251. *The Nature of the Diffusion-controlled Reactions following Neutron Capture in Alkyl Bromides.*

By Miriam Milman and P. F. D. Shaw.

The variation of retention caused by adding 1 : 2-dibromoethylene to ethyl bromide, ethylene and ethylidene dibromide, and 1 : 1 : 2-tri- and 1 : 1 : 2 : 2-tetra-bromoethane has been investigated in an attempt to elucidate the nature of diffusion-controlled reactions undergone by radicals resulting from neutron capture in these bromides. It is concluded that a large proportion of the radio-bromine atoms, which diffuse from the site of neutron capture, is probably produced by reaction of organic radicals with HBr* and Br_2* formed by high-energy processes.

A major difficulty in the quantitative treatment of the diffusive reactions following neutron capture in organic halides is the lack of knowledge of their chemical nature. It has been shown [1,2] that, in ethyl bromide and ethylene dibromide, the radioactive products from such reactions are relatively simple, consisting chiefly of the parent compound. If the latter are produced predominantly (in diffusive processes) by combination of the active atoms with free radicals, other reactions removing radicals will also be important, since the extent to which they occur will partly determine the number of radicals available for reaction with the active atom. These reactions cannot be completely determined because, in some cases, no radio-bromine will be involved, and the quantities of the inactive products are too small for conventional analysis; however, it was expected that some evidence for their nature might be found by studying the variation of R_D and A (defined below) as a function of the relative number of hydrogen and bromine atoms in the parent compound.

In this and the following paper, A is defined as the fraction of the total radio-bromine produced which diffuses from the second (diffusion-dependent) stage, and which reacts with small quantities ($\sim 10^{-4}$ molar fraction) of 1 : 2-dibromoethylene present in the

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[1] Milman and Shaw, *J.*, 1957, 1308.

[2] Milman, Shaw, and Simpson, preceding paper.

irradiated bromide; R_E and R_D are, respectively, the retentions produced by the high-energy and diffusion-dependent processes and refer to the pure (bromine-free) liquid.

Goldhaber and Willard,[3] and Roy, Williams, and Hamill [4] interpreted the rise in retention, from 32% to 60%, caused by 1 : 2-dibromoethylene to mean that A is 28% and that the remaining inorganic activity (40%) is present as molecules formed by the high-energy processes. They do not appear to have considered the possibility that reactions such as

$$\mathrm{R + BrBr^* \longrightarrow RBr^* + Br} \tag{a}$$

$$\mathrm{R + BrBr^* \longrightarrow RBr + Br^*} \tag{b}$$

or

$$\mathrm{R + HBr \longrightarrow RH + Br^*} \tag{c}$$

(where R = Et) might also be important in the diffusive stage. If this were so, the yield of inorganic molecules from high-energy processes would be greater than that estimated.[3,4]

Reactions (*a*), (*b*), and (*c*), where R = Et or C_2H_4Br, require little or no activation energy,[5,6,7] and it will be assumed that they are equally probable, given a suitable collision, to recombination of radicals (or atoms).

To simplify discussion, let us temporarily neglect the possibility that an active bromine atom, produced by high-energy reactions, may escape diffusive reaction, and also the possible occurrence of the diffusive reactions

$$\mathrm{R + Br^* \longrightarrow RBr^*} \tag{d}$$

$$\mathrm{Br + Br^* \longrightarrow BrBr^*} \tag{e}$$

$$\mathrm{H + Br^* \longrightarrow HBr^*} \tag{f}$$

In these conditions the only active bromine atoms produced are those from reactions (*b*) and (*c*), and the diffusive yield of the parent compound will be from reaction (*a*). A will therefore be determined by (*b*) and (*c*), and R_D by (*a*), which is as probable as (*b*). The quantity $(A - R_D)$ should therefore be a measure of the amount of HBr* produced in the high-energy processes, and this should decrease as the ratio of hydrogen to bromine atoms decreases in the parent compound.

