[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Exchange of Br^{80} Atoms with Bromoölefins; Induced Rearrangement of the Bromopropenes[1,2]

BY RUSSELL R. WILLIAMS, JR., WILLIAM H. HAMILL, HAROLD A. SCHWARZ[3] AND ELLIOTT J. BURRELL

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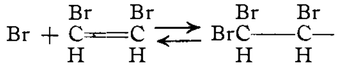
It has been found that various bromoölefins, present to the extent of a few mole per cent. in ethyl bromide or bromobenzene during neutron bombardment, undergo an efficient isotopic exchange reaction with the nascent Br^{80}. The ratio of the rates of such exchange with allyl bromide and α,β dibromoethylene has been measured over a range of temperatures. In addition to the exchange an isomerization also occurs among the three bromopropenes. When one of these isomers is present during bombardment, and carrier amounts of the other isomers are added after bombardment, radioactive bromine may appear in all three components. Some suggestions concerning the mechanism of these reactions are offered.

Considerable experimentation and speculation have been directed toward elucidation of the role played by free halogen atoms in the chemical processes induced by slow neutron capture[4-7] (the Szilard–Chalmers reaction) and isomeric transition[8,9] by the halogen of organic halides. It is generally agreed that a significant fraction of the activated halogen atoms pass through the atomic state at some stage of the life which they begin as energetic recoil atoms or ions and end in some form of chemical combination. It has been inferred that a portion of the halogen recoils escape reaction and reach thermal energies in the atomic state, there to react or persist according to the chemistry of the system. Unfortunately the chemical form of the product of thermal halogen atom reactions is likely to be indistinguishable from the product of hot halogen atom reactions in many systems and therefore the disentanglement of these two kinds of reactions must rest on indirect evidence such as kinetic interpretations.

With the object in mind of finding an efficient reagent for the detection of thermal halogen atoms produced by nuclear reactions in organic halides, we have investigated the isotopic exchange reaction between Br^{80} and some bromoölefins, a reaction which is presumed to proceed through a reversible addition–dissociation reaction such as (1).



$$\mathrm{Br} + \underset{\mathrm{H}}{\overset{\mathrm{Br}}{\mathrm{C}}}{=}\underset{\mathrm{H}}{\overset{\mathrm{Br}}{\mathrm{C}}} \rightleftarrows \mathrm{Br}\underset{\mathrm{H}}{\overset{\mathrm{Br}}{\mathrm{C}}}{-}\underset{\mathrm{H}}{\overset{\mathrm{Br}}{\mathrm{C}}}{-} \qquad (1)$$

The presence of two bromine atoms in equivalent positions in the free radical permits isotopic exchange with a maximum probability of 0.5 for each addition–dissociation cycle if no reshuffling of Br atoms within the radical occurs. If the concentration of molecular bromine and other reagents which would react efficiently with the radical is kept sufficiently low, the exchange equilibrium state, where essentially all active atoms are in the form of bromoölefin, can be closely approached.

A preliminary communication[10] has indicated the success of this technique for detection of thermal Br^{80} atoms, which has been successfully adopted by others.[5] In our own investigations we have used bromoölefins to assess the importance of thermal bromine atoms in studies of the chemical reactions induced by neutron capture,[7] isomeric transition[9] and to elucidate the mechanism of the addition of bromine to the double bond.[9] The present report is concerned with isotopic exchange of bromine atoms with allyl bromide in the liquid phase and with the bromine atom-induced isomerization of the bromopropenes.

Experimental

Chemicals.—The bromopropenes were obtained from the Halogen Chemical Co. and purified by distillation at a reflux ratio of 50/1 and a take-off rate of 2 cc. per hour in a Podbielniak miniature Hyper-Cal fractionating column with metal parts fabricated from the halogen-resistant alloy Hastelloy B. The boiling range of fractions used was less than 0.3°. The products were kept under an inert atmosphere, usually helium, when they were intended for use in an air-free experiment.

Bromobenzene and ethyl bromide, used as target compounds for neutron capture, were purified by shaking with concentrated sulfuric acid, caustic and water. They were distilled at a reflux ratio of 10/1 and a take-off rate of 40 cc. per hour in a glass helix-packed Todd fractionating column. The boiling range of the fractions used was less than 0.1°.

Other alkyl halides were used as obtained from commercial suppliers.

