

**250. *The Szilard-Chalmers Reaction in Ethylene Dibromide.***

By MIRIAM MILMAN, P. F. D. SHAW, and I. B. SIMPSON.

The retentions of radio-bromine produced by neutron capture in purified ethylene dibromide are not reproducible. This can be largely explained by the presence of vinyl bromide which is formed, on storage and by radiolysis, by dissociation of the parent compound. When present, vinyl bromide causes increased retentions by exchanging with radio-bromine atoms produced by neutron capture; subsequent addition of bromine or hydrogen bromide gives increased yields of active tribromoethane or ethylene dibromide respectively.

Analysis of the products from the neutron irradiation of bromine-ethylene dibromide mixtures, shows that the predominant diffusion-controlled reactions result in the formation of ethylene dibromide and vinyl bromide, which is subsequently saturated to give tribromoethane.

THE work described earlier <sup>1</sup> supports the suggestion of Willard and others <sup>2,3</sup> that the reactions following neutron capture in ethyl bromide occur in two stages. A considerable fraction of the high-energy products consisted of ethyl bromide; according to Libby's <sup>4</sup> "billiard ball" hypothesis (see p. 1203), a high yield of the parent substance would be expected. Although Libby's theory is subject to criticism, since most collisions by the recoiling atom are inelastic, it is possible that some collisions between the recoiling atom and a bound bromine atom might result in relatively little activation of the group attached to the struck atom, and in these conditions a high yield of the parent compound might be produced. Since such processes could only occur when Br-Br collisions are involved, <sup>4</sup> substances containing a greater number of bromine atoms per carbon atom than ethyl bromide should give an increased yield of the parent compound from the high-energy

<sup>1</sup> Milman and Shaw, preceding paper.

<sup>2</sup> Goldhaber and Willard, *J. Amer. Chem. Soc.*, 1952, **74**, 318.

<sup>3</sup> Levey and Willard, *ibid.*, p. 6161.

<sup>4</sup> Libby, *ibid.*, 1947, **69**, 2523.

reactions. In order to investigate this, and also to see whether the production of the parent compound from the second (diffusive-recombination) stage is a general feature of the Szilard-Chalmers effect in aliphatic bromides, a study similar to that for ethyl bromide was made with ethylene dibromide.

The Szilard-Chalmers effect in ethylene dibromide has been relatively little investigated. Shaw and Collie<sup>5</sup> found difficulty in obtaining reproducible results, and preliminary experiments indicated that the processes following neutron capture were more complex than those occurring in ethyl bromide.

*Retention in Pure Ethylene Dibromide.*—As no reproducible results were obtained for the retention in this compound, experiments were generally performed in pairs by using two portions of the same specimen and varying a single parameter likely to influence the retention. The retentions obtained were greater for <sup>82</sup>Br (half-life 35 hr.) than for <sup>80</sup>Br\* (4.4 hr.). As the retentions in pure substances are the same for all the bromine isotopes,<sup>6-8</sup> this suggested the occurrence of slow reactions capable of returning the inorganic radio-bromine to the organic fraction. Such effects have been observed<sup>7</sup> in impure substances, and in bromobenzene<sup>9</sup> where a  $\gamma$ -ray induced exchange occurs between elementary bromine and bromobenzene.

Shaw and Collie,<sup>5</sup> using less carefully purified ethylene dibromide, observed slow reactions of this type and suggested that exchange between active hydrogen bromide and ethylene dibromide might occur. To test this, hydrogen [<sup>82</sup>Br]bromide was passed into ethylene dibromide, and the solution kept near a 500 mc Ra-Be neutron source for eight days. If it is assumed that the activity in the organic fraction was produced by exchange, the observed rate was much too small to account for the difference in retention between the isotopes, and another explanation was sought.