The possibility of reactions (*d*), (*e*), and (*f*) must now be considered. If (*d*) is important in the diffusion-dependent reactions (as has been postulated [3,4]) it would be expected that (*e*) and (*f*) might also be important, since it is improbable that in a single recoil the radio-bromine is the only atom produced. Small quantities of 1 : 2-dibromoethylene (10^{-4}—10^{-3} molar fraction) are unlikely to affect the course of the reactions occurring in the diffusive stage, the observed increase in retention being due to exchange with radio-bromine atoms which were produced either in the high-energy or the diffusive process, and which escape further reactions [such as (*d*), (*e*), or (*f*)]. If the latter reactions were important in the diffusive stage, greater concentration of 1 : 2-dibromoethylene should lead to the interception and exchange of radio-bromine atoms by the reaction :

$$\mathrm{CHBr{:}CHBr + Br^* \longrightarrow CHBr{:}CHBr^* + Br}$$

so that radio-bromine atoms which previously formed inorganic molecules by (*e*) or (*f*) would be returned to organic combination. The curve of retention against molar fraction of 1 : 2-dibromoethylene might then be expected to show a sharp initial increase in retention in the same way that addition of bromine to the pure bromide causes the retention to fall rapidly.

This argument presupposes that, for suitable collisions, the probability of exchange by reaction (*d*) is comparable with that for recombination by (*c*). This is supported by the formation in ethylene dibromide of tribromoethane by diffusive reactions,[2] and indicates

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[3] Goldhaber and Willard, *J. Amer. Chem. Soc.*, 1952, **74**, 318.

[4] Roy, Williams, and Hamill, *ibid.*, 1954, **76**, 3274.

[5] Sherman, Quimby, and Sutherland, *J. Chem. Phys.*, 1936, **4**, 732.

[6] Muller and Schumacher, *Z. phys. Chem.*, 1939, *B*, **42**, 327.

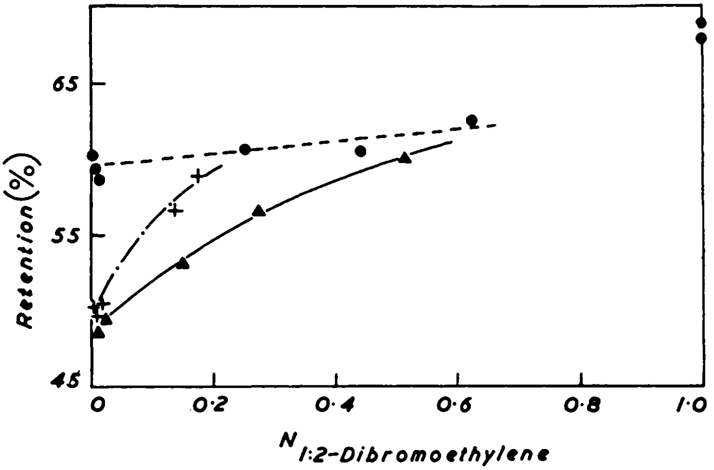
[7] Anderson and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 479.

that vinyl bromide, which reacts similarly to 1 : 2-dibromoethylene, can compete with atoms or free radicals for the active atom.

Part of the object of this work was therefore to investigate the nature of the diffusion-dependent reactions following neutron capture.

The molecular products from the high-energy reactions must be affected by the probability that, when the active atom is thermal, a high density of radicals or atoms is

FIG. 1. *Retention of ethyl bromide, ethylene dibromide, and tribromoethane as a function of the molar fraction of* 1 : 2-*dibromoethylene.*



● EtBr, ▲ $C_2H_4Br_2$, + $C_2H_3Br_3$.

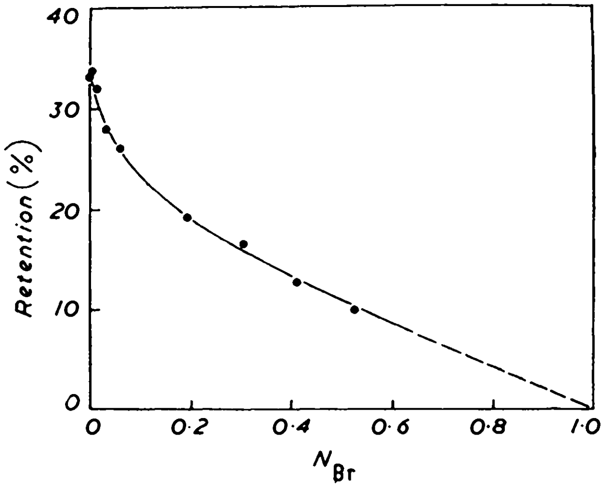


FIG. 2. *Retention of ethylidene dibromide as a function of the molar fraction of bromine.*

