in the pure compounds is not grossly in error. Pure compound cross-sections calculated on the assumption that only a single ion reacts do not agree with the mixture values as well as the values given in Table IV.

In somewhat the same regard, we might point out that the compounds and systems reported in this paper constitute all of our investigations in this area except for an investigation of pure methane, and in all but pure methane the hydride transfer reaction has been observed. This indicates to us that the reaction is one of considerable generality with respect to both ions and neutral molecules. We attribute our failure to observe reaction in methane to experimental difficulties involving the small reactant ion intensity and the fact that CH_3^+ and CH_4^+ serve as reactants in other ion-molecule reactions.

The observed decrease in reaction cross-section with increasing molecular weight is interesting and puzzling. As the molecular weight increases the polarizability increases, and theoretically[1,6] the reaction cross-section should increase with the square root of the polarizability. Furthermore, with increasing molecular weight the number of available hydrogens per hydrocarbon molecule increases, and the carbon–hydrogen bond dissociation energies in the molecules should decrease somewhat. One would expect both of these factors to contribute to an increase in reaction cross-section with increasing molecular weight.

We have considered the possibility that the observed decrease in cross-section may be the result of the rapid decomposition of the product ion of mass $M - 1$ into product ions of lower molecular weight, which would generally not be detected in our experiments. However, while for the two heaviest molecules one cannot completely exclude this possibility, it can be excluded on the basis of energetics for the lighter molecules. Thus no decompositions of $C_2H_5^+$ ion from ethane are energetically possible. In propane the reactions of $C_2H_3^+$ and $C_2H_5^+$ with C_3H_8 will produce $C_3H_7^+$ containing enough energy to decompose to $C_3H_5^+$ if it be assumed that the neutral molecule formed in the hydride ion transfer reaction carries away none of the heat of reaction. However, if one makes a more reasonable assumption concerning the distribution of the heat of reaction, the decomposition to $C_3H_5^+$ becomes energetically impossible. In accordance with this view, an inspection of the mass 41 intensities in propane shows no evidence of the growth to be expected if appreciable amounts of secondary $C_3H_5^+$ ions were being formed. Thus we certainly cannot attribute the fact that the hydride ion transfer reaction cross-section in propane is only 25% that in ethahe to decomposition of the $C_3H_7^+$ ion. Similar, although less unequivocal, considerations apply to the other molecules studied. We are forced to the admission that we do not at all understand the observed decrease in the reaction cross-sections.

Discussion

Hydride ion transfer reactions have been postulated for many years and are considered to be of much importance in many processes, but to our knowledge these are the first observations of the elementary reactions and the first measurements of their rates. These rates are of the same large order of magnitude as those found for other gas phase ionic reactions, and thus hydride ion transfer can be expected to occur readily in any system containing ions. We think that our results coupled with chemical intuition support the tentative postulate that the hydride ion transfer reaction is a general phenomenon which will occur with many ions and many molecules. It is certain that these results will have to be considered in possible mechanisms for gaseous radiation chemistry systems, and it may be that the occurrence of these reactions make the systems simpler than has previously been thought. Because of these reactions the number of types of ions present in the radiation plasma may be diminished, which could simplify the over-all reaction mechanism. Similar considerations might apply to certain catalytic systems.

Acknowledgment.—We wish to thank Mr. B. L. Clark for helping with the experimental work reported in this paper.

BAYTOWN, TEXAS

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(6) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1956).

[CONTRIBUTION FROM THE NUCLEAR PHYSICS GROUP OF THE ECOLE NORMALE SUPÉRIEURE]

The Szilard–Chalmers Effect in Solid Ethyl Bromide

BY MIRIAM MILMAN

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The contribution of diffusion dependent reactions following radiative neutron capture by the bromine atom in solid ethyl bromide, has been investigated. The scavenger effect of elementary bromine and 1,2-dibromoethylene, as well as the influence of irradiation temperature and crystalline structure were examined. It was found that the high yield of radioactive organic species is due to a great enhancement of "hot" processes, the "diffusion controlled" reactions having a smaller relative importance than in the case of the neutron irradiation of liquid ethyl bromide.

