposition can involve collisions between  $\text{C}_2\text{H}_5\text{-wall}$  and Br or  $\text{C}_2\text{H}_4\text{Br}$ ; or between  $\text{C}_2\text{H}_4\text{Br}$  and Br. Other products found in the decompositions such as ethane can be explained also on the basis of collisions with HBr,  $\text{C}_2\text{H}_4$  and with  $\text{C}_2\text{H}_5\text{-wall}$ .

The authors are indebted to the Research Committee of the Graduate School of the University of Wisconsin and to the Wisconsin Alumni Research Foundation for a continuing assistantship which made this work possible.

### Summary

1. Bromine reacts with ethyl bromide below 350° to give the dibromide. Direct exchange of radioactive bromine into ethyl bromide occurs only through reaction with the products of the reaction.

2. The bromine of hydrogen bromide exchanges with ethyl bromide from 180 to 310° with an activation energy of 31.5 ± 1.0 kcal. per mole. The reaction is first order with respect to ethyl bromide and zero order with respect to  $\text{HBr}^*$ . The rate depends on the surface area and nature of the wall.

3. The deuterium of deuterium bromide exchanges with all five hydrogens of ethyl bromide between 258 and 306° with an activation energy of 40 ± 4 kcal. per mole. The reaction is roughly first order with respect to ethyl bromide and first order with respect to deuterium bromide.

4. The exchange of bromine and deuterium were studied simultaneously, also, using deuterium bromide containing radioactive bromine.

5. A mechanism for the exchange reactions is proposed which involves free radicals produced on the walls. It is believed that the bromine exchange is a wall reaction and that deuterium exchange is a chain starting and ending on the wall.

6. The mechanisms proposed for exchange are applicable also to the thermal decomposition of ethyl bromide at higher temperatures.