Early in this work, the retentions in purified ethylene dibromide were found to increase with the time elapsing between purification and extraction. This was most pronounced when the samples were kept either near the neutron source or in daylight, and suggested that an impurity from the decomposition of the ethylene dibromide was introduced. Dissociation into vinyl and hydrogen bromide, which occurs readily<sup>10</sup> at 350°, might occur at room temperature to yield sufficient vinyl bromide to react with the elementary bromine formed by neutron capture to give tribromoethane. To test this explanation, a freshly purified ethylene dibromide sample was split into two portions, to one of which a small quantity of vinyl bromide was added. The retentions found [Table I, (a) and (b)] showed the expected increase when vinyl bromide was present, the fractions chiefly affected being vinyl bromide, ethylene dibromide, and tetrabromoethane. The last was recovered as a residue from the separation, and might therefore also contain higher-boiling compounds. In view of the sensitivity of the retention to the presence of vinyl bromide, experiments were always performed with fresh samples of ethylene dibromide, specimens to which vinyl bromide had been added, either before or after irradiation (as carrier), being permanently discarded.

Williams, Hamill, and Schwartz<sup>11, 12</sup> have shown that rapid exchange occurs between bromine atoms and a number of vinylic compounds containing bromine. Small quantities of 1 : 2-dibromoethylene added to ethyl bromide before irradiation increase the retention from 32 to 60%;<sup>2, 13</sup> this increase has been interpreted to mean that 28% of the radio-bromine atoms produced escape from the site of their formation as atoms, thus enabling exchange with the dibromoethylene.

<sup>5</sup> Shaw and Collie, *J.*, 1951, 434.

<sup>6</sup> Fox and Libby, *J. Chem. Phys.*, 1952, 20, 487.

<sup>7</sup> Rowland and Libby, *ibid.*, 1953, 21, 1495.

<sup>8</sup> Chien and Willard, *J. Amer. Chem. Soc.*, 1954, 76, 4735.

<sup>9</sup> Milman and Shaw, *J.*, 1956, 2101.

<sup>10</sup> Iredale and Maccoll, *Nature*, 1937, 140, 24.

<sup>11</sup> Hamill and Williams, *J. Amer. Chem. Soc.*, 1950, 72, 2813.

<sup>12</sup> Hamill, Williams, and Schwartz, *ibid.*, p. 2813.

<sup>13</sup> Roy, Williams, and Hamill, *ibid.*, 1954, 76, 3274.

On irradiating ethyl bromide containing  $10^{-3}$  molar fraction of vinyl bromide, a retention of 60% was obtained, indicating that a similar exchange occurs with vinyl bromide. This might partly account, therefore, for the large activity in this fraction observed throughout the results shown in Table 1. The increased activity of the ethylene dibromide fraction when vinyl bromide was present could be explained by addition of hydrogen bromide. By comparison with the smaller ethylene dibromide activity found

TABLE 1.

	(a) Containing $5.5 \times 10^{-3}$ molar fraction of vinyl bromide		(b) As (a), but no vinyl bromide		(c)	(d) Same specimen as (c)		(e)		(f) Same specimen as (e)	
	11 d.		10 d.			21.8 hr.	16 d.		14.9 hr.	5 d.	
Irradiation time .....	$^{80}\text{Br}^*$	$^{82}\text{Br}$	$^{80}\text{Br}^*$	$^{82}\text{Br}$	$^{80}\text{Br}^*$	$^{80}\text{Br}^*$	$^{82}\text{Br}$	$^{80}\text{Br}^*$	$^{80}\text{Br}^*$	$^{82}\text{Br}$	$^{82}\text{Br}$
Bromine isotope .....											
Vinyl bromide .....	16.10	11.71	7.46	7.20	12.31	5.85	5.00	4.00	9.92	7.29	
Methylene dibromide...	5.85	2.22	5.40	3.81	4.30	5.44	1.91	3.07	3.96	2.78	
Ethylidene dibromide	4.87	3.51	3.42	3.10	3.92	4.61	2.81	1.37	3.81	3.24	
Ethylene dibromide ...	27.90	31.02	20.62	24.81	28.75	23.30	29.00	16.71	21.85	36.42	
Bromoform .....	5.51	6.51	3.67	4.40	6.26	4.82	8.06	3.54	3.71	11.01	
1 : 1 : 2-Tribromoethane	4.81	6.40	3.94	6.47	11.48	5.14	6.74	2.36	3.62	8.24	
1 : 1 : 2 : 2-Tetrabromo- ethane (residue) .....	8.64	11.75	3.76	6.71	9.49	3.32	5.76	1.34	3.49	9.75	
Observed retention ...	69.40	70.04	55.5	64.61	79.45	52.52	66.21	35.52	51.45	72.58	