Procedures.—Experiments to determine the fate of recoil atoms from bombarded ethyl bromide were performed as follows: 10 cc. of ethyl bromide, containing a small, measured amount of allyl bromide was subjected to neutron bombardment in the annular space formed by two concentric soft-glass test-tubes. The neutrons were generated by a 300 mg. Ra–Be neutron source placed inside the central tube. The bombardments extended for a period of approximately 15 minutes and separations were completed in less than 30 minutes in order to produce sufficient 18-minute Br^{80} activity without serious contamination ($< 10\%$) by the 4.4-hour Br.^{80} At the end of bombardment, the amount of allyl bromide was made up to 10 cc. and 10 cc. of 1,2-dibromopropane was added. The inorganic activity was extracted from this mixture with dilute aqueous thiosulfate, the organic layer was washed with water, dried and distilled in a small fractionating column containing a glass-packed section about 12 inches long and 1 inch in diameter. Fractions of approximately 1° boiling range, corresponding to ethyl bromide (38°) and allyl bromide (71°) were collected. After the head temperature had risen to the boiling point of the dibromopropane (142°) the distillation was halted and the residual liquid in the still-pot taken as the third fraction, considered to be 1,2-dibromopropane. Intermediate fractions were discarded. The radioactivity of the three organic fractions and the aqueous extract was determined with a liquid sample Geiger counter, making appropriate corrections for decay, self-absorption and volume of the various samples. The results of these experiments are given in Table I as per cent. of total activity in each fraction.

The relative reaction rates of two bromoölefins, allyl

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(3) Atomic Energy Commission predoctoral fellow 1948–1951.

(4) W. F. Libby, THIS JOURNAL, **69**, 2523 (1947).

(5) S. Goldhaber and J. Willard, *ibid.*, **74**, 318 (1952).

(6) J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 579 (1950).

(7) R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **18**, 783 (1950).

(8) D. DeVault and W. F. Libby, THIS JOURNAL, **63**, 3216 (1941).

(9) W. H. Hamill and J. A. Young, *J. Chem. Phys.*, **20**, 888 (1952).

(10) W. H. Hamill, R. R. Williams, Jr., and H. A. Schwarz, THIS JOURNAL, **72**, 2813 (1950).

TABLE I

ACTIVITY DISTRIBUTION, PER CENT.

Mole % allyl bromide	EtBr	AB	1,2-DBP	Aqueous
0	32	..	..	68 (Ref. 5)
.009	27	29	..	44
.009	22	33	..	45
.44	23	45	0	32
2.21	22	48	0	30

bromide and α,β-dibromoethylene,[11] were determined by production of Br^{80} atoms by neutron bombardment of 100 cc. of bromobenzene containing one volume per cent. of each bromoölefin. After bombardment for approximately four hours, carrier amounts (*ca.* 10 cc.) of the bromoölefins were added and distilled from the organic liquid. The large difference in boiling points permitted ready isolation of relatively pure fractions whose activity was determined not less than two hours after separation to ensure radioactive decay equilibrium between the nuclear isomers 4.4-hour Br^{80*} and 18-minute Br^{80}. These competitive exchange reactions were carried out at three different temperatures by use of appropriate cooling or heating baths around the bombardment vessel. The results were as follows: at −29°, the activity ratio allyl bromide/dibromoethylene = 0.89 ± 0.05; at 19°, 0.96 ± 0.03; at 90°, 1.01 ± 0.03. (The data reported are the average from two experiments at each temperature. In each case, the differences did not exceed the sum of the standard deviations due to counting error, which is reported with the ratios.) These data correspond to a difference in activation energies of 0.2 ± 0.1 kcal./mole.

Experiments to investigate the isomerization of the bromopropenes which accompanies the exchange with thermal bromine atoms were performed using bromobenzene as the target substance. 99 cc. of this substance, containing 1 cc. of one of the bromopropenes, was subjected to neutron bombardment for 9 to 15 hours in a vessel similar to that described above. At the end of the bombardment carrier amounts (3.5 cc.) of all three bromopropenes were added and a rough distillation used to concentrate them from the large amount of bromobenzene. Separation of the three isomers was accomplished by careful fractionation on the Podbielniak column under conditions described above. It was possible to collect fractions of constant boiling point (±0.2°) amounting to 1.0 to 1.5 cc. of each isomer. These were diluted with inactive bromobenzene for radioactivity determinations, which were made not less than two hours after separation in order to ensure radioactive equilibrium of the 18-minute and 4.4-hour isomeric activities.

