BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1746—1750 (1971)

The Effect of Benzene on the Reaction of the Recoil Bromine Atom with Ethyl Bromide[1)]

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(Received December 17, 1970)

An attempt was made to estimate the effect of benzene on the recombination reactions of the recoil bromine atoms activated by the $^{81}\mathrm{Br}(n,\gamma)^{82m}\mathrm{Br}\xrightarrow{\mathrm{I.T}}{}^{82}\mathrm{Br}$ and $^{81}\mathrm{Br}(n,2n)^{80m}\mathrm{Br}$ reactions in ethyl bromide and benzene mixtures. It seems to be reasonable to conclude, from the consideration of the parent yield, that the reactions leading to the formation of parent molecules in the thermal and high-energy regions can be classified into two reaction types. Judging from the results of the $^{81}\mathrm{Br}(n,\gamma)^{82m}\mathrm{Br}\xrightarrow{\mathrm{I.T}}{}^{82}\mathrm{Br}$ reaction, approximately 53% of the parent yield from the high energy reactions in the pure ethyl bromide system is formed through the de-excitation process of the excited ethyl bromide labelled by the direct substitution reaction of the energetic recoil atom, while 47% is formed by the reaction of the recoil atom with ethyl radicals in the cage. The reaction of ethylene with hydrogen bromide, which is produced by the decomposition of the labelled excited ethyl bromide, contributes about 51% of the parent yield from the thermal energy reaction; the rest is formed by the other thermal reactions. Furthermore, no essential difference was observed between the recombination reactions of the recoil ^{82}Br and ^{80m}Br atoms produced by the $^{81}\mathrm{Br}(n,\gamma)^{82m}\mathrm{Br}\xrightarrow{\mathrm{I.T}}{}^{82}\mathrm{Br}$ and $^{81}\mathrm{Br}(n,2n)^{80m}\mathrm{Br}$ reactions respectively.

Many investigations have been carried out into the chemical effects associated with the nuclear transformations of bromine atoms in organic bromide systems, with emphasis laid especially on the recombination processes of recoil bromine atoms in the pure organic bromide systems.

Recently, binary and ternary mixtures of the organic bromides and hydrocarbons, such as benzene or cyclohexane, have been employed in order to evaluate precisely the recombination processes of the recoil bromine atoms in the high- and thermal-energy regions.[2—8a)] However, most of these studies have been made in terms of overall organic yields.

It has now been attempted to estimate the individual yields of labelled products and to make more detailed interpretations of the recombination processes of recoil bromine atoms.

The individual yields resulting from the $^{81}\mathrm{Br}(n,\gamma)^{82m}\mathrm{Br}\xrightarrow{\mathrm{I.T}}{}^{82}\mathrm{Br}$ and $^{81}\mathrm{Br}(n,2n)^{80m}\mathrm{Br}$ reactions in the mixtures of benzene and ethyl bromide were examined. Important information was obtained from the correlation between the parent yields from the high- and the thermal-energy reactions upon the addition of benzene, and from the isotope effects between ^{80m}Br and ^{82}Br recoil atoms.

Experimental

Materials. E.P.-grade ethyl bromide and G.R.-grade benzene, supplied by the Junsei Chemical Co., Ltd., were purified with the ordinary method described in Ref. 8, and their purities were checked by means of a gas chromatograph. The contents of the impurities in the ethyl bromide and benzene used for the experiments were less than 0.025% and 0.001% respectively. The bromine used was the highest grade available.

Irradiation. About 0.3—0.5 m*l* portions of the mixtures of ethyl bromide and benzene or bromine was sealed into a quartz ampoule. Thermal neutron irradiations were made 3—5 min in a pneumatic tube of JRR-1 of the Japan Atomic Energy Research Institute at room temperature at a neutron flux of 3×10^{11}n/cm^2/sec, with a concomitant gamma ray dose rate of 10^4R/hr. In the case of the $^{81}\mathrm{Br}(n,2n)^{80m}\mathrm{Br}$ reaction, all the irradiations were made for 2 hr with 14 MeV neutrons at a flux of 10^6n/cm^2/sec resulting from the $^3\mathrm{H}(^2\mathrm{H},n)^4\mathrm{He}$ reaction, where the effect of thermal neutrons and γ-dose on the organic yield was neglected.