Specimens (a), (b), (c), and (d) were pre-treated by boiling of a small quantity of ethylene dibromide before irradiation; only specimen (a) contained added vinyl bromide. Specimens (e) and (f) were purified by fractional crystallisation. The standard deviations due to counting were approximately 2–3% for  $^{80}\text{Br}^*$  and 5–8% for  $^{82}\text{Br}$ .

when small quantities of elementary bromine were present during the neutron irradiation [Table 2, (a)], it appears that such addition must occur in nearly all specimens of purified ethylene dibromide.

In order to determine the conditions under which vinyl bromide might be produced by the decomposition of ethylene dibromide, a sample of the latter was refluxed in daylight in a closed system at  $131^\circ$ ; after 20 days the first fraction distilling from the ethylene dibromide was collected in a freshly purified sample, and the mixture irradiated simultaneously with another portion of the pure specimen. The retention for  $^{80}\text{Br}^*$  in the latter (44%) was less than that in the mixture (55%); an analysis was made after adding a trace of elementary bromine and allowing the solution to stand in daylight to saturate vinyl bromide present. The difference in retention (10%) was reflected in the increased yields of ethylene dibromide (3.7%) and tribromoethane fractions (7.2%), and the results were therefore consistent with the presence of vinyl bromide in the products from the boiled specimen.

The variation of retention with the time near the neutron source was also investigated; the results from two sets of experiments are given in Table 1 [experiments (c) and (d), and (e) and (f)]. They are apparently erratic, the retentions increasing with time when the initial concentration of vinyl bromide (as indicated by the activity in this fraction for short irradiations) was small, and decreasing for larger initial concentrations. This effect was also observed in other (unpublished) experiments. The ethylene dibromide used in experiments (e) and (f) was probably purer than that used in (c) and (d), since the final purification consisted of fractional crystallisation in darkness, thus avoiding heat treatment.

Further, when active bromine is added to ethylene dibromide previously subjected to the action of daylight or  $\gamma$ -rays, a large part of the activity is found in the tetrabromoethane (residue) fraction, approximately half the activity of which was present as high-boiling compounds. This, together with the fact that vinyl bromide polymerises in daylight suggests that polymerisation of vinyl bromide might also affect the ultimate distribution of activity in purified ethylene dibromide.

*Retentions in Bromine-Ethylene Dibromide Mixtures.*—Values of these are plotted against bromine concentration in the Figures. It was difficult to obtain reproducible results when only small quantities of bromine were present, since it was sometimes lost during irradiation. Addition of elementary [<sup>82</sup>Br]bromine showed that the loss of bromine was accompanied by a growth of activity in the ethylene dibromide and tri- and tetra-bromoethane fractions. This was consistent with the presence, as impurities, of vinyl and hydrogen bromide.

In view of this irreproducibility, the equality of the retentions for the different isotopes, which has been found to hold in a number of bromides, was adopted as a criterion for the

FIG. 1. *Retention of ethylene dibromide as a function of the molar fraction of bromine.*

+ <sup>80</sup>Br, ● <sup>80</sup>Br\*, ▼ <sup>82</sup>Br.

