Chemistry of ^{82g}Br Recoils in Neutron-Irradiated Crystalline Alkali Metal Bromates[1]

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Abstract: The analysis of neutron-irradiated crystalline alkali metal bromates by anion-exchange chromatography showed that the ^{82g}Br recoils produced in the crystals were distributed in varying amounts among four oxidation states of the element: BrO_3^-, BrO_2^-, BrO^-, and Br^-. The species BrO^- and BrO_2^- were labile and disappeared on heating the irradiated crystals. A nearly complete recombination of all radiobromine to bromate was effected by heating neutron-bombarded $LiBrO_3$, $KBrO_3$, and $CsBrO_3$ for 1 hr at temperatures approaching their melting points. Irradiation with ^{60}Co γ rays also induced the recombination to bromate, and significant differences in annealing rates depending on the cation in the salt were observed. The transfer to bromate by heating of radiobromide added to pure alkali metal bromate crystals was demonstrated. Neutron irradiations of mixed crystals of $NaBrO_3$ + $NaClO_3$ showed that the fraction of ^{82g}Br combined as bromate doubled on going from pure $NaBrO_3$ crystals to a 1% by weight solid solution of $NaBrO_3$–$NaClO_3$. A model based on the production of radiobromine recoils in small, isolated regions of localized disorder in the crystal was employed in a discussion of the kinetics of their thermal and radiation annealing to form radiobromate.

The alkali metal and alkaline earth bromates among all crystalline inorganic salts are perhaps the most studied as regards the chemical consequences of nuclear transformations caused to occur within them. In the earliest work[2–4] on the effects of slow neutron capture it was observed, when the irradiated crystals were analyzed, that more than three-fourths of the recoil radiobromine produced appeared as bromide ion but that a minor fraction of the bromine activity was always "retained" in the bromate ion. Subsequent researches have demonstrated that the fraction of activity occurring as bromate ion may be increased by solid-state reactions induced by heat[5–8] and energetic ionizing radiations.[5,7] Thermal and radiation annealing effects are inevitably present during neutron irradiations, particularly in nuclear reactors, so that the primary or initial distribution of recoil activity between bromide, bromate, and the other bromine oxidation states is probably never observed.

The only radiobromine valence states positively identified are bromide and bromate. It has been suggested[6] that radiohypobromite may be formed in crystalline $LiBrO_3$, but this was not confirmed by later work[8] with this compound. The production of radiobromite, or fragments which give BrO_2^- ion on dissolving irradiated $KBrO_3$, has been postulated,[9] but no experimental identification of this species has been reported. However, micro amounts of hypobromite, bromite, and bromide together with oxygen gas have been observed in the radiolysis of the crystalline alkali metal bromates by ^{60}Co γ rays,[10] by neutron reactor irradiations,[11] and by ^{6}Li fission recoil particles.[12,13] Neutral bromine was not detected except in salt irradiated to *ca.* 10% bromate decomposition where Br_2 may have been formed by the reaction of BrO^- with Br^- ions in the presence of water. The formation of Br^-, BrO^-, and BrO_2^-, but not Br_2, in crystalline $KBrO_3$ irradiated at $-78°$ with 10-Mev electrons has also been reported recently.[14]

Several new valence states of the radiobromine recoils produced by neutron capture in the crystalline alkali metal bromates were identified in this research. Crystalline $LiBrO_3$ was employed in many of the experiments because it is stable toward thermal decomposition up to and above its melting point. The isotopic lithium compound, $^7LiBrO_3$, moreover shows the least radiolysis of all the alkali metal bromates when exposed to nuclear reactor radiations, and radiobromine is the only long-lived activity produced by thermal neutrons. Experiments also were conducted with crystalline $NaBrO_3$, $KBrO_3$, $CsBrO_3$, and $AgBrO_3$. A rapid and efficient anion-exchange column analysis method for determining the relative yields of radiobromine in the various bromine oxidation states was developed. Measurements were made of the changes in these yields caused by thermal and radiation annealing reactions induced in the irradiated crystals by heat and ^{60}Co γ rays.