Determination of Organic Yields. The irradiated samples were separated into organic and inorganic fractions by using the ordinary extraction method,[8)] and the overall organic yield was determined as a ratio of the activity in the organic fraction to the total activity. All the extraction procedures were performed after the irradiated samples had been allowed to stand long enough for the $^{78}\mathrm{Br}(t_{1/2}$: 6.5m) produced by the $^{79}\mathrm{Br}(n,2n)^{78}\mathrm{Br}$ reaction in the fast neutron experiment and the $^{80m}\mathrm{Br}(t_{1/2}$:4.38hr) produced by the $^{79}\mathrm{Br}(n,\gamma)^{80m}\mathrm{Br}$ reaction in the thermal neutron experiment to decay out. The organic fraction was then divided into two aliquots: one (Aliquot I) was used as the standard, and the other (Aliquot II) was submitted to gas chromatographic separation after the addition of various organic bromides as carriers. Each fraction of the organic bromides was collected in a coiled glass tube cooled in a dry-ice ethanol bath at the outlet of the column. The various products were separated by means of a gas chromatograph in a temperature-programmed all-stainless-steel column (0.6 cm in diameter and 3 m long), using tricresyl phosphate or silicone DC 703 as

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[1)] Presented at "The International Symposium on Chemical Effects of Nuclear Transformations," Cambridge, July, 1969.

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[2)] P. F. D. Shaw and J. E. C. Macrae, *Radiochim. Acta*, **2**, 76 (1963).

[3)] P. F. D. Shaw and J. E. C. Macrae, *J. Inorg. Nucl. Chem.*, **24**, 1327 (1962).

[4)] P. F. D. Shaw, *ibid.*, **24**, 1337 (1962).

[5)] M. Milman, *J. Phys. Chem.*, **67**, 537 (1963).

[6)] S. S. Kontis, P. Sanitowangs, and M. Weston, "Chemical Effects of Nuclear Transformations," Vol. 1, Vienna (1963), p. 333.

[7)] E. S. Filatov, An. N. Nesmeyanov, and Yu. B. Chepyzhev, *Vest. MGU. Ser. Khim.*, **6**, 46 (1963).

[8)] a) T. Shiokawa, T. Sato, K. Kondo, and K. Sato, *Nippon Kagaku Zasshi*, **87**, 922 (1966); b) T. Shiokawa, T. Sato, G. Izawa, K. Kondo, and K. Sato, *ibid.*, **86**, 1006 (1965).

staionary phase and helium as the eluent gas. Furthermore, the collected ethyl bromide and the Aliquot I mentioned above were each allowed to completely react with the sodium metal by using ethanol as the solvent; then the concentration of bromine present in these fractions was determined by the Volhard method. The parent (P) and other product yields (Q) are given by the following formulas:

$$P = \frac{A_p}{A_o} \times \frac{S_o}{S_p} \times R\ (\%)$$

$$Q = \frac{A_q}{A_p} \times P\ (\%)$$

R: overall organic yield
A_p: activity of the collected ethyl bromide fraction
A_o: activity of the Aliquot I
A_q: activity of the product
S_o: concentration of bromine of the Aliquot I
S_p: concentration of bromine in the collected ethyl bromide fraction

The higher-boiling-point products, which were inseparable by means of the gas chromatograph, were observed in this system, so these procedures were necessary to obtain the absolute yields of the organic products. Only the products having boiling points lower than that of dibromobenzene were investigated; no attempt to obtain the yields of the various products other than ethyl bromide was made in the (n, 2n) experiment.