available for combination with it. This high density is most probable immediately after the passage of a highly energetic atom, since they will recombine rapidly, and consequently the yield of high-energy products must depend on the efficiency of retardation of an energetic atom to thermal velocities. Since a single Br–Br collision (regarded as elastic) can reduce the energy of a recoiling atom to the thermal region, the yield of active molecules from the high-energy processes should increase with the density of bromine atoms in the bromide irradiated. Such an effect has been found in ethyl bromide and ethylene dibromide,[1,2] and the work now described was undertaken partly to see whether this was a general feature of Szilard–Chalmers reactions.

Effect of 1 : 2-*Dibromoethylene*.—Preliminary experiments with short irradiation times and measurement of the retentions of ^{80}Br (half-life, 18 min.) confirmed results obtained with ethyl bromide, [3,4] but the retentions for ^{80}Br* (half-life, 4·4 hr.), obtained after longer irradiation periods, were anomalously large, especially if the bromo-olefin was carefully purified. This suggested that a more general exchange occurred, probably induced by γ-radiation from the neutron source. This was confirmed by analysis of a specimen which contained 10^{-3} molar fraction of 1 : 2-dibromoethylene and gave a high retention (81%), the activity present as 1 : 2-dibromoethylene being 51%. If a little nitrogen dioxide (approximately 10^{-3} molar fraction of NO_2) was dissolved in the olefin, the γ-ray induced exchange was inhibited, probably by the breaking of a self-propagating chain reaction (cf. Milman and Shaw [8]) but the non-homogeneous exchange, involving active atoms diffusing from the sites of neutron capture, still took place and reproducible

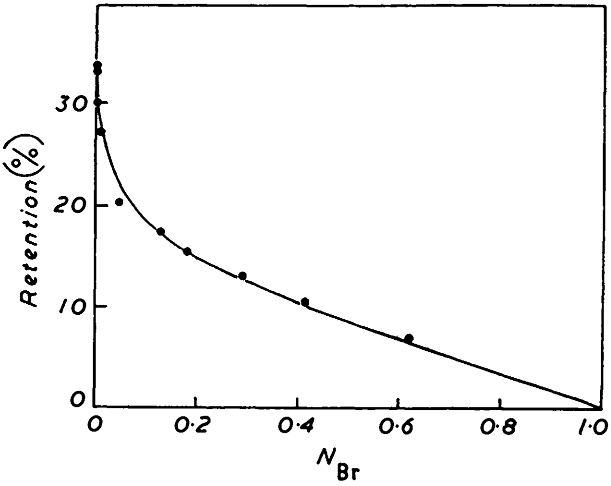


FIG. 3. *Retention of tribromoethane as a function of the molar fraction of bromine.*

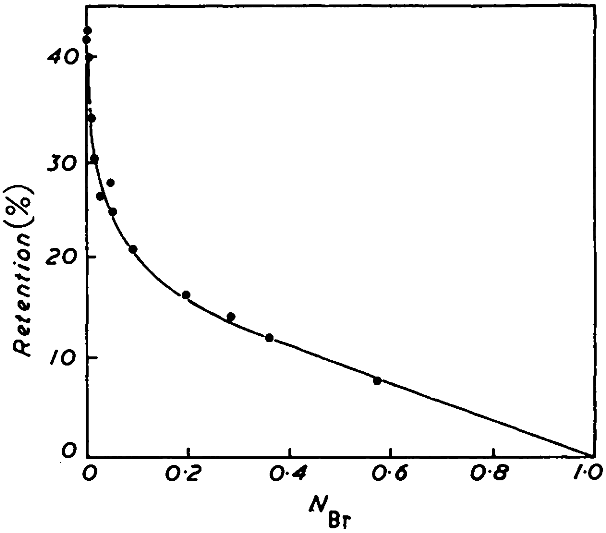


FIG. 4. *Retention of tetrabromoethane as a function of the molar fraction of bromine.*

