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Isomer, Neutron Energy, and Radiation Dosage Effects
on Reactions Activated by Radiative Neutron
Capture in Organic Bromides

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Capron and co-workers¹ have shown recently that the $\text{Br}^{79} (n, \gamma)$

(1) P. C. Capron and E. Crevecoeur, J. Chem. Phys., 21, 1843 (1953).

Br^{80m} (4.4 hr.) process gives higher organic yields² in propyl bro-

(2) The "organic yield" is the fraction of the (n, γ) events which lead to organically bound radiobromine.

mides, bromobenzene³ and bromoform⁴ than the $\text{Br}^{79} (n, \gamma) \text{Br}^{80}$ (18 min.)

(3) P. C. Capron and E. Crevecoeur, J. Chim. Phys., 49, 29 (1952).

(4) P. C. Capron and Y. Oshima, J. Chem. Phys., 20, 1403 (1952).

process, when commercial reagents are used without further purification. They have reasoned that impure reagents should give isomer effects similar to pure organic compounds even though the absolute values of the organic yields are different. Fox and Libby⁵ and

(5) M. S. Fox and W. F. Libby, J. Chem. Phys., 20, 487 (1952).

Rowland and Libby⁶ have reported, however, that the organic yields

(6) F. S. Rowland and W. F. Libby, J. Chem. Phys., 21, 1495 (1953).

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for Br^{som} , Br^{so} and Br^{sz} produced by the (n, γ) process in highly purified liquid propyl bromides are identical. They have pointed out that if impurities were present which could react with inorganic bromine (Br_2 or HBr) to return it to organic combination, these might increase the apparent organic yield of the 4.4 hr. isomer relative to that of the 18 min. isomer because of its longer radioactive lifetime in solution⁷. The experiments summarized below were

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- (7) The average age of the 18 min., 4.4 hr. and 36 hr. atoms produced by a 1 hr. neutron irradiation and present at the end of the irradiation is 19.3 min., 29.21 min. and 29.93 min. respectively; the average ages after a 6 hr. bombardment are 25.8 min., 160 min. and 176 min.
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designed to determine whether the reported isomer effects can be obtained reproducibly. Related information on reported neutron energy effects and on the effect of gamma ray dosage on organic yields is also given.

Experimental

Several methods of purification and irradiation similar in type to those reported previously⁸⁻¹³ were used.

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- (8) E. G. Bohlmann and J. E. Willard, J. Am. Chem. Soc., 64, 1342 (1942).
- (9) R. S. H. Chiang, S. Goldhaber and J. E. Willard, J. Am. Chem. Soc., 73, 2271 (1951).
- (10) S. Goldhaber and J. E. Willard, J. Am. Chem. Soc., 74, 318 (1952).
- (11) G. Levey and J. E. Willard, J. Am. Chem. Soc., 74, 6161 (1952).
- (12) J. F. Hornig and J. E. Willard, J. Am. Chem. Soc., 75, 461 (1953).
- (13) J. C. W. Chien and J. E. Willard, J. Am. Chem. Soc., 75, 6160 (1953).
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The organic yield due to the $\text{Br}^{79} (n, \gamma) \text{Br}^{80} (18 \text{ min.})$ process was determined independently of that due to the $\text{Br}^{\text{eom}} (4.4 \text{ hr.}) \rightarrow \text{Br}^{80} (18 \text{ min.})$ isomeric transition process by two methods. In the first, advantage was taken of the fact that, for a 2 min. irradiation, the 18 min. activity produced by the isomeric transition was negligible (ca. 2%) compared to that produced by the (n, γ) process. In the second method the organic yields of both the 18 min. and 4.4 hr. activities present at the end of 180 min. neutron irradiations of the organic bromides were determined with the aid of decay curves taken on the aqueous and organic fractions. Immediately after such an irradiation, the disintegration rate due to the 18 min. isomer formed by the (n, γ) process is about ten times that due to isomeric transition. Hence the observed organic yield of the 18 min. species could not be greatly influenced by the contribution from the isomeric transition process unless the latter gave a distribution widely different from the former. The organic yield of $\text{Br}^{80} (18 \text{ min.})$ due to the isomeric transition of the Br^{eom} in the chemical forms in which it exists in n-propyl bromide which has been irradiated with neutrons for 180 min. was determined by allowing the samples to stand for 180 min. before extraction and then determining the decay curves of the aqueous and inorganic fractions. The initial points showed only slight evidence of a different distribution of the 18 min. activity from the isomeric transition than the 4.4 hr. activity from the (n, γ) process.

Test of Isomer Effect

n-Propyl Bromide. --In eleven determinations of the organic yield of the 18 min. isomer, and nine of the 4.4 hr. isomer, from

the neutron irradiation of purified n-propyl bromide we have obtained yields of $31.7 \pm 0.9\%$ and $32.5 \pm 1.1\%$ respectively. The results are in good agreement with those of Libby and co-workers^{5,6} and indicate that there is no significant isomer effect in pure n-propyl bromide. Other experiments gave identical organic yields for the two isomers at each of a series of bromine concentrations in n-propyl bromide up to 8×10^{-3} mole fraction, proving that the "scavenger"¹⁰⁻¹³ effect is the same for the two species.