Activity Measurements. The activities of the ^{82}Br from the ^{81}Br(n,γ)^{82m}Br$\xrightarrow{\text{I.T}}$^{82}Br reaction and of the ^{80m}Br from the ^{81}Br(n,2n)^{80m}Br reaction were meaured by using a sodium iodide crystal scintillation counter. The experimental error arising from the activity measurements were of the following magnitudes: (1) for overall organic yields: ±2—3%, and (2) for the product yield: ±3—15%. No correction was made for the ^{82}Br formed by (n,γ) on ^{81}Br, which accounts for 7% of the total ^{82}Br activity.[9]

Results

In order to estimate the contribution of the thermal reaction (scavenger sensitive reaction) and the high-energy reaction (scavenger insensitive reaction) to the product yields in ethyl bromide and benzene mixtures, it is necessary to establish the scavenger curves for a number of mixtures of ethyl bromide and benzene. As a typical example, Fig. 1 indicates the scavenger curve of each product obtained in the mixture of ethyl bromide (0.87 mf: mole fraction)-benzene (0.13 mf) in the ^{81}Br(n,γ)^{82m}Br$\xrightarrow{\text{I.T}}$^{82}Br reaction and of ethyl bromide (0.89 mf)-benzene (0.11 mf) in the ^{81}Br(n,2n)^{80m}Br reaction. Although, in this experiment, the organic yields were not corrected for the ^{82}Br directly formed by the ^{81}Br(n,γ)^{82}Br reaction, which accounts for about 7% of the total ^{82}Br,[9] it can be expected that its contribution to the organic yields is very small, since the overall organic yields for the ^{82}Br formed by the ^{81}Br(n,γ)^{82}Br and ^{81}Br(n,γ)^{82m}Br$\xrightarrow{\text{I.T}}$^{82}Br processes were almost the same as those for the ^{80m}Br and ^{80}Br produced by (n,γ) on ^{79}Br in the pure ethyl bromide.[8a,10]

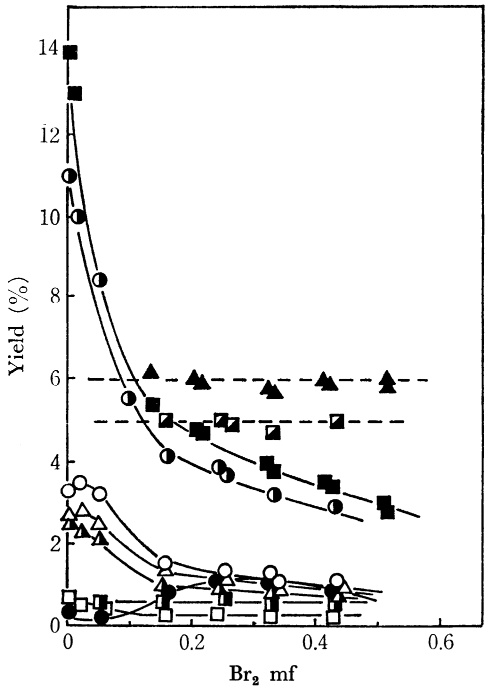

Fig. 1. Scavenger curves of various products obtained in the systems of ethyl bromide (0.87 mf)-benzene (0.13- mf) in the ^{81}Br(n,γ) ^{82m}Br$\xrightarrow{\text{I.T}}$^{82}Br reaction and ethyl bromide (0.89 mf)-benzene (0.11 mf) in the ^{81}Br(n,2n) ^{80m}Br reaction.

a) ^{81}Br(n,γ) ^{82m}Br$\xrightarrow{\text{I.T}}$ ^{82}Br

◭: C_6H_5Br △: 1.1-$C_2H_4Br_2$ ○: 1.2-$C_2H_4Br_2$
●: $C_6H_4Br_2$ □: CH_2Br_2 ◨: CH_3Br
◑: C_2H_5Br ◪: parent yield normalized by $(1-C)/(1+C)$

b) ^{81}Br(n,2n) ^{80m}Br

■: C_2H_5Br ▲: parent yield normalized by $(1-C)/(1+C)$

The fraction of the high-energy-reaction yield for each labelled product is given as an intercept on the coordinate axis by extrapolating each scavenger curve to zero scavenger concentration. The scavenger curve for dibromobenzene shows a minimum at a bromine concentration of 0.05 mf, and the yield gradually increases at higher bromine concentrations. The value of 0.23% at 0.05 mf of bromine was employed as the approximate yield due to the high-energy reaction.