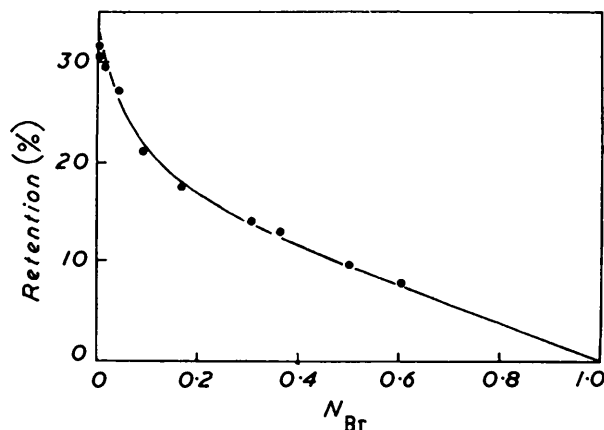
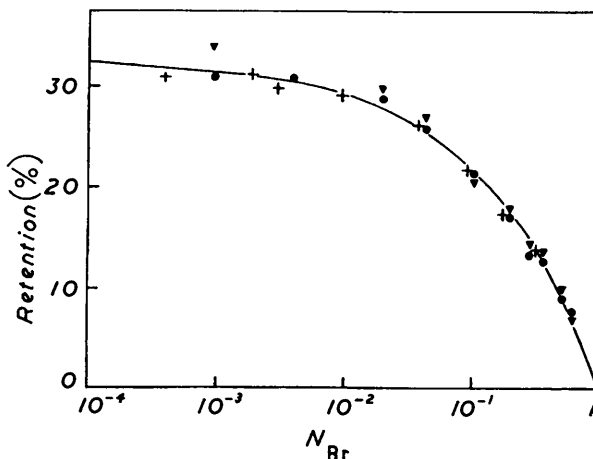


FIG. 2. *Retention of ethylene dibromide as a function of the molar fraction of bromine. The points shown are the weighted mean of the values, shown in FIG. 1, taken at the same molar fraction of bromine.*

acceptance of results obtained for the <sup>80</sup>Br\* and <sup>82</sup>Br isotopes. It can be seen from Fig. 1 that the retentions of all isotopes are equal for large bromine concentrations; at low concentrations some values for <sup>82</sup>Br lie considerably higher than those corresponding for <sup>80</sup>Br\*; these were included since the equality of the latter with those obtained for <sup>80</sup>Br indicated the general validity of the lower group of points. The curves drawn in Figs. 1 and 2 will be discussed later.<sup>14</sup>

The products from neutron irradiation are given in Table 2, the results shown being obtained from the weighted mean of the activities found for <sup>80</sup>Br\* and <sup>82</sup>Br; for a given fraction, the latter were equal within the errors of counting.

<sup>14</sup> Milman and Shaw, *J.*, 1957, 1325.

TABLE 2.

	Percentage activity in fraction shown:		(c) % activity in (a) % activity in (b)	(d) Activity at $N_{Br} = 0$ due to	
	(a) $N_{Br} = 10^{-3}$	(b) $N_{Br} = 0.312$		(i) High-energy processes	(ii) Diffusive processes
Methylene dibromide ...	2.05 ± 0.11	1.27 ± 0.07	1.61 ± 0.13	1.84 ± 0.10	0.21 ± 0.15
Ethylidene dibromide ...	1.51 ± 0.08	0.89 ± 0.03	1.70 ± 0.06	1.29 ± 0.04	0.21 ± 0.09
Ethylene dibromide.....	15.81 ± 0.43	5.89 ± 0.07	2.69 ± 0.08	8.50 ± 0.10	7.31 ± 0.44
Bromoform .....	2.05 ± 0.11	1.21 ± 0.11	1.70 ± 0.18	1.75 ± 0.16	0.30 ± 0.19
1 : 1 : 2-Tribromoethane	5.18 ± 0.16	2.85 ± 0.05	1.82 ± 0.06	{ 4.00 ± 0.07 2.36 ± 0.06 *	{ 1.18 ± 0.18 2.82 ± 0.17 *
1 : 1 : 2 : 2-Tetrabromoethane (residue) .....	1.47 ± 0.13	0.95 ± 0.04	1.45 ± 0.14	1.38 ± 0.06	0.09 ± 0.14
Observed retention .....	30.42 ± 0.75	14.08 ± 0.18	—	—	—

\* Calculated from the results of Table 1, experiment (e).