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[8] Milman and Shaw, *J.*, 1956, 2101.

retentions of 60% were obtained. Under these conditions prolonged irradiation still caused high retentions, and in order to complete the experiment within the induction period caused by the inhibitor, the irradiation-times were kept small (10 min.) and the retentions of ^{80}Br were measured. The results obtained for ethyl bromide, ethylene dibromide, and 1 : 1 : 2-tribromoethane are shown in Fig. 1. The retentions observed when small quantities ($\sim 10^{-3}$ molar fraction) of 1 : 2-dibromoethylene were present in ethylidene dibromide and 1 : 1 : 2 : 2-tetrabromoethane were 50 ± 1 and 57 ± 2% respectively.

Retentions with Bromine Present.—These for ethylidene dibromide and tri- and tetra-bromoethane are shown as a function of the molar fraction of bromine present in Figs. 2, 3, and 4. They were measured by using short irradiation times and by counting the ^{80}Br produced. This ensured that the effect of slow addition reactions, of the type found in ethylene dibromide, was not important, even when the bromine concentration was small.

The high energy retentions can be obtained[3,4] by extrapolation of the curves found for large molar fractions (N) of bromine. Since R_D should be a continuous function of bromine concentration, the observed retentions should reach the straight line joining R_E (at $N_{Br} = 0$) to zero (at $N_{Br} = 1$) asymptotically; consequently it is difficult to estimate the best line for the extrapolation since the best line through the experimental points will tend to include a small contribution due to diffusive retention. Hence, the values for R_E in the Table are slightly lower than those which would have been obtained by direct extrapolation through the experimental points, the magnitude of the reduction being based empirically on the curve-fitting to be described.[9] Values of R_E for ethyl bromide and ethylene dibromide are also included in the Table; their slight reduction from the values previously given[1,2] does not affect the arguments previously based on them.

In view of the difficulty experienced with ethylene dibromide[2] no attempt was made to obtain the retention in the bromine-free bromides, except in the case of ethyl bromide. Values of the retention at zero bromine concentration were obtained by extrapolation from those found when small quantities of bromine were present; this is justified by the equality of the retentions found in ethyl bromide directly, and by using this technique. The retentions produced by diffusive reactions (R_D) are given in the Table, and were obtained by subtraction of R_E from the total retention (R). The percentage of radio-bromine escaping as atoms (A) was found by subtraction of R from the retention obtained in the presence of small quantities of 1 : 2-dibromoethylene.

DISCUSSION

The Table shows that the increase of R_E for ethyl bromide and ethylene dibromide is not sustained when the number of bromine atoms per molecule is further increased; consequently, if arguments such as those advanced by Libby[10] or on p. 1319 are relevant to the high-energy processes, some sort of " saturation effect " occurs. If the concentration of bromine atoms (taken independently of their state of combination) is low, as in ethyl bromide, the energy lost by collision with atoms other than bromine may be of comparable importance in the slowing-down process. Since such collisions can only produce " thermal " atoms relatively slowly, considerable recombination of the radicals

	Ethyl bromide	Ethylene dibromide	Ethylidene dibromide	1 : 1 : 2-Tri-bromoethane	1 : 1 : 2 : 2-Tetra-bromoethane
R (%)	32	33	34	35	42
R_E (%)	14	17	19	17	18
R_D (%)	18	16	15	18	24
A (%)	27·5	16	16	15	15
$(A - R_D)$	9·5	0	1	−3	−9
P_B	0·39	0·50	0·48	0·54	0·61

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[9] Milman and Shaw, following paper.