All measurements were conducted with 35.3-hr ^{82g}Br, which was formed to greater than 99.9% by the decay of 6.1-min ^{82m}Br generated in short irradiations. The 6.1-min ^{82m}Br isomer[15] is produced with a relatively large reactor neutron capture cross section and decays primarily (*i.e.*, 97.6%) by a highly internally converted 46-kev level ($\alpha_K = 268$) to ^{82g}Br. All experiments were performed after a time sufficient (*i.e.*, 48 hr) for complete decay of the 4.4-hr ^{80m}Br and its 18-min ^{80g}Br daughter also produced in the bombardments.

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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Experimental Section

Materials. The preparation and analysis of anhydrous crystals of $LiBrO_3$ and $^7LiBrO_3$ have been described elsewhere.[12] The purified, crystalline $NaBrO_3$, $KBrO_3$, and $CsBrO_3$ preparations from earlier studies[11] were used.

Neutron Irradiations. Neutron bombardments were carried out at different times in three reactors possessing differing thermal and fast neutron fluxes and differing reactor γ-ray intensities. Most of the irradiations were conducted at the terminus of the pneumatic transfer tube of the low-intensity test reactor (LITR), a heterogeneous, light water-moderated, aluminum–uranium alloy fueled tank-in-pool facility, where the thermal flux, ϕ_{th}, determined with dilute (0.15 atom %) Co–Al alloy monitors, was 1.5×10^{13} cm^{-2} sec^{-1}. The radiolysis rate at the same position measured with $^7LiBrO_3$ was $4.2_1 \times 10^{-3}$ mole of BrO_3^- decomposed per mole of $^7LiBrO_3$ per hour. Other bombardments were performed in hole 71 of the Oak Ridge graphite reactor (ORGR) where the thermal flux was 7.4×10^{11} cm^{-2} sec^{-1}. A description of this facility has been given;[11] the radiolysis rate measured with $^7LiBrO_3$ was much lower (*i.e.*, $0.11_6 \times 10^{-3}$ mole mole^{-1} hr^{-1}) than in the LITR.[16]

Irradiations in a highly thermalized neutron flux freed from reactor γ rays were conducted in a special facility in the bulk shielding reactor (BSR), a pool-type heterogeneous, light water-moderated reactor. This facility[17] consisted of a massive bismuth metal block positioned at the center of a large aluminum tank filled with D_2O. Small samples were placed at the center of the bismuth block where γ radiation from the reactor is reduced to very low levels. The entire assembly was movable and could be located adjacent to the active lattice of the reactor for neutron irradiations. The neutron flux at the center of the Bi block when the reactor operated at 1 mw was $4.8_8 \times 10^{11}$ cm^{-2} sec^{-1}. The γ-ray dose rate has been reported[17] as 1.4×10^5 roentgens per hour, but this was shown to be caused by neutron capture in the wall of the 2.81-in. i.d. aluminum tube liner extending to the center of the block. Our samples, which were placed in a cylindrical bismuth shield, which fitted inside the aluminum tube, showed a much reduced radiation level; thus, the radiolysis rate measured with $KBrO_3$ was 0.11×10^{-3} mole mole^{-1} hr^{-1}, which is essentially the self-radiolysis rate caused by thermal neutron capture in the sample itself (*i.e.*, *via* capture γ rays and radioactive decay radiations).

The neutron-irradiated samples were stored in CO_2–ice. Several bombardments were made at liquid nitrogen and at Dry Ice temperatures with quartz dewars in the BSR neutron thermalizer. In the former instance, the samples were stored in liquid nitrogen.

Yield and Retention Determinations. The distribution of the 35.3-hr ^{82g}Br in the neutron-irradiated crystalline bromates among the bromine valence states was determined by analyses of aqueous solutions of the crystals at room temperature. The compounds were dissolved in pure water in the initial experiments in which the yield of activity combined as bromate (*i.e.*, the "retention") was measured with the bromine extraction technique.[5,7,9] However, because of the instability of Br(I) and Br(III) in neutral solutions[18] and the possibility of an isotopic exchange reaction between Br^- and BrO_3^- ions, in most of the experiments the crystals were dissolved either in 0.1 *N* $NaHCO_3$ or 0.1 *N* NaOH solutions. In alkaline solution, however, a rapid and complete exchange reaction between Br^- and BrO^- ions was observed when a small quantity of Br_2(l) was added to the solution, as might be expected from the equilibrium

$$Br_2 + 2OH^- \rightleftharpoons BrO^- + Br^- + H_2O \qquad (A)$$

Because of this complication "carrier" bromide plus hypobromite ions were not added to the aqueous solutions in which the irradiated alkali metal bromates were dissolved.[19]