Introduction

Previous work on the nuclear activation of halogen atoms in liquid organic media[1a] has shown that the reactions of the tagged atom occur in two stages. In the first, the recoiling atom loses

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(1) (a) S. Goldhaber and J. E. Willard, THIS JOURNAL, **74**, 318 (1952); (b) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952); (c) J. C. Roy, R. R. Williams and W. H. Hamill, *ibid.*, **76**, 3274 (1956); (d) M. Milman, P. F. D. Shaw and I. B. Simpson, *J. Chem. Soc.*, 1303 (1957); (e) J. C. W. Chien and J. E. Willard, THIS JOURNAL, **79**, 4872 (1957).

energy by inelastic collisions producing a high local concentration of molecular fragments with which it can combine after being thermalized. If the radioactive atom escapes from the "cage" containing the molecular fragments, it diffuses into the liquid together with some of the free radicals it has produced. In this second stage the radicals can either combine among themselves or react with the radioactive thermalized halogen. These reactions proceed until the concentration of reactants is so reduced by diffusion that their reaction probability is insignificant; the radio-bromine atoms which escape reaction, ultimately form inorganic compounds, possibly by reaction with the solvent. Most of the information available on the chemical consequences of nuclear processes in liquid organic halides was obtained by the addition prior to irradiation of varying concentrations of substances (currently called "scavengers") that react readily with organic radicals or atoms. The large drop of the retention[2] observed when small quantities of elementary halogen are present during irradiation, was attributed to its reactions with free radicals and atoms in the diffusion-controlled reactions, and the main product of this stage was found to be the radioactive parent compound.[1d,e] At large concentrations of this scavenger the formation of radioactive organic halides by diffusion dependent reactions becomes negligible and the inactive halogen also reacts with the molecular fragments which might otherwise combine with the active atom in the initial "hot" stage. The organic halides formed in the vicinity of the recoil were found[1d,e] to be the result of the disruption of the solvent molecules by the energetic atom, and of the displacement of the halogen from the parent molecule. Hamill, *et al.*,[3a,b] have found that 1,2-dibromoethylene exchanges quickly with bromine atoms but not with bromine molecules; consequently this substance was used as scavenger of bromine atoms.[1a,c,d] The addition of 10^{-5} molar fraction of this olefin,[1d] brought an appreciable increase in retention due to its exchange with the radiobromine atoms that have escaped recombination or reaction with radicals and diffuse away from the site of neutron capture.

The information available about (n,γ) and (n, 2n) reactions in solid organic halides is of a more conflicting nature. The organic yields were found to be greater than in liquids for certain substances, *e.g.*, normal and isopropyl iodide and bromide, ethyl chloride and bromide[4] and unchanged or smaller in others, *e.g.*, secondary butyl iodide, ethyl iodide.[1b] In the cases of increased retention in solid phase, a negligible increase was found in the yield of the parent compound, as compared to the enhanced yield of new organic species. *A priori*, it might be expected that the increased retention observed in some of the solid organic halides would be due to more effective "caging" favoring the formation of substances produced by high energy processes. However, the possibility that diffusion plays an important part cannot be excluded. The literature gives now evidence for diffusion occurring in solid media; in our particular case the energy available is even sufficient to cause local melting.[5] This paper describes an attempt using the scavenger techniques previously applied to liquids, to investigate the extent to which diffusion controlled reactions contribute to the total retention in solid ethyl bromide.

Experimental

Purification of Reagents.—The ethyl bromide (chemically pure Touzart et Matignon) was stored in daylight with elementary bromine to saturate olefinic impurities. After removal of the free bromine by extraction with a dilute solution of sodium sulfite, the ethyl bromide was separated and dried over calcium chloride; it was then twice distilled in a column (50 cm., 1.5 cm. diameter) packed with glass helices, the middle 50% being retained.

The bromine (p.a. Merck) was dried with phosphorus pentoxide and filtered in a dry box.

The 1,2-dibromoethylene (B.D.H.) was used as such, after it was proved that it did not react with elementary bromine in the dark.