## DISCUSSION

By using the extrapolation method described previously<sup>1</sup> the value of  $R_E$  (retention due to high-energy processes) obtained from Fig. 2 is approximately 18%. A similar linear form for the variation of  $R_E$  with molar fraction of bromine being assumed, the ratio of  $R_E$  at  $N_{Br} 0$  and 0.312 is 1.45, and the corresponding ratios of the percentage activities of any fraction produced by high-energy processes might be expected to be the same. The observed ratios for the individual fractions are given in Table 2, column (c), and, with the possible exception of the tetrabromoethane fraction, the ratios are all greater than this, indicating that diffusive processes are partly responsible for their formation. If it is assumed that the active compounds produced when 0.312 molar fraction of bromine was present are entirely due to high-energy processes, the corresponding values at zero bromine concentration can be obtained, and hence also the degree to which diffusive reactions contribute to the different products. The results are given in Table 2, (d), from which it can be seen that the predominant diffusive reactions result in the formation of ethylene dibromide and tribromoethane.

The greater value of  $R_E$  for ethylene dibromide than for ethyl bromide suggests that Br-Br collisions play an important part in the high-energy processes, possibly by their ability to "thermalise" energetic atoms in a single encounter,<sup>4</sup> so that the active atom is surrounded by the radicals previously produced by inelastic collisions. In the absence of such collisions a slower degradation of the energy associated with the active atom might occur, so that when the atom was finally thermal there would be a smaller concentration of neighbouring free radicals, and hence a smaller chance of recombination. The greater concentration of (bound) bromine atoms in ethylene dibromide than in ethyl bromide might therefore be expected to give an increased yield of high-energy products. Evidence for the occurrence of processes of the type postulated by Libby<sup>4</sup> may also be afforded by the greater yield of parent compound produced by high-energy processes (8.5%) than with that found in ethyl bromide (6.1%).

In the presence of small quantities of bromine the percentage of tribromoethane is often greater than that found in the pure substance [compare, for example, Table 1, (e) with Table 2, (a)]. This implies that the reactions producing this substance involve the addition of elementary bromine to active vinyl bromide. Also, the "diffusive" dependence of the tribromoethane fraction on bromine concentration suggests that part of the active vinyl bromide is formed at this stage, the most probable mechanism for this being by exchange of inactive vinyl bromide (formed by high-energy processes) with active atoms. The observed reduction in activity of the tribromoethane when the bromine concentration is increased can then be explained by the removal of inactive vinyl bromide by addition, or, more probably, of active atoms by the reaction:

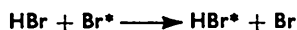


The ethylene dibromide activities found in the pure system were greater than those obtained when bromine was present and are consistent with the view that the homogeneous reactions



partly account for the activity in this fraction. The rôle of bromine, when present, is most probably to saturate vinyl bromide produced on storage or by radiolysis, thus preventing such reactions. Further evidence for the formation of ethylene dibromide by slow reactions (in the absence of bromine) is given by the greater percentage activity of  $^{82}\text{Br}$  (than of  $^{80}\text{Br}^*$ ) in this fraction since, by virtue of its greater half-life, molecules of vinyl or hydrogen bromide containing  $^{82}\text{Br}$  are available for such reactions for longer than similar molecules containing  $^{80}\text{Br}^*$ . Similar effects are observed for the tri- and tetra-bromoethane (residue) fractions, both of which are partly derived from vinyl bromide.

The erratic variation of retention with the time of irradiation [cf. Table 1, (c), (d), (e), (f)] can be explained if the purification of specimens (c) and (d) were more effective in removing hydrogen bromide than vinyl bromide. The large initial activity of vinyl bromide would then be expected; subsequent formation of vinyl bromide by radiolysis would be accompanied by the liberation of hydrogen bromide, and the latter might reduce the rate of formation of vinyl bromide by the competing exchange :



For experiments (e) and (f), in which there was a much smaller initial vinyl bromide concentration, the simultaneous formation of vinyl and hydrogen bromide could cause an increased vinyl bromide fraction.