A suitable technique for separating the anionic radiobromine species present in alkaline solutions is by ion-exchange chromatography with a strong-base-type anion exchanger. This method was applied previously[20] to the separation of radiobromate from radiobromide ions by differential elution with aqueous 0.5 and 2 *M* KNO_3 solutions. No bromine-containing anions other than BrO_3^- and Br^- were observed, however. In our investigations, a cylindrical bed of 100–200 mesh Dowex-1, 9-mm diameter by 15–18 cm deep, initially in the bicarbonate salt form, was employed. Neutron-irradiated bromate (50–100 mg) was dissolved in 0.1 *M* $KHCO_3$ solution, which was made accurately to 25 ml volume. A 5-ml aliquot of this solution was placed on the top of the bed where all the bromine activity was absorbed. A selective elution of the radiobromine-containing anions was accomplished by pumping 0.5 *M* $KHCO_3$, 1.0 *M* $KHCO_3$, and 1.0 *M* KNO_3 solutions successively through the bed at *ca.* 10–15 ml min^{-1}. The effluent solutions passed through a thin-walled quartz glass coil wound about a halogen quenched G.M. counter whose response to the radioactivity in the liquid was measured with a logarithmic count-rate meter and recorded continuously on a Brown recorder. A concentration history (*i.e.*, radiochromatogram) of the activity in a typical separation is shown in Figure 1. The γ rays emitted by aliquots taken from effluent fractions containing the peaks shown were measured with a 3 × 3 (Na + Tl)I crystal connected with a 400-channel analyzer. The γ-ray spectra showed that only ^{82g}Br was present. The chemical identity of the last peak to emerge from the column was demonstrated to be bromide ion by separation performed with aqueous solutions of neutron-irradiated LiBr. The first peak was assigned to BrO_2^- ion based on the fact that it could be eliminated when the starting solution was treated with dilute $NaAsO_2$ solution containing OsO_4 as a catalyst for the reduction to bromide (*cf.* Figures 1A and 1B). A small fraction of the radiobromine (*ca.* 5–10%) was strongly absorbed at the top of the bed and could not be eluted, presumably because of a chemical reaction with the organic ion exchanger. Radiohypobromite was demonstrated to be the species responsible for this behavior; a pretreatment of the alkaline solution of irradiated bromate with AsO_2^- which coverts BrO^- to Br^- ion acted to lower the irreversibly bound activity to negligibly small levels.

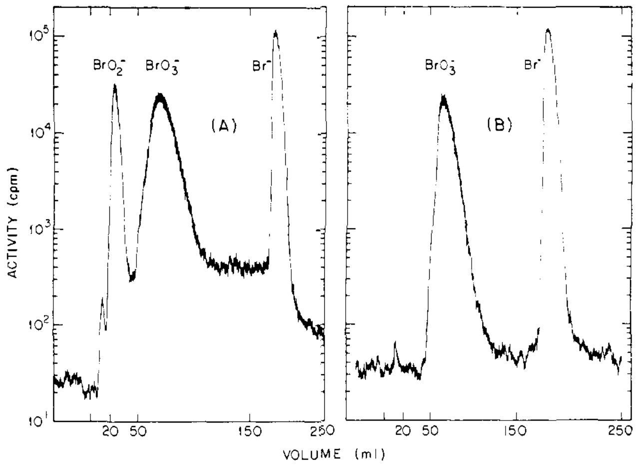

Figure 1. Anion-exchange chromatographic separations of radiobromine activity in neutron-irradiated $LiBrO_3$: (A) irradiated crystals dissolved in 0.1 *M* $KHCO_3$; (B) irradiated crystals dissolved in 0.1 *M* $KHCO_3$ containing AsO_2^- + OsO_4.

Highly efficient separations of BrO_2^-, BrO_3^-, Br^-, and BrO^- ions from one another were accomplished, and a quantitative recovery and assay of the ^{82g}Br in each of the foregoing valence states was realized. As little as 0.1% of the activity present as BrO_2^-, BrO_3^-, or Br^- ion could be detected and measured. The sum of all the bromine activity from the column fractions agreed to within 1% with the activity in an unprocessed 5-ml aliquot of the starting solution. The yield values reported below were determined with this method, and an activity balance check was always obtained.