[10] Libby, *J. Amer. Chem. Soc.*, 1947, **69**, 2523.

produced might occur before a reaction such as (*d*) is possible. The free-radical concentration immediately surrounding the thermalised atom might therefore be less for ethyl bromide than for ethylene dibromide, and therefore a smaller value of R_E might be expected in the former. If the efficiency of thermalisation increases sharply with the concentration of (bound) bromine atoms, a state of " saturation " can be envisaged where nearly all the recoil atoms are slowed down so rapidly that, when thermal, they are initially surrounded only by atoms and molecular fragments. Under these conditions, R_E will be determined solely by the relative number of atoms or radicals competing for the active atom. Since the organic products from the high-energy processes in ethyl bromide and ethylene dibromide [1,2] consist predominantly of the parent compound or its singly substituted derivatives, it might be expected that in all bromides roughly equal numbers of atoms and radicals would surround the active atom, so that R_E would be roughly constant under " saturation " conditions. The relatively low values of R_E can be explained by assuming that steric effects are more important in the combination of the active atom with an organic radical than with another (hydrogen or bromine) atom. In consequence, the yield of high-energy active products should consist predominantly of molecules rather than atoms, though the latter might result if the surrounding radicals and atoms combined with each other, leaving the active bromine atom surrounded by the newly formed molecules.

The lack of a sharp initial rise in the curve of retention against molar fraction of 1 : 2-dibromoethylene in ethyl bromide (Fig. 1) indicates that reactions (*e*) and (*f*) [and also, by implication, (*d*)] are not important in the diffusive stage. Since active atoms are known to be produced by the high-energy *and* diffusion-dependent reactions, this strongly suggests that the diffusive reactions (*b*) and (*c*) are responsible for the production of free active atoms, and that the active inorganic high-energy products consist predominantly of molecules rather than atoms.

If it is temporarily assumed that A measures the total number of active bromine atoms produced by reactions (*b*) and (*c*), and R_D measures the RBr^* molecules from reaction (*a*), the quantity $(A - R_D)$ should be related to the amount of HBr^* produced by high-energy reactions, and should decrease as the number of hydrogen atoms per molecule of the irradiated bromide is reduced. The Table shows that this effect was found, although the negative values for tri- and tetra-bromoethane cannot be explained without further assumption, since, on the above premises, R_D cannot exceed A because of the equal probabilities of reactions (*a*) and (*b*). If the efficiency of thermalisation is increased as the number of (bound) bromine atoms in the parent substance increases, the products from the high-energy reactions would be confined to a smaller volume of liquid near the site of neutron capture. Under such conditions the diffusive reactions might become more complex, first leading to the formation of bromine atoms from the high-energy molecular products by reactions (*a*), (*b*), and (*c*); if this happened before the radicals which had not reacted had been greatly dispersed by diffusion, reactions (*d*), (*e*), and (*f*) could then occur so that R_D would increase at the expense of A, the quantity $(A - R_D)$ becoming negative. Conversely, in a relatively more disperse system of radicals, etc., the probability of the active bromine atom's being involved in two consecutive reactions in the diffusive stage will be considerably decreased.

The shapes of the curves (Fig. 1) for ethylene dibromide and tribromoethane are in qualitative agreement with this argument, for they indicate that the atomic recombinations (*e*) and (*f*) occur in the diffusion-dependent processes. Further, the initial slope (for low molar fractions of 1 : 2-dibromoethylene) of the curve for tribromoethane is greater than that for ethylene dibromide, showing that the recombination reactions become more important as the number of bromine atoms per molecule of the parent compound is increased.

The interpretation of the processes following neutron capture given above is reasonably consistent with the data obtained, and will be used as a basis for the treatment of the diffusive reactions which is attempted in the following paper.

For this, it is desirable to estimate the probability that collision between an organic radical and the inorganic species containing radio-bromine will lead to the formation of an organic radio-bromine compound. Such probabilities depend on the relative amounts of hydrogen bromide and bromine present, and therefore on the irradiated halide; also, they might be expected to vary when the overall density of bromine atoms is altered by addition of elementary bromine to a given bromide. Adopting the above arguments, we see that reactions (*a*), (*b*), (*c*), and (*d*) produce either an organic radio-bromide or a radio-bromine atom. If we assume that, given a suitable collision, the probabilities of these reactions are equal, the extent to which such reactions occur is proportional, approximately, to $(A + R_D)$; the fraction of such collisions leading to organic retention is therefore approximately $R_D/(A + R_D)$. Values of this quantity (P_R) are listed in the Table, and are given approximately by the empirical relation

$$P_R = 0{\cdot}30 + [0{\cdot}92 \times 10^{-3} \times (\text{Molecular weight of irradiated substance})]$$