The scavenger curves of 1,1- and 1,2- dibromoethane were very similar to the results previously reported by Shaw *et al.*[11] for their recoil study of the ^{80m}Br produced by (n,γ) on ^{79}Br in the pure ethyl bromine system; it showed almost a $(1-C)$ dependency at bromine concentrations higher than 0.15 mf (C: mole fraction of bromine). On the other hand, the parent scavenger curve showed a $(1-C)/(1+C)$ dependency at bromine concentrations higher than 0.15 mf. and the parent yield due to the high-energy reactions was obtained by the normalization by $(1-C)/(1+C)$. The experimental data for each product due to the thermal and the high-energy reactions obtained in this way are summarized in Figs. 2 and 3, together with the total yields from both the thermal and high-energy reactions in the ^{81}Br(n,γ)^{82m}Br$\xrightarrow{\text{I.T}}$^{82}Br reaction. The total organic

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[9] J. F. Emery, *J. Inorg. Nucl. Chem.*, **27**, 903 (1965).

[10] a) M. Milman and P. F. D. Shaw, *J. Chem. Soc.*, **1957**, 1303. b) B. Knight, G. E. Miller, and P. F. D. Shaw, *J. Inorg, Nucl. Chem.*, **23**, 15 (1961).

[11] A. J. Cole, M. D. Mia, G. E. Miller, and P. F. D. Shaw, *Radiochim. Acta*, **6**, 150 (1961)

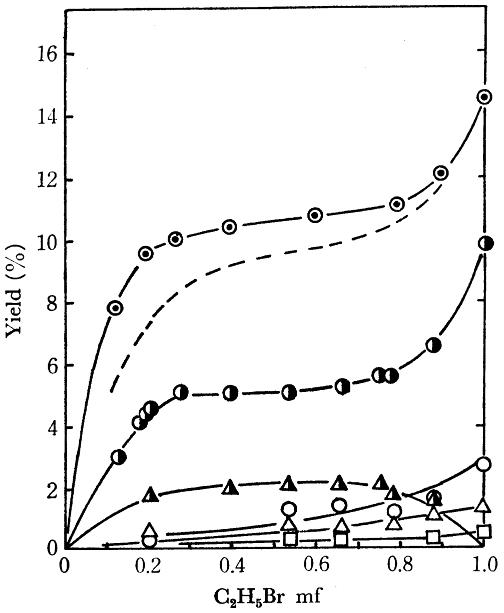

Fig. 2. Yields of various products due to the thermal energy reactions resulting from the $^{81}Br(n,\gamma)$ $^{82m}Br \xrightarrow{\text{I.T}} {}^{82}Br$ reaction in ethyl bromide and benzene mixtures as a function of ethyl bromide concentration.
⊙: total organic yields
---: sum of individual yields
Other symbols are listed in caption for Fig. 1.