Freezing Technique.—Twenty-five or 50 cc. of either 1,2-dibromoethylene–ethyl bromide or bromine–ethyl bromide mixtures to be irradiated, were contained in a narrow necked glass vessel, into which a quartz tube was fitted. Two methods of freezing were tried. In the first, liquid nitrogen was poured into the central quartz tube, and complete freezing occurred in about one hour; using the second method, the freezing time was reduced to 5 minutes by also immersing the vessel in liquid nitrogen. X-Ray photographs were taken of a crystalline mixture containing 10^{-1} molar fraction of bromine, using the Laue back-reflection method. They showed that slow freezing leads to the formation of big single crystals of ethyl bromide, while the second method yields very small crystals.

Neutron Irradiation.—A 1.5 curie polonium–beryllium source was lowered into the central quartz tube and the specimen irradiated for 30 minutes; only Br^{80} (half-life 18 min.) was studied. During irradiation the samples were kept in a non-silvered blackened Dewar filled with liquid nitrogen and surrounded by paraffin wax.

Determination of Organic Yields.—After irradiation the samples were allowed to melt and a trace of bromine was added in the case of the pure substance (irradiated without bromine scavenger) and the 1,2-dibromoethylene–ethyl bromide mixtures, to avoid losses on the walls of the vessel. In the latter case, the preparation, freezing and irradiation of the samples were made in a dark room.

In all experiments the retention was determined from the ratio of the activity of the organic media (after reducing extraction with dilute sodium sulfite solution, separating and drying over calcium chloride) to the total activity.

Analysis of the Organic Activity.—The fractionation of the organic phase was done in a distillation column (20 cm. high, 1.5 cm. diameter) packed with glass helices. Because of the short life of the isotope studied, only a middle cut fraction of the parent compound was collected, other radioactive organic halides being first distilled or held back by the prior addition of suitable carriers.

Counts were taken with an immersion type Geiger counter (20th Century Electronics GM6). All chemical processing and measurements were made in less than 30 minutes after irradiation, to avoid cumbersome corrections for the activity due to any Br^{80*} (4.4 hours half-life) present.

Results

Influence of the Crystalline Structure and Irradiation Temperature.—The crystalline structure has an interesting influence on the results obtained. It was found that to get a reproducible

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(2) The retention is defined as the fraction of the total activity present in organic combination.

(3) (a) W. H. Hamill, R. R. Williams and H. A. Schwartz, This Journal, **72**, 2813 (1950); (b) R. R. Williams, W. H. Hamill, H. A. Schwartz and E. J. Burrell, *ibid.*, **74**, 5737 (1952).

(4) (a) M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952); (b) R. H. Schuler and C. E. McCauley, This Journal, **79**, 821 (1957); (c) J. C. W. Chien and J. E. Willard, *ibid.*, **75**, 616 (1953); (d) M. Milman, *ibid.*, **79**, 5581 (1957).

(5) If the latent heat of fusion is considered to be about 50 cal./g. and the available energy of 50 e.v. this would allow the melting of about 200 molecules of ethyl bromide (cooling effects being neglected).

scavenger effect in solid ethyl bromide, the quick freezing method must be used; in this way the bromine molecules are trapped between extremely small crystals of ethyl bromide, their distribution in the mixture being similar to that in the liquid state. The slow freezing of the mixtures did not influence the organic retention in pure ethyl bromide, but no scavenger effect could be observed (see Table I); this is probably due to the isolation of the bromine molecules between big crystalline masses of ethyl bromide, their surfaces of contact being greatly reduced.[6]

TABLE I

Mole fraction of bromine	Freezing time	Retention, %
0	1 hr.	84.0 ± 2.6
0	5 min.	83.2 ± 2.6
5.7×10^{-2}	1 hr.	79.0 ± 2.3
5.7×10^{-2}	5 min.	69.5 ± 2.2

To test the stability of the quickly frozen crystalline ethyl bromide–bromine mixture, it was kept at −196° for 8 hours and then irradiated for 30 minutes. No change in retention was found, as would be expected if there was a migration of the bromine molecule in the lattice.

The effect of the temperature change of the solid mixture was examined by irradiating two samples containing, respectively, zero and 1×10^{-2} molar fraction of inactive bromine at −123°, using a butyl chloride slurry as cooling agent. The results showed no difference from those obtained at −196°.