Thermal-Annealing Experiments. The irradiated crystals were heated for varying times at constant temperature (*i.e.*, isothermal annealing) and at various temperatures for a constant-time interval (isochronal annealing) to determine if the initial yields of ^{82g}Br among the bromine valence forms could be altered. An electric tube furnace controlled to ±2° was used. The crystals were heated in air in a porcelain boat placed at the center of the furnace inside a

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(16) Assuming $G(-BrO_3^-) = 0.47$ (ref 11), a decomposition rate of 1×10^{-3} mole mole^{-1} hr^{-1} corresponds to a dose rate of 1.6×10^{19} ev g^{-1} min^{-1}.

(17) B. C. Kelley and C. E. Klabunde, "International Symposium on Developments in Irradiation Capsule Technology," USAEC Conference-660511, May 3–5, 1966, Paper 8.7.1.

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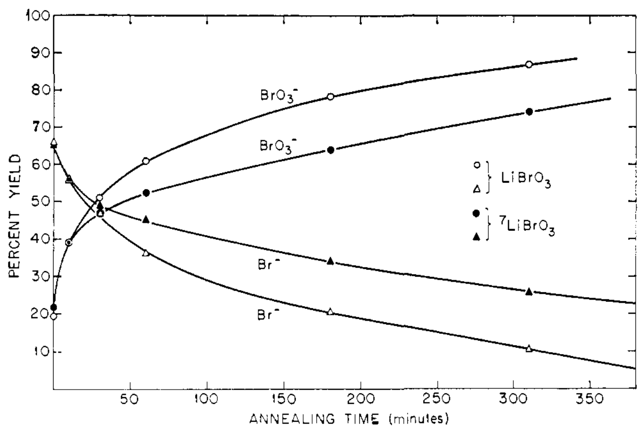

Figure 2. Changes in radiobromide and bromate ion yields caused by heating neutron-irradiated $^7LiBrO_3$ at 200°.

quartz tube. The temperature was measured to ±1° with a thermocouple. At the end of the anneal, the crystals were cooled abruptly and stored in CO_2–ice until analysis.

Radiation-Annealing Experiments. The effect of energetic ionizing radiations on the relative yields of radiobromine in its various valence forms was investigated. The crystals were irradiated at *ca.* 105° with Co γ rays in a previously described source arrangement.[10] Irradiations also were conducted at −78, 0, and 32.8° with CO_2–ice + acetone, ice–water, and $Na_2SO_4 \cdot 10H_2O$ mixtures held in dewars. The doses absorbed by the samples were computed from measurements of the decomposition of $KBrO_3$ monitors with $G(-BrO_3^-)$ = 1.3 molecules/100 ev. The γ-ray annealed samples were stored at −78°.

Results

The Chemical Identity of Recoil Radiobromine. The data (Figure 1 and Table I) reveal that small fractions of recoil radiobromine produced by neutron capture in crystalline alkali metal bromates may occur in valence states other than bromate and bromide. In $LiBrO_3$ which contained the naturally occurring abundance of ^6Li, for example, as much as 13% of the ^{82g}Br was combined as radiobromite plus radiohypobromite. The amount of radiobromine in these latter species varied depending on the nature of the cation. With $AgBrO_3$ and $KBrO_3$ 1% or less of the activity appeared in BrO_2^- + BrO^-. Interestingly, the fraction of ^{82g}Br retained as BrO_3^- was nearly independent of the cation in the alkali metal bromate.

Table I. Dependence of Yields on Nature of Cation[a]

Salt	$R(BrO_3^-)$	$R(BrO_2^-)$	$R(BrO^-)$	$R(Br^-)$
$LiBrO_3$	23.0 ± 0.5	9.6 ± 1.3	3.5 ± 1.3	63.2 ± 1.0
$^7LiBrO_3$	23.5 ± 0.6	5.3 ± 1.3	3.7 ± 1.0	66.9 ± 0.5
$NaBrO_3$	23.8	3.5	0.5	69.8
$KBrO_3$	24.5	1.0	...	...
$CsBrO_3$	24.7	3.7	...	...
$AgBrO_3$	26.0	0.7	0.2	71.2

[a] 5 *m* LITR irradiations at 35°.