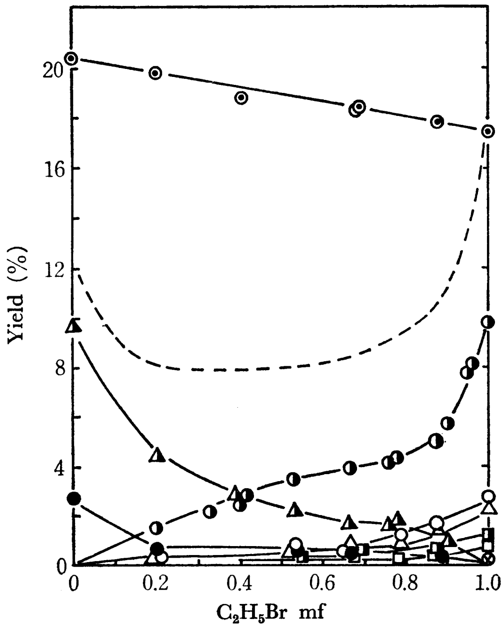

Fig. 3. Yields of various products due to the high energy reactions resulting from the $^{81}Br(n,\gamma)$ $^{82m}Br \xrightarrow{\text{I.T}} {}^{82}Br$ reaction in ethyl bromide and benzene mixtures as a function of ethyl. bromide concentration
⊙: total organic yield
⊗: $CHBr_3$
---: sum of individual yields
Other symbols are listed in caption for Fig. 1.

yields obtained in the (n,2n) experiment were shown in Ref. 8a.

For the systems in which the overall organic yield were not obtained experimentally, the overall organic yields, as estimated graphically, were used for the calculation.

The most interesting aspect of the results shown in Figs. 2 and 3 is that the parent yields from the thermal and the high-energy reactions are affected similarly by the addition of benzene. This suggests that there is a close correlation between the formations of the labelled parent molecules in both the reaction regions. The sum of the product yields in the two reaction regions in the $^{81}Br(n,\gamma)^{82m}Br \xrightarrow{\text{I.T}} {}^{82}Br$ reaction is given by a dotted line in Figs. 2 and 3. Here, the yields of other products, such as tetra-bromomethane, tri- and tetra-bromoethane, were less than 0.2 percent at most and are not included in Figs. 1, 2, and 3.

As is shown in Fig. 2, the total organic yield from the thermal energy reaction was very close to the sum of the yields of the individual products obtained experimentally. On the other hand, Fig. 3 shows that the sum of each product yield from the high-energy reactions was very low, compared with the total organic yield; especially, it was only about 40—60% of the total organic yield at benzene concentrations higher than 0.2 mf. This difference corresponds to the yields of the higher-boiling-point products which were not analyzed in this experiment. Furthermore, the sharp increase in the yields of higher-boiling-point products from the high-energy reactions at 0—0.2 mf of benzene can be practically accounted for as compensation for the decrease in both parent yields due to the thermal and the high-energy reactions as is shown in Fig. 4. This definitely suggests that, in the presence of benzene, there are some reaction

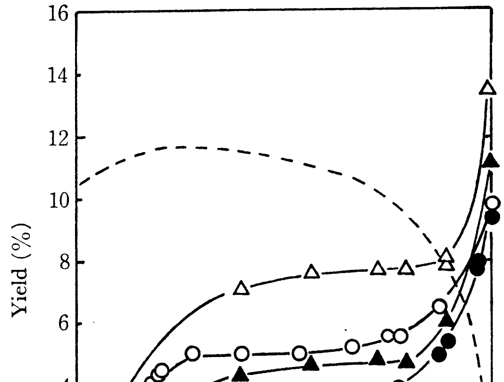

Fig. 4. Parent yields in both energy regions in ethyl bromide and benzene mixtures as a function of ethyl bromide concentration
a) $^{81}Br(n,\gamma)$ $^{82m}Br \xrightarrow{\text{I.T}} {}^{82}Br$
○: yield due to the thermal energy reactions
●: yield due to the high energy reactions
---: yield of the higher boiling point products due to the high energy reactions
b) $^{81}Br(n,2n)$ ^{80m}Br
△: yield due to the thermal energy reactions
▲: yield due to the high energy reactions

paths interrupting the formation of the labelled parent molecules from the thermal and the high-energy reactions. On the other hand, the yields of CH_3Br, CH_2Br_2, $CHBr_3$, 1,1- and 1,2-$C_2H_4Br_2$ decreased gradually as the benzene concentration became higher; however there were no remarkable effects on the formation of these labelled molecules by the addition of benzene. The parent yields from the thermal and the high-energy reactions are approximately 0.5—3.9 percent higher in the $^{81}Br(n,2n)^{82m}Br$ reaction than those in the $^{81}Br(n,\gamma)^{82m}Br\xrightarrow{I.T}{}^{82}Br$ reaction, as is shown in Fig. 4. However, the parent-yield curves very similar tendency for the addition of benzene in both nuclear transformations.