The Scavenger Effect of Inactive Bromine.—The retentions observed for different solid mixtures of ethyl bromide and inactive bromine are given in Fig. 1, where the organic yield is plotted against the logarithm of the molar fraction of added bromine. The reproducibility of the results was tested at several points on the curve, and no variation bigger than the limit of the statistical error (±2% to ±3%) was found, although the freezing time varied from two to five minutes.

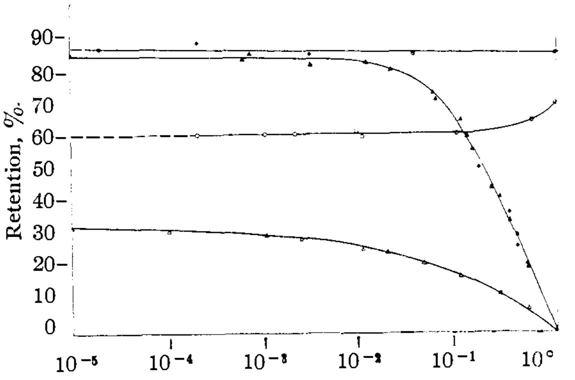

Fig. 1.—△, liquid mixtures of ethyl bromide–bromine; ▲, solid mixtures of ethyl bromide–bromine; ○, liquid mixtures of ethyl bromide–1,2-dibromoethylene; ●, solid mixtures of ethyl bromide–1,2-dibromoethylene.

The results of the separation of the active parent compound are given in Table II. A comparison is made of the activity as ethyl bromide in the liquid and solid state, at zero and 4×10^{-1} molar fraction of inactive bromine.

TABLE II[a]

	Solid ethyl bromide		Liquid ethyl bromide	
	No bromine present	4×10^{-1} M.F. of bromine	No bromine present	4×10^{-1} M.F. of bromine
Retention, %	84.0	29.6	31.5	9.0
Ethyl bromide, %	45.5	11.6	22.6	3.6
Other products, %	38.5	18.0	8.9	5.4
Ethyl bromide(h), %	25.7	12.0	5.8	3.6
Ethyl bromide(d), %	19.8	−1	16.8	0
% of retention as ethyl bromide(d)	23.5	...	53.5	...

[a] Ethyl bromide(h) = ethyl bromide produced by hot reactions; ethyl bromide (d) = ethyl bromide produced by diffusion controlled reactions.

Effect of 1,2-Dibromoethylene.—The experimental results are shown in Fig. 1 and indicate that the organic yield is independent of 1,2-dibromoethylene concentration the curve extrapolating smoothly to the retention of pure 1,2-dibromoethylene.

Discussion

A nuclear transformation imparts to an atom a recoil energy large compared to bond energies; from the order of magnitude involved, it can be inferred that primary acts are temperature independent. If the atom becomes thermalized before reacting, its fate in the "diffusive region" might well depend on the activation energies of the possible reactions and on the irradiation temperature. The evidence obtained in this work confirms earlier data published by Libby, *et al.*,[4a] as no changes were found between retentions at two different temperatures of the irradiated solid. The temperature independence could be explained if (a) diffusion controlled reactions do not occur; alternatively, if they do take place, it implies either that (b) this type of reactions have extremely small activation energies, as at such low temperatures quite important changes in rate constants should be expected[7] or that (c) the diffusion dependent reactions take place between "frozen in" radicals and atoms while the system is melted prior to extraction. A study of the results obtained using the scavenger techniques, allows, to a certain extent, a choice between the three alternatives described.

The addition to ethyl bromide of 1,2-dibromoethylene brings no increase of the organic yield in the case of the solid ethyl bromide. This lack of scavenger effect seems to eliminate the possibility of survival in the crystalline mixture of radioactive bromine atoms during and after the diffusion controlled region; it must also be taken into account that as the pure solid 1,2-dibromoethylene was found to have the same retention as the solid ethyl bromide, no marked scavenger effect could be expected. From the evidence now available it is not clear whether the existence of trapped organic radicals can be denied altogether; Maddock[8]

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[6] Consequently, all results given in Table II and Fig. 1 were obtained using the quick freezing method.

[7] *E.g.*, a reaction with an activation energy of 500 cal./g. mole is 5 times more probable at −123° than at −196°.