Several features, however, are not explained by the above arguments, which suggest that R_D should increase with the number of bromine atoms per molecule; for example, if the slowing-down is more efficient in a medium containing a high density of bromine atoms, the initial radical concentration should be greater, so that diffusive reactions become more important. It can be seen from the Table that in moving from ethyl bromide to ethylene dibromide R_D decreases, and then increases steadily for the remaining bromides. This could be explained if ethyl radicals were more stable than bromoethyl and similar radicals, which may dissociate into a bromine atom and an olefin molecule before the termination of the diffusive processes. The activation energy for such dissociation for the bromoethyl group has been reported [5] as 13 ± 2 kcal./mole, whereas for the dissociation into ethylene and a hydrogen atom the ethyl radical would require at least 45 kcal./mole, the endothermicity of the reaction (calculated from bond energies given by Pauling [11]).

An alternative explanation is that the probability of reaction with bromine, etc., is less for a bromoethyl than for an ethyl radical. This could arise by stabilisation due to the greater electron density available from the bromine atoms in bromoethyl radicals. Sherman *et al.*[5] have calculated that the activation energy of the reaction

$$CH_2Br{\cdot}CH_2 + Br_2 \longrightarrow CH_2Br{\cdot}CH_2Br + Br$$

is 2·3 kcal./mole; experimentally, Muller and Schumacher [6] found this to be greater than 5 kcal./mole, but the other results [7, 12] are consistent with the assumption that the similar reactions involving methyl or ethyl radicals have zero, or a very small, activation energy.

A further point requiring explanation is the difference in R_E found for ethylene and ethylidene dibromides. On the model used for the high-energy processes (*i.e.*, where inelastic processes are important, but the effectiveness of atoms in slowing the recoiling atom is based on Libby's " billiard-ball " hypothesis) equality of R_E might have been expected, since the constituent atoms are the same in each case. The difference therefore illustrates the inadequacy of such a treatment, which was chosen primarily for its simplicity. However, it is possible that the explanation of the difference in R_E is that different steric effects operate in the combination of the thermalised atom with the surrounding molecular fragments.

An alternative explanation of the more effective thermalisation, postulated in bromides containing more than one bromine atom, can be based on the degree of inelasticity of the collisions. For example, as the mass of the molecules increases, it might be expected that the walls of the cage holding a molecule hit by a recoiling atom would become more " rigid " owing to the greater inertia of the surrounding molecules. Consequently, more energy could be transferred to the molecular bonds in heavily brominated compounds than in ethyl bromide, so that the recoil energy should be dissipated more rapidly and within a

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[11] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1940, 2nd Edn.

[12] Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469.

smaller volume; also, the products from the high-energy reactions should indicate greater fragmentation of the parent molecules. Possible evidence for the latter might be given by the sum of the methylene dibromide and bromoform activities found in ethylene dibromide [2] (4·1%) which is greater than the corresponding quantity for ethyl bromide [1] (2·8%). On this basis, differences in R_E for substances containing different arrangements of the same atoms might arise from the ability of the molecules to group themselves in formations corresponding to greater or less " rigidity " in the wall of the liquid cage.

Summarising the conclusions of this and the preceding papers,[1, 2] we obtain the following picture of the processes following neutron capture :

(i) The recoil atom moves through the liquid, losing its energy by inelastic processes until it is finally thermal. The local concentration of free radicals, molecular fragments, and atoms existing after the passage of the recoil atom is extremely high, so that an immediate recombination occurs in which most of the radicals, etc., will form stable molecules. Owing to the random nature of such recombination, some radicals will be isolated from each other, and thus remain to react in the subsequent diffusive stage. The more highly fragmented molecules thus isolated must disproportionate, or react with solvent molecules to form ethyl or bromoethyl radicals, since there is little evidence for their existence in the subsequent diffusive reactions. After the termination of the high-energy reactions, the radio-bromine atom will be either in organic combination (contributing to R_E) or otherwise present predominantly as HBr* or BrBr*. It seems improbable that the amount remaining as atomic bromine is as large as thought previously.[3, 4]

(ii) The radicals resulting from (i) diffuse from the sites of their formation and react with inorganic compounds produced in (i) or recombine mutually. Reaction with Br*Br or Br* gives molecules of the parent substance contributing to R_D. It appears that a considerable fraction of the atomic radio-bromine present at the end of this stage results from diffusive, rather than high-energy, reactions. In ethylene dibromide, and probably also in compounds containing more bromine atoms per molecule, exchange reactions between radio-bromine atoms and vinyl bromides [produced in stage (i)] may also contribute to the diffusive retention.