Experiments conducted as described above, in the presence of air, were not reproducible (some typical results are given in Table II) and did not agree with later results obtained when air was excluded from the system. Although some lack of reproducibility still existed in this case, we prefer these results in view of the well-known effects of oxygen on free radical reactions. Air was removed through use of the following procedure: about 0.01 cc. of methylene iodide and 1 cc. of mercury were put into the bombardment vessel (all glass, with side-arm and stopcock for evacuation) in addition to the bromobenzene and bromopropene. The vessel was cooled with liquid air, evacuated, warmed and filled with helium, a treatment which was repeated several times in order to flush out air. Next, the vessel was sealed and irradiated for 30–60 minutes with a mercury arc lamp through a Corning No. 738 filter. Under these conditions actinic light is absorbed by methylene iodide but not by the bromides. It was expected that radicals produced by photodissociation of methylene iodide would react with the last traces of oxygen or other interfering substances and convert them to a non-reactive form. The color change observed indicated a production of iodine amounting to 10^{-5}–10^{-4} mole. This color disappeared when the mercury was shaken with the organic liquid. Separation of isomers after the bombardment was accomplished as previously described. The results of experiments on isomerization of the bromopropenes are given in Table II.

TABLE II

REARRANGEMENT OF BROMOPROPENES

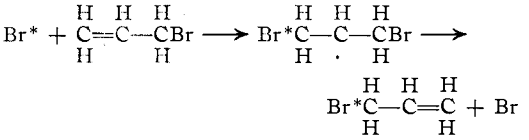
Starting material	Active products, % 2BP	1BP	AB
2-Bromopropene (2BP)	4	19	77[a]
	5	20	75
	20	17	63
	14	17	69
	9	17	74
1-Bromopropene (1BP)	4	45	51[a]
	2	64	34[a]
	0	30	70
	2	44	54
	3	40	57
Allyl bromide (AB)	1	24	75[a]
	0	5	95
	0	4	96

[a] Air present.

The proportion of the products resulting from photobromination of 2-bromopropene in carbon tetrachloride was determined in one experiment using 34-hour Br^{82} tracer[12] as follows: 0.1 g. of molecular bromine containing the tracer activity was added to a solution of 0.25 cc. of 2-bromopropene in 25 cc. of carbon tetrachloride under an atmosphere of helium. This mixture was illuminated to ensure complete reaction. Three cc. each of 1,2,3-tribromopropane and 1,2,2-tribromopropane were added to the solution, the bulk of the carbon tetrachloride was removed in a simple distillation and the two tribromopropanes separated by careful fractionation in the Podbielniak column. The relative activities of 1,2,2- and 1,2,3-tribromopropane were 99:1.

Discussion

The considerable shift of bromine activity from inorganic to organic form produced by adding small amounts of allyl bromide to ethyl bromide before neutron bombardment (Table I) indicates that this reagent is affecting some intermediate of thermal energy. We assume this intermediate to be bromine atoms and further assume that they undergo a reversible addition–dissociation reaction such as (2)



$$Br^* + \overset{H}{\underset{H}{C}}{=}\overset{H}{C}{-}\overset{H}{\underset{H}{C}}Br \longrightarrow Br^*\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}\overset{H}{\underset{H}{C}}Br \longrightarrow Br^*\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{\underset{H}{C}} + Br \quad (2)$$

which leads to exchange. It is improbable under these experimental conditions that net addition involving Br* could compete with exchange. This was confirmed by adding carrier 1,2-dibromopropane which gave an inactive fraction. Since it was recovered from the still-pot this strongly indicates the absence of active tribromopropane. The limiting 45–48 per cent. of total activity in the bromoölefin fraction may be identified with those recoil atoms which escape hot atom reactions and reach thermal energy. Of the remainder which undergo hot atom reactions, the yield of active ethyl bromide (Table I) indicates that 23% of all Br* re-form the primary compound

$$Br\cdot^* + C_2H_5Br \longrightarrow C_2H_5Br^* + Br\cdot$$

while 32% of all Br* form an inorganic compound by reaction such as

$$Br\cdot^* + C_2H_5Br \longrightarrow HBr^* + C_2H_4Br\cdot$$

This division of the bromine recoil atoms into the

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[11] The same supply of α,β-dibromoethylene was used in all experiments to ensure constant proportions of the *cis* and *trans* isomers.