Discussion

Recombination Reactions of Recoil ^{82}Br and ^{80m}Br Atoms. It appears from Fig. 4 that, in the presence of 0—0.2 mf of benzene, the parent yields from the thermal and the high-energy reactions in the $^{81}Br(n,\gamma)^{82m}Br\xrightarrow{I.T}{}^{82}Br$ reaction decreased abruptly in a similar fashion, and that, furthermore, this decrement in both the parent yields was almost equal to the increase in the yields of the higher-boiling-point products due to the high-energy reactions. This suggests that a part of the recoil bromine atoms react with ethyl bromide during the slowing-down process, thus contributing to the formation of some excited species labelled with ^{82}Br, and that, in the presence of benzene, higher-boiling-point products are produced by the reactions of those exicted species with benzene.

These trends can be explained by assuming that a part of the recoil atoms can undergo the substitution reaction with the bromine atom of ethyl bromide by means of billiard ball-type elastic collisions, or inelastic collisions with ethyl bromide molecules, thus forming a labelled excited ethyl bromide. As is illustrated in Fig. 5, the labelled excited ethyl bromide should be partially de-excited by the interaction with neighbouring molecules, and it gives the parent yield from the high-energy reaction through the path 2. The residual is decomposed to give ethylene and hydrogen bromide through the path 1 by the analogy with the pyrolysis of ethyl bromide.[12] Then, the radioactive hydrogen bromide formed through the path 1 reacts thermally with the ethylene which is produced either through path 1 or by the pyrolitic decomposition of ethyl bromide molecules at the near site of recoil events, thus contributing to the formation of the labelled ethyl bromide due to the thermal reactions, as is shown in Eq. (1). Ethylene produced by a reaction other than path 1 also reacts with the radioactive bromine molecule and contributes to the formation of labelled 1,2-dibromoethane by means of the thermal reactions shown in Eq. (2);

$$CH_2{=}CH_2 + H^*Br \longrightarrow CH_3CH_2{}^*Br \quad (1)$$

$$CH_2{=}CH_2 + {}^*Br_2 \longrightarrow CH_2BrCH_2{}^*Br \quad (2)$$

It may be reasonable to assume that the reaction (1)

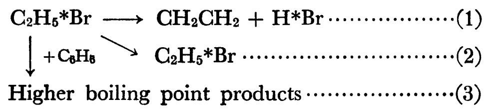

Fig. 5. Reaction paths of the excited ethyl bromide

of ethylene with hydrogen bromide will be predominant over the reaction (2) from the viewpoint of radiolysis and pyrolysis. However, in the presence of a bromine scavenger, ethylene will be immediately scavenged, and both the reactions, (1) and (2), are suppressed. Meanwhile, it is conceivable that, in the presence of benzene, these labelled excited ethyl bromide molecules may react instantaneously with benzene molecules through the path 3 in Fig. 5, thus contributing to the formation of higher-boiling-point products due to the high-energy reactions. The reaction mechanisms for the path 3 are not clear because these higher-boiling-point products have not been identified experimentally. However, it may be presumed that these excited ethyl bromide molecules have sufficient energies in excess of the activation energy required for the path 3.[13]

Similarly, Rowland *et al.*[14–16] indicated that the decomposition and the de-excitation of the tritiated parent molecules in the excited state play an important role in determining the distribution of the yields of the various labelled products in the gas-phase reactions of recoil tritium with alkyl chlorides and hydrocarbons. Since little attention has been paid to the analysis of higher-boiling-point products, only the yields of thep roducts separated by gas chromatography were discussed. The authors have found that a considerable portion of the overall organic yields in the systems containing benzene, such as $C_6H_6+Br_2$ and $C_6H_6+C_6H_5Br$ systems, consists of higher-boiling-point products.