These reactions proceed until the concentrations of the reactants are so reduced by diffusion that their reaction probability is insignificant. Radio-bromine atoms which escape reaction ultimately form inorganic compounds, probably by reactions of the type : [4]

$$\mathrm{EtBr} + \mathrm{Br}^* \longrightarrow \mathrm{C_2H_4Br}\cdot + \mathrm{HBr}$$

EXPERIMENTAL

Organic bromides were obtained from British Drug Houses Ltd., and, except for 1 : 2-dibromoethylene, all were distilled and then kept with bromine in daylight for a few hours. The bromine was then removed by sulphite extraction; the bromide was dried ($CaCl_2$) and fractionally distilled in a dark room with a column (40 × 1·5 cm.) packed with glass helices; a middle fraction was retained. The 1 : 2-dibromoethylene was fractionally distilled in darkness without pre-treatment; " AnalaR " bromine was used without further purification.

Experiments with 1 : 2-*Dibromoethylene*.—Known volumes of the organic bromide and 1 : 2-dibromoethylene were mixed in diffuse light, and were irradiated as already described.[1] Extractions were made with bromide–sulphite solutions in diffuse light to reduce the possibility of light-induced exchange or addition reactions between the extractable radio-bromine and 1 : 2-dibromoethylene. The retentions in ethylidene dibromide and tri- and tetra-bromoethane, and mixtures containing a large proportion of 1 : 2-dibromoethylene were measured by using 5 ml. irradiated specimens. The total activity was measured after dilution of 2 ml. of these with 10 ml. of carbon tetrachloride; 2 ml. were extracted and similarly diluted before separation from the aqueous layer. Counts and precautions were as previously described.[1]

Preliminary experiments with ethyl bromide containing a little 1 : 2-dibromoethylene showed that overnight irradiations gave higher retentions for ^{80}Br* than short (4 hr.) irradiations. Organic products were analysed by adding carriers, including 1 : 2-dibromoethylene, to an extracted portion of a specimen giving high retention (81%) and separating them by fractional distillation; methylene and ethylidene dibromide and 1 : 2-dibromoethylene were collected together, the activity of this mixed fraction being 55% of the total. After allowance for the expected activity of methylene and ethylidene dibromide (4% [1]) the activity of 1 : 2-dibromoethylene (51%) corresponds closely to the rise in retention (81 − 32 = 49%) caused by addition of this substance, thus showing that exchange reactions are responsible for the anomalously high retention observed.

The behaviour of ethyl bromide–1 : 2-dibromoethylene mixtures was erratic when the molar fraction of the latter was large, high retentions being sometimes observed even for short irradiation times. When this occurred, traces of bromine added to the mixture in daylight disappeared rapidly, there being no noticeable induction period. Experiment showed that nitrous fumes dissolved in the olefin caused an induction period, and the use of such mixtures gave consistent results providing that the irradiation times were short; these were therefore restricted to 10 min., and measurements were confined to ^{80}Br. Air was not excluded, so that the inhibiting agent was probably nitrogen dioxide, the concentration of which was found by shaking the olefin with dilute sodium hydroxide and separating. Dissolved olefin was removed by four extractions with carbon tetrachloride and the aqueous layer was acidified and titrated with 0·01N-potassium permanganate.

The solution of nitrogen dioxide in 1 : 2-dibromoethylene was always checked before use by ascertaining that the retention of ethyl bromide containing a trace (10^{-4}—10^{-3} molar fraction) of the bromo-olefin gave a retention of about 60%.

Retentions with Bromine Present.—These were measured as described previously; [1] the activities were corrected for solution density and the volume of bromine present. Retentions in ethylidene dibromide and tri- and tetra-bromoethane were determined for 5 ml. samples by using the dilution technique described above.

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