[8] M. M. de Maine, A. G. Maddock and K. Taugbol, *Faraday Soc. Discussions*, **23**, 211 (1957).

found recombination reactions taking place after irradiation of the solid hexabromoethane; Libby[4a] dissolved the solid propyl bromide in ethylene at $-126°$, and Milman[4d] melted the solid ethyl bromide in the presence of a bromine solution, without finding any change in retention. The above observations on the survival of organic radicals in solid media are still in need of a correlating explanation.

The scavenging effect of inactive bromine is less sharp in the solid than in the liquid phase (Fig. 1). In fact no detectable change in retention occurs up to a molar fraction of 10^{-2}. If the bromine molecules are homogeneously distributed (the Laue photograph allows this approximation) their concentration is high enough to ensure that mainly the atoms which take part in hot reactions, or have reacted with a radical before diffusing more than a few molecular diameters from the place of neutron capture, could appear in organic form. In the liquid, the retention is decreased by 20% by the addition of 10^{-2} molar fraction of bromine; in the solid system only by 2%. This smallness of the effect indicates the lesser importance of diffusion dependent reactions in the case of the crystalline ethyl bromide.

A confirmation of this hypothesis can be found in the analysis of the results given in Table II, and a comparison with similar work done with liquid ethyl bromide. In the liquid halide it was established that probably the entire yield from diffusion dependent reactions consists of ethyl bromide, the high energy reactions producing new species of active organic substances as well as the mother compound. The amount of ethyl bromide produced by hot and diffusion dependent reactions was established in the case of the pure liquid system at zero bromine concentration, by use of the extrapolation technique described elsewhere.[9] The data also showed that the ratio of the ethyl bromide produced by hot reactions to the amount of other products formed by the same processes is constant whatever the bromine concentration, and equal to approximately 1.5. The retention at a 0.4 molar fraction of bromine was found to be due only to high energy processes and, by analogy, the same assumption was made in the case of the solid system. This assumption was confirmed by the application of the proportionality factor 1.5 (defined above) which was then used in the deduction of the amount of ethyl bromide formed by hot processes from the experimentally found percentage of new products obtained in neutron irradiated solid ethyl bromide (data to be found in the first column of Table II). Although this constant factor was found empirically, it seems reasonable to assume—at a first approximation—that the hot reactions produce ethyl bromide and other new products in constant relative proportions, whatever the phase or bromine concentration. The amount of ethyl bromide produced by diffusion controlled reactions (ethyl bromide(d)) was found by subtraction of "ethyl bromide(h)" from the total yield of the active parent compound. It appears from Table II that while in the pure liquid ethyl bromide more than half the total retention is due to diffusion controlled reactions, in the solid 76.5% of the retention is due to high energy processes, and only 23.5% to diffusion dependent reactions.

The experiments therefore confirm the enhancement of the yield of new organic species in solid ethyl bromide; the result was to be expected if inelastic collisions are important in the high energy region, since such processes would be favored by the greater rigidity of the cage walls. However, it is also possible that other factors (density, temperature and orientation), not yet properly understood, may lead to similar effects. Diffusion controlled reactions also occur, but their relative importance is greatly reduced in the solid and the field of the reactions taking place after neutron capture appears to be restricted to isolated regions that are only reached by high concentrations of bromine scavenger

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[9] The linear form—at high bromine concentrations—of the curve representing the retention function of scavenger concentration in liquid ethyl bromide[1d] has allowed the following interpretation of the data: (a) the retention at high bromine concentration is due to hot reactions, since the probability of a recoiling atom forming organic bromides at this stage should be directly proportional to the concentration of radicals in the vicinity of the recoil track, *i.e.*, to the concentration of ethyl bromide molecules, (the latter being proportional to (1 − molar fraction of bromine present)). Consequently, the retention due to high energy processes at zero bromine concentration (R. hot) was found by extrapolating the linear part of the curve. (b) On the above interpretation, the ratio of "R. hot" at zero bromine concentration to that found at high bromine concentration is the same as the corresponding ratio for those products the formation of which is by high energy processes. It was thus found that all the new organic species are formed by hot reactions, the diffusion controlled reactions producing mainly the parent compound.