TABLE I

UNIT CELL DIMENSIONS OF RARE EARTH OXYFLUORIDES, RHOMBOHEDRAL LaOF STRUCTURE TYPE[a]

	a in Å.	α in deg.	Fluorine, %		Metal, %	
			Found	Theor.	Found	Theor.
LaOF[a]	7.132 ± 0.001	33.01 ± 0.01				
LaOF	7.132 ± .001	32.99 ± .01	10.80	10.93	79.68	79.87
PrOF	7.016 ± .004	33.03 ± .03	10.26	10.80	80.68	80.10
NdOF	6.953 ± .001	33.04 ± .01	10.54	10.60	80.21	80.43
SmOF	6.865 ± .002	33.07 ± .02	10.00	10.25	81.77	81.13
EuOF	6.827 ± .002	33.05 ± .02				
GdOF	6.800 ± .001	33.05 ± .01	9.75	9.90	82.03	81.76
TbOF	6.758 ± .011	33.02 ± .09				
CeOF[b]	6.985 ± .001	33.56	9.59	10.85	80.01	79.00
CeOF	5.703 ± .001	Cubic, face-centered				
CeOF[c]	5.66 ± .01 to 5.73 ± 0.01					

[a] See reference 3. [b] Rhombohedral cell dimensions corresponding to the face-centered cubic cell actually observed. [c] See reference 4.

dimensions of a series of rare earth oxyfluorides were obtained and are listed in Table I together with values previously found by other investigators. All the oxyfluorides examined with the exception of cerium oxyfluoride had the rhombohedral structure found by Zachariasen[3] for lanthanum oxyfluoride. The cubic cell dimensions found for cerium oxyfluoride are within the range of values reported by Finkelnburg and Stein[4] who found that the cell constant of the fluorite type structure varied with the amount of fluorine in the lattice.

The oxyfluorides of lanthanum, praseodymium, neodymium, samarium, europium and gadolinium were made by hydrolysis of the anhydrous fluoride by heating at about 800° in a current of moist air. In the case of praseodymium some higher oxide also was formed. Cerium and praseodymium oxyfluorides were prepared by hydrolysis in a moist ammonia stream at 800°. Hydrolysis in air led to cerium dioxide. Terbium oxyfluoride was formed accidentally as the result of fluorination of Tb_4O_7 followed by hydrolysis in a stream of undried hydrogen.

The cell dimensions were determined from the back reflection lines of films exposed in a Debye-Scherrer type powder camera (rad. = 5.73 cm.) using Cu Kα or Fe Kα radiation. The data were treated using Cohen's[5] analytical extrapolation method. The errors listed are the standard errors from one determination.

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(3) W. H. Zachariasen, *Acta Cryst.*, **4**, 231 (1951).

(4) W. Finkelnburg and A. Stein, *J. Chem. Phys.*, **18**, 1296 (1950).

(5) E. R. Jette and F. Foote, *ibid.*, **3**, 605 (1935).

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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-workers[1] have shown recently that the Br^{79} (n,γ) $\mathrm{Br}^{80\mathrm{m}}$ (4.4 hr.) process gives higher organic yields[2] in propyl bromides, bromobenzene[3] and bromoform[4] than the Br^{79} (n,γ) Br^{80} (18 min.) 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 Libby[5] and Rowland and Libby[6] have reported, however, that the organic yields for $\mathrm{Br}^{80\mathrm{m}}$, Br^{80} and Br^{82} 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 solution.[7] The experiments summarized below were designed to determine whether the reported isomer effects can be obtained reproducibly. Related information on reported neutron energy effects and on the effect of γ-ray dosage on organic yields is also given.

Experimental

Several methods of purification and irradiation similar in type to those reported previously[8-13] were used.

The organic yield due to the Br^{79} $(n,\gamma)\mathrm{Br}^{80}$ (18 min.) process was determined independently of that due to the $\mathrm{Br}^{80\mathrm{m}}$ (4.4 hr.) $\rightarrow$ Br^{80} (18 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

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

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

(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).

(5) M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

(6) F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953).

(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, 29.2 and 29.9 min., respectively; the average ages after a 6 hr. bombardment are 25.8, 160 and 176 min. The usual irradiation time used by Capron and Crevecoeur was three hours. They did one experiment with a one hour irradiation which they felt showed that the isomer effects which they observed could not be due to the different average lifetimes of Br^{80} and $\mathrm{Br}^{80\mathrm{m}}$.

(8) E. G. Bohlman and J. E. Willard, THIS JOURNAL, **64**, 1342 (1942).

(9) R. S. H. Chiang, S. Goldhaber and J. E. Willard, *ibid.*, **73**, 2271 (1951).

(10) S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

(11) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

(12) J. F. Hornig and J. E. Willard, *ibid.*, **75**, 461 (1953).

(13) J. C. W. Chien and J. E. Willard, *ibid.*, **75**, 6160 (1953).

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 Br^{80} (18 min.) due to the isomeric transition of the Br^{80m} 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 which were carried out 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 ± 0.9% and 32.5 ± 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^{-2} 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 ± 1.2% (8 detn.) for the 18 min. isomer and 66.1 ± 1.1% (4 detn.) for the 4.4 hr. isomer. The same yields were obtained with 20, 180 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 results similar 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 compound,[3] 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

Capron and co-workers suggested that neutron energies[3] and neutron intensities[1] 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 ± 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 CP3′ nuclear reactor at the Argonne National Laboratory. These values agree with those obtained elsewhere at different fluxes and degrees of moderation using a cyclotron[5] as a neutron source and using a Po–Be neutron source.[6] 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 capture[8-13] we have never observed effects due to neutron energies or neutron intensities.

Apparent Isomer Effect Following High γ-Dosage

It has been firmly established that wide variations of γ-ray intensity and total γ-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 indicates[11] 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 formed by the Szilard Chalmers process could react to give fictitiously high organic yields. We have found that the minimum γ-ray dosage required to show the effect for the 4.4 hr. species in air-free *n*-propyl bromide is about 20,000 roentgens.[14] Purified degassed *n*-propyl bromide which gave organic yields of 33.7 and 32.6% (single detn.) for the 18 min. and 4.4 hr. isomers after 4 hr. irradiation with a 5 curie Sb–Be photoneutron source at a distance of 4 cm. through paraffin gave very little change in the 18 min. yield up to 132 hr. while the 4.4 hr. yield increased to 45% at 24 hr., 53% at 40 hr. and 73% at 132 hr. Corresponding yields of Br^{82} (36 hr.) determined for 40, 80 and 132 hr. irradiation were 67, 88 and 90. A similar sample subjected a γ-irradiation of 3×10^6 r. from a 40 curie Co^{60} 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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[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.

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Heats of Reaction of Sodium and Potassium with Water and the Standard Heats of Formation of Aqueous Sodium and Potassium Hydroxides at 25°

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The standard heats of formation of aqueous sodium and potassium hydroxides are of considerable thermochemical significance since they are employed in establishing much of the thermochemical data for other sodium and potassium com-