On the other hand, several radicals should be produced during the slowing-down processes of the energetic recoil bromine atoms, and a part of the recoil atoms which have escaped from the direct substitution reaction will recombine with such radicals in both the energy regions. In the cage, the recombination reactions of the recoil atoms with these radicals take place before the radicals start diffusing away, and consequently, contribute to the yields due to the high-energy reaction (immediate recombination reaction).

The recoil bromine atom which has escaped from the cage reacts with radicals or other reactants (C_2H_5Br, *etc.*) and thus contributes to the formation of labelled products in the thermal-energy region. The parent yield from the recombination reaction in the cage depends on the concentration of ethyl radicals, which will gradually be diminished by the addition of benzene because of the decrease in the collision probability of the recoil atom with the ethyl bromide molecule. Thus, the fact that the parent yield from the high-energy reactions shows a gradual decrease at benzene concentrations of more than 0.2 mf may be ascribed to the gradual

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[12] N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, London (1958), p. 228.

[13] Path 3 will probably involve the reaction of the excited ethyl bromide with C_6H_5 or C_6H_7 radicals formed in the recoil site.

[14] F. S. Rowland, Y. M. Tang, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **86**, 1280 (1964).

[15] E. K. C. Lee and F. S. Rowland, *ibid.*, **84**, 3027 (1962).

[16] R. S. Rowland and Y. M. Tang, *ibid.*, **87**, 3304 (1965).

decrease in the recombination reaction of the recoil bromine atom with the ethyl radical in the case. If it is assumed that the parent yield from the recombination reaction in the cage at 0—0.2 mf of benzene shows a dependence on the benzene concentration in the same manner as that obtained at about 0.2—0.8 mf of benzene, it is possible to divide the parent yield from the high-energy reaction in the pure ethyl bromide system into two parts by extrapolating the yield curve to zero mole fraction of benzene in Fig. 4.

The parent yield from the recombination reaction in the cage is estimated to be about 47% from the intercept of the yield curve in Fig. 4; the remaining 53% results from the de-excitation of the excited ethyl bromide molecules formed by the substitution reactions (path 2 in Fig. 5). Similarly, the parent yield from the thermal energy reactions can be classified into two parts by extrapolating the plateau of the yield curve at 0.2—0.8 mf of benzene in Fig. 4. It may be presumed that approximately 49% of the parent yield from the thermal energy reaction is formed by the reactions indicated by Eqs. (3), (4), and (5), while about 51% arises from the reactions of ethylene with the labeled hydrogen bromide produced through the path 1 in Fig. 5. The reaction shown in Eq. (5) may be disregarded because its activation energy is 25 kcal/mol,[17] too high for the thermal atoms to be involved.

$$C_2H_5 + {}^*Br \longrightarrow C_2H_5{}^*Br \qquad (3)$$

$$C_2H_5 + {}^*Br_2 \longrightarrow C_2H_5{}^*Br + Br \qquad (4)$$

$$C_2H_5Br + {}^*Br \longrightarrow C_2H_5{}^*Br + Br \qquad (5)$$

The active bromine atoms escaped from the site of recoil events normally form inorganic compounds such as H^*Br, as has already been shown.[18,19] The scavenger curve of 1, 2-dibromoethane in Fig. 1 shows a slight increase in the yield at low bromine concentrations. This fact indicates that there are $CH_2CH_2{}^{82}Br$ radicals formed by the reaction of ^{82}Br with CH_3CH_2Br in the high-energy region, as was postulated by Shaw *et al.*[11] in their study of the recombination reaction of the ^{80m}Br produced by the (n,2n) reaction of ^{81}Br in the pure ethyl bromide system. Another explanation would be possible for the sharp fall of the parent yield at 0—0.2 mf of benzene in Fig. 3 if the $CH_2CH_2{}^{82}Br$ radical could be considered a labeled excited species instead the labelled excited ethyl bromide. However, this explanation is not acceptable since there is no correlation between the parent and 1,2-dibromoethane yields upon the addition of bromine, as is illustrated in Fig. 1.