[12] Obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee.

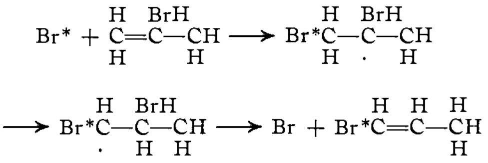
categories of hot atom organic, hot atom inorganic and thermal is in approximate agreement with the values reported by Goldhaber and Willard,[5] using α,β-dibromoethylene as the reagent for thermal bromine atoms.

Allyl bromide is very rapidly brominated at room temperature, while α,β-dibromoethylene photobrominates much more slowly. Nevertheless, the rates of exchange of these two compounds with atomic bromine are very nearly equal over a range of temperatures. The data for competitive exchange indicate that the difference in activation energies for the addition of bromine atoms to the appropriate position on the double bond of these two compounds is approximately 0.2 kcal./mole. Furthermore, since bromine atoms react efficiently with bromoölefins at concentrations as low as 0.009 mole per cent. in ethyl bromide, where the competing reaction of hydrogen abstraction has an activation energy in the region of 12–13 kcal./mole, the atom addition to the double bond must have an activation energy no greater than 7–8 kcal. The contrasting rates of addition of these compounds cannot therefore be attributed to a difference in rates of addition of the bromine atom to the double bond, which is generally accepted as the first step in bromination of an olefin.

Isomerization accompanying the exchange of atomic bromine with allyl bromide and its isomers is indicated in Table II. This effect certainly occurred in the preceding experiments with allyl bromide, but since the isomers have boiling points much closer to each other than to the other compounds used, the isomers should all appear in the allyl bromide fraction. In any event, the data in Table II indicate that isomerization of allyl bromide is quite limited.

The fractional distribution of activity among the isomers, even in air-free samples, is not as reproducible as could be desired, but a fairly consistent pattern appears. No matter which isomer is present for the initial atom exchange, allyl bromide predominates among the products, while 1-bromopropene and 2-bromopropene are successively less important.

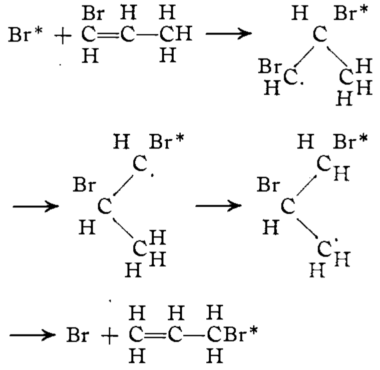
The observed rearrangements must occur in the free radical form after the addition of a bromine atom. Furthermore the failure to detect rearrangement[13] in the course of photobromination of 2-bromopropene indicates that, in the presence of molecular bromine, the lifetime of the radicals is too short to permit the rearrangement. The radical isomerizations required can be accomplished through various combinations of two processes: (1) hydrogen atom shift and (2) electron shift in a cyclic structure. The latter process could also be described as the migration of a methyl radical. Keeping in mind the limitations of two-dimensional representation of structural formulas the radical rearrangement yielding 1-bromopropene from 2-bromopropene may be represented as



$$\mathrm{Br^* + \overset{H}{\underset{H}{C}}{=}\overset{Br}{C}{-}\overset{H}{\underset{H}{C}}H \longrightarrow Br^*\overset{H}{\underset{H}{C}}{-}\overset{Br}{\underset{\cdot}{C}}{-}\overset{H}{\underset{H}{C}}H}$$

$$\mathrm{\longrightarrow Br^*\overset{H}{\underset{\cdot}{C}}{-}\overset{Br}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}H \longrightarrow Br + Br^*\overset{H}{C}{=}\overset{H}{C}{-}\overset{H}{\underset{H}{C}}H}$$

and that yielding allyl bromide from 1-bromopropene as



In all such reactions, addition of the bromine atom to the other position on the double bond, the one already containing a bromine atom, could lead to simple exchange. A slightly enhanced activity in the parent isomeric species implies limited exchange by this path.

Whether or not the particular mechanisms proposed here are correct it is probable that the effect observed is to be attributed to a rearrangement process whose rate-controlling activation energy is comparable to that for the elimination of a bromine atom from the intermediate free radical to regenerate the olefin.

NOTRE DAME, INDIANA

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[13] Qualitative observations with α,β-dibromoethylene, however, show that exchange occurs rapidly with bromine under usual photochemical conditions.