In contrast to the above results, experiments in which commercial n-propyl bromide (Eastman white label) was used without further purification always gave a higher organic yield for the longer lived isomer, in agreement with the results of Capron and co-workers^{1,3,4}. Typical values were 45% and 66% for the 18 min. and 4.4 hr. isomers in the absence of added bromine and 38% and 44% when 1×10^{-3} mole fraction of bromine was present during irradiation.

Bromoform. --Purified degassed bromoform irradiated with neutrons in sealed quartz tubes gave organic yields of $65.6 \pm 1.2\%$ (8 detn's) for the 18 min. isomer and $66.1 \pm 1.1\%$ (4 detn's) for the 4.4 hr. isomer. The same yields were obtained with 20 min., 180 min., and 720 min. irradiation times. Purification was accomplished by adding Br_2 , illuminating for eight hours with a 1000 watt lamp, washing with sulfite solution, drying, fractionally distilling under reduced pressure and degassing on a vacuum system.

When Eastman white label bromoform, which contains diphenylamine as stabilizer, was used, either as received or after fractional distillation in a Vigreux column, it gave organic yields of 76% and

94% for the 18 min. and 4.4 hr. isomers. Degassed samples of this impure material gave similar results to those irradiated in the presence of air.

Bromobenzene. --Attempts to obtain reproducibly pure bromobenzene for investigation of isomer effects have not yet been successful. ^{Mr. Robert Chiang and} ~~Mr. James Evans~~ of our laboratory have found that slight variations in a variety of apparently rigorous procedures for the purification of C_6H_5Br yield samples which give organic yields varying from 47% to 88%. This makes it seem probable that the apparent isomer effect obtained from this compound³, like that from the propyl bromides and bromoform, was due to impurities. The "scavenger" effect on this compound is very great; the organic yield with 3 mole % of added Br_2 present is only about 29%. One or more of the organic products of the (n, γ) process on C_6H_5Br in the absence of Br_2 scavenger is slowly hydrolyzable by the aqueous extracting solution, which further complicates the determination of precise organic yields.

Absence of Neutron Energy Effects

It has been suggested by Capron and co-workers that neutron energies³ and neutron intensities¹ may affect the organic yields obtained from the (n, γ) process. Such effects have not been observed by other workers using highly purified samples. We obtain $32 \pm 2\%$ as the organic yield for highly purified n-propyl bromide with samples exposed to Sb-Be photoneutron sources of different intensities, and with samples exposed at different intensities and different degrees of neutron moderation in the CP3¹ nuclear reactor at the Argonne National Laboratory. These values agree with those obtained elsewhere at different fluxes and degrees of moderation

using a cyclotron⁵ as a neutron source and using a Po-Be neutron source⁶. We likewise have found the organic yields from bromoform to be independent of whether a Sb-Be photoneutron source was used or a Ra-Be source with a paraffin moderator duplicating that described by Capron and co-workers. In a variety of other studies on activation by radiative neutron capture⁸⁻¹⁰ we have never observed effects due to neutron energies or neutron intensities.

Apparent Isomer Effect Following High Gamma Dosage

It has been firmly established that wide variations of gamma ray intensity and total gamma dose during neutron irradiation do not alter the organic yields obtained from alkyl halides^{6, 11, 12} if these variables are within the ranges normally prevailing in studies of the chemical effects of the (n, γ) process. This is a very important fact because it indicates¹¹ that the chemical fate of the recoil atom must be determined in or near the spot where it is born and is not affected by radicals generated elsewhere in the solution.

Just as initially impure organic bromides show an apparent isomer effect on organic yields from the (n, γ) process, it might be expected that sufficiently prolonged radiolysis of some compounds would produce impurities with which the Br_2 and/or HBr ~~originally~~ formed by the Szilard Chalmers ^{process could} react to give fictitiously high organic yields. We have found that the minimum gamma ray dosage required to show the effect for the 4.4 hr. species in air-free n-propyl bromide is about 20,000 roentgens¹⁴. Purified degassed

(14) We have investigated this "secondary radiation effect" on the organic yields of the three bromine nuclides and expect to report the detailed results later.

n-propyl bromide which gave organic yields of 33.7% and 32.6%^(single det'ns) for the 18 min. and 4.4 hr. isomers after 4 hrs. irradiation with a 5c Sb-Be photoneutron source at a distance of 4 cm. through paraffin gave very little change in the 18 min. yield up to 132 hrs. while the 4.4 hr. yield increased to 45% at 24 hrs., 53% at 40 hrs. and 73% at 132 hrs. Corresponding yields of Br^{82} (36 hr.) determined for 40, 80, and 132 hrs. irradiation were 67, 88, and 90%. A similar sample subjected a gamma irradiation of 3×10^6 r from a ^{60}Co source just prior to a 4 hr. irradiation with the Sb-Be source gave organic yields of 44% and 58% for the 18 min. and 4.4 hr. isomers.

Conclusion

There appears to be no basis for believing that an isomer, isotope, or neutron energy effect is important in determining the organic yields of bromine in pure liquid alkyl bromides, although apparent isomer effects due to the reaction of stabilized products of the (n, γ) process with impurities may be observed easily.

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