As is shown in Fig. 2, the parent and the total organic yields from the thermal-energy reactions show quite different features at 0.2—0.8 and at 0.8—1.0 mf of benzene. This can be understood by considering that, at high benzene concentrations, the reaction of recoil bromine atoms with hydrogen radicals resulting from Eq. (6) becomes predominant and contributes to the sharp decrease in the parent and the total organic yields from the thermal reactions. Similar reactions have been postulated by Shaw[4] to account for the overall organic yield obtained in the solution of ethyl iodide and iodine in benzene. As to the yields of the other products, such as dibromomethane, 1,1- and 1,2-dibromoethane, no remarkable effect was observed in either energy region on the addition of benzene, indicating that benzene acts almost as a diluent.

$$C_6H_6 + C_6H_5 \longrightarrow C_6H_5C_6H_5 + H \qquad (6)$$

Isotope Effect between the $^{81}Br(n,2n)^{80m}Br$ *and* $^{81}Br(n,\gamma)^{82m}Br \xrightarrow{I.T} {}^{82}Br$ *Reaction.* In the case of the $^{81}Br(n,\gamma)^{82m}Br \xrightarrow{I.T} {}^{82}Br$ reaction, various products labelled with ^{82m}Br, such as $H^{82m}Br$, $CH_3{}^{82m}Br$, $Br^{82m}Br$, and $C_2H_5{}^{82m}Br$, undergo further isomeric transition to the ground state of ^{82}Br. As a consequence of the isomeric transition, followed by the Auger electron emission, ^{82}Br should have a high positive charge. It is postulated that this highly positive charge is partially neutralized by electron transfer from the remainder of the molecule or the neighbouring molecule, and that the recoil ^{82}Br obtains a considerable recoil energy (~10eV) resulting from Coulombic repulsion.[20] The individual product yields resulting from the $^{81}Br(n,\gamma)^{82m}Br \xrightarrow{I.T} {}^{82}Br$ reaction in the pure ethyl bromide were almost equal to those previously reported by other investigators for the $^{79}Br(n,\gamma)^{80}Br$ and $^{79}Br(n,\gamma)^{80m}Br$ reaction.[10,11] The absence of any isotope effect between these nuclear transformations seems reasonable, since the chemical fate of the recoil atom must be determined after it has lost most of its energy and can thus be expected not to be influenced by the slight difference in the initial energy.

However, in the case of the $^{81}Br(n,2n)^{80m}Br$ reaction with a recoil energy about 1000 times greater than that of the $^{81}Br(n,\gamma)^{82}Br$ reaction, an energy dependency of the organic yield might be expected. The parent yields due to the thermal and the high-energy reactions from the $^{81}Br(n,2n)^{80m}Br$ reaction were a little higher than those in the $^{81}Br(n,\gamma)^{82m}Br \xrightarrow{I.T} {}^{82}Br$ reaction, as is illustrated in Fig. 4.

However, the yield curve in Fig. 4 indicates a very similar dependence on the benzene concentration in both nuclear transformations. These results suggest that there is no essential difference in the mechanisms between these nuclear transformations. The differences between the parent yields for ^{82}Br and ^{80m}Br at 0—0.2 mf of benzene can be explained mainly in terms of the different probability of the formation of labeled excited ethyl bromide because of the low collision probability of ^{82}Br with a lower recoil energy in comparison with ^{80m}Br. Furthermore, it can be understood that a much higher recoil energy, causing disturbance over a wide range in the system, serves to enhance the parent yields resulting from the reactions in the cage and thermal recombination reactions after the recoil atoms have diffused away.

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[17] B. Liberator and F. Wiig, *J. Chem. Phys.*, **8**, 349 (1940).

[18] S. Goldharber and J. E. Willard, *J. Amer. Chem. Soc.*, **74**, 318 (1952).

[19] J. C. Roy, R. R. Williams, and W. H. Hamill, *ibid.*, **76**, 3274 (1954).

[20] A. R. Kazanjian and W. F. Libby, *J. Chem. Phys.*, **42**, 2778 (1965).