A further observation, in empirical agreement with the above arguments, is the smaller percentage of active vinyl bromide containing  $^{82}\text{Br}$  rather than  $^{80}\text{Br}^*$ ; this can be seen in experiments (a), (d), and (f) (Table 1) and has also been found in three other analyses (unpublished). Such an effect would be expected if the rate of removal of active vinyl bromide by addition reactions was greater than its rate of production by the reactions described, or by slow  $\gamma$ -ray induced exchange with extractable radio-bromine. Evidence for such exchange in ethyl bromide containing 1 : 2-dibromoethylene is given later.<sup>15</sup> If precautions are taken to avoid such reactions, the retention of ethylene dibromide in the presence of 1 : 2-dibromoethylene is about 50%,<sup>15</sup> and the retentions in ethyl bromide containing either this substance or vinyl bromide are equal. In these conditions, the maximum retention expected in ethylene dibromide in the presence of vinyl bromide is therefore 50% also; the greater retentions found (Table 1) therefore indicate that  $\gamma$ -ray induced exchange might also contribute to the formation of active vinyl bromide.

The bromoform activities in Table 1 show a similar difference in the percentage activities for the two isotopes to that found in the neighbouring fractions. Since the separation of bromoform from the other carriers is difficult to perform quickly, it seemed possible that this effect was spurious and due to poor fractionation. However, this was disproved by comparing the ratio (% activity as  $^{82}\text{Br}$ /% activity as  $^{80}\text{Br}^*$ ) for the ethylene dibromide, bromoform, and tribromoethane fractions from the results of twelve analyses; in four cases the observed ratio for bromoform was significantly greater than that for the corresponding neighbouring fraction, showing that the increased  $^{82}\text{Br}$  activity cannot always be ascribed to poor separation. It may be observed empirically that large activities in the bromoform fraction are generally accompanied by large residual activities. Since the latter are probably due to compounds derived from polymerised vinyl bromide, this suggests that the activity collected with the bromoform fraction might be due to other chemical species produced by addition of free radicals to vinyl bromide.

Another puzzling feature of the analyses is the similarity between the vinyl bromide and the methylene and ethylidene dibromide fractions, all of which tend to give smaller activities for the longer-lived isotope. This suggests the presence of an impurity (e.g.,

<sup>15</sup> Milman and Shaw, following paper.

1 : 2-dibromoethylene) which reacts similarly to vinyl bromide and boils between 100° and 110°. However, the complexity of the slow processes occurring in bromine-free ethylene dibromide can be largely explained by the formation of vinyl bromide, and no attempt was made to investigate the latter surmise.

#### EXPERIMENTAL

*Materials.*—Ethylene bromide was obtained from The Associated Ethyl Company; samples were kept in daylight with excess of bromine for 2 hr., then extracted with sulphite, washed with water, and dried (CaCl<sub>2</sub>). The samples were then filtered and fractionally distilled as described for ethyl bromide.<sup>1</sup> Specimens were then stored in the dark until required. Preliminary experiments showed that this purification did not give more irreproducible results than specimens purified by Willard's method; <sup>1</sup> in view of the similarity of the results obtained with ethyl bromide purified by the two methods, the former was always used. Vinyl bromide was made from ethylene dibromide by refluxing the latter with alcoholic potassium hydroxide. A Drikold trap at the top of the reflux condenser collected most of the vinyl bromide, which was purified by fractional distillation in a vacuum-jacketed column cooled externally with melting ice. The fraction, b. p. 15.5–16°, was collected and sealed in small glass ampoules which were kept in darkness until needed. Specimens left in daylight formed white crystals which were assumed to be polymer.

Bromine ("AnalaR") was used without further purification.

*Technique.*—The neutron irradiation, and methods of extracting and counting ethylene dibromide, were exactly as described for ethyl bromide.

In order to check that no exchange occurred between ethylene dibromide and hydrogen bromide, a mixture of them was prepared by passing hydrogen bromide from pile-produced NH<sub>4</sub><sup>82</sup>Br into ethylene dibromide, as described by Milman and Shaw,<sup>9</sup> the only modification being that traces of bromine were removed by bubbling the hydrogen bromide through ethylene dibromide instead of bromobenzene. The sample was placed near the radium-beryllium source for eight days, and then extracted. A period of two days was allowed before measurement to reduce the activity of <sup>80</sup>Br\* produced from the source. The corresponding <sup>82</sup>Br activity was negligible compared with that from the H<sup>82</sup>Br introduced. If it is assumed that the activity in the extracted fraction was produced by exchange, the rate found corresponded to a fraction exchanging per hour of  $7 \times 10^{-4}$ .

The products from neutron irradiation were analysed by extracting about 37 ml. of a 50 ml. irradiated specimen. The unextracted portion was used to determine the total activity; 12 ml. of the rest were used to determine the retention which was corrected <sup>1</sup> for any activity adhering to the walls of the irradiation flask. After being dried (CaCl<sub>2</sub>), 25 ml. were mixed with 10 ml. each of all carriers except vinyl bromide, and the mixture was re-extracted to ensure the removal of bromine. After being dried (CaCl<sub>2</sub>), the mixture was cooled in Drikold, and 10 ml. of pre-cooled vinyl bromide was added. After filtration, the mixture was fractionally distilled,<sup>1</sup> the column and collecting vessel being cooled initially in melting ice. The vinyl bromide recovered was diluted to 50 ml. with pre-cooled carbon tetrachloride; other samples were prepared for measurement as described previously.<sup>15</sup>

In addition to the purification described above, a little of the ethylene dibromide was boiled off at atmospheric pressure in samples (a), (b), (c), and (d) (Table 1) to remove most of the vinyl and hydrogen bromide which might have been formed during storage. Samples (e) and (f) were purified before irradiation by cooling a stoppered flask containing ethylene dibromide in an ice-bath; when about three quarters had frozen, the liquid was poured off in a dry-box and the solid was allowed to melt. The process, which was performed in diffuse light, was repeated twice, the product from the final melt being used.

The retention of <sup>80</sup>Br in ethyl bromide containing vinyl bromide (10<sup>-3</sup> molar fraction) was measured by irradiating the mixture for 10 min. and extracting with a bromide-sulphite reagent.

Attempts to produce ethylene dibromide enriched in vinyl bromide by boiling were made by refluxing it in a glass system. The exit tube from the reflux condenser was held under more ethylene dibromide contained in a bubbler, the outlet of which was attached to a tube containing sodium hydroxide pellets to remove any hydrogen bromide evolved and to prevent ingress of moisture. After 20 days, the ethylene dibromide from the boiling flask and the bubbler were mixed and distilled, the first ml. being collected in a freshly purified ethylene dibromide sample.

This, together with another sample from the same batch, was irradiated overnight, and the retentions were measured. The analysis was performed after the extracted solution had been treated with bromine to saturate vinyl bromide present; the latter was not added as carrier in this case.

By keeping aliquot portions of the same specimen of ethylene dibromide in darkness, daylight, and near a 500 mc Ra source production of hydrogen bromide was found to be greatest for the specimen held in daylight and least for that kept in the dark. These results might indicate the relative dissociation of ethylene dibromide under such conditions. The results obtained by adding bromine labelled with  $^{82}\text{Br}$  (prepared as described previously<sup>9</sup>) to these samples were inconclusive, but activity was always found in the ethylene dibromide and the tri- and tetra-bromoethane (residue) fraction. The latter was further distilled at 1.5 cm. admixed with pentyl benzoate, benzyl benzoate, 1:3:5-tribromobenzene, and dibutyl phthalate to provide higher-boiling carrier material. The residual activity was approximately equally distributed between tetrabromoethane and higher-boiling compounds. Of the latter, it was estimated that 10% boiled above 300° (at atmospheric pressure), the activity per unit temperature range between 260° and 300° being roughly constant.

*Retentions in Bromine-Ethylene Dibromide Mixtures.*—These and the analysis of the products were determined as described for ethyl bromide.<sup>1</sup>

The authors thank Professor Lord Cherwell, F.R.S., for the facilities of the Clarendon Laboratory, and the Associated Ethyl Company Limited for a gift of ethylene dibromide.

THE CLARENDON LABORATORY, OXFORD.

[Received, July 19th, 1956.]

---