The variability of the yields of radiobromite and hypobromite ions may be explained by the fact that these species, or their precursors in the crystals, are unstable and slowly decompose thermally. The existence of a thermally activated reaction which altered the concentration of ^{82g}Br-labeled BrO_2^- and BrO_3^- in irradiated $^7LiBrO_3$ is suggested by the data of Table II.

Table II. Dependence of Yields on Storage for 1.0 Hr at Various Temperatures after Irradiation of $^7LiBrO_3$ at −195° for 1.0 Hr[a]

Storage temp, °C	$R(BrO_3^-)$	$R(BrO_2^-)$	$R(Br^-)$
−195	15.1	5.6	...
−78	15.1	5.7	...
0.0	17.1	3.8	75.0
25	19.4	3.3	...

[a] BSR, D_2O + Bi facility.

At and below the temperature of a CO_2-ice plus acetone bath (−78°) there was no change in the yields of BrO_3^- or BrO_2^-. However, the yield of bromite decreased to 3.3% and that of bromate increased to 19.4% on removing the crystals from liquid nitrogen and allowing them to stand in air for 1 hr at room temperature. Numerous observations have shown that the yield of radiobromite plus hypobromite may be reduced virtually to zero by heating the irradiated crystals at temperatures approaching their melting points. Thus, with $LiBrO_3$ irradiated in the LITR for 1 hr, the yield of BrO_2^- + BrO^- at 25° was 13.3%; on heating the crystals for 1 hr at 99, 200, and 252° the yields were 8.9, 4.1, and 0.1%, respectively.

Thermal-Annealing Processes. Solid-state reactions involving bromide ion also occurred on heating neutron-irradiated $^7LiBrO_3$ and $LiBrO_3$ at elevated temperatures (Figure 2). It has been demonstrated[5–7] that the yield of radiobromate, $R(BrO_3^-)$, increased with time on heating the alkali metal and alkaline earth bromates at constant temperature, and that the value of $R(BrO_3^-)$ itself after long times increased with temperature. Results from this research show further that the increase in $R(BrO_3^-)$ is related directly to the decrease in the yield of radiobromide, $R(Br^-)$. The rate of oxidative annealing of bromide ion appears to be enhanced by radiation damage produced in the crystal during neutron bombardment. Crystals of $LiBrO_3$, for example, are subject to appreciable radiolysis during neutron irradiation because of energetic ionizing tritons and α particles produced by the fission of ^6Li in the compound. It is of interest to note in Figure 2 that almost 90% of the radiobromide in the $LiBrO_3$ was oxidized to radiobromate after heating for 6 hr at 200°. Although it is not shown in Figure 2, the yields of radiobromite, $R(BrO_2^-)$, decreased from 8.5 to 1.4% after 10 min at 200° and then slowly to 0.4% after 6 hr. At the same time the yield of radiohypobromite in $LiBrO_3$ decreased from 3.5 to 1.3% and then slowly to 0.2%. The apparent persistence of thermally quite unstable bromite and hypobromite for many hours at 200° is of interest.

Isochronal annealing experiments (Figure 3) revealed that recoil radiobromine in $^7LiBrO_3$ may be recombined quantitatively into bromate by heating the irradiated crystals for 1 hr at their melting point (254°). Increases in $R(BrO_3^-)$ also occurred on heating $KBrO_3$ and $CsBrO_3$. These compounds, however, began to decompose at temperatures below their melting points of 396 and 420°, respectively, causing the yield of radiobromate to decrease and that of bromide to increase. The curves in Figure 3 suggest an apparent threshold in the annealing reaction at *ca.* 110°, which is significantly higher than the ambient temperature during the neutron irradiation. The possibility that this difference may have been caused by radiation annealing during the neutron bombardment appears to be ruled out by the similarity in the results with $^{7}LiBrO_3$ irradiated in the LITR and in the neutron thermalizer in the BSR. Although at a given temperature $CsBrO_3$ and $KBrO_3$ appear to anneal to a lesser extent than $^{7}LiBrO_3$, actually this may be shown not to be the case when the reduced temperature, T/T_m, where T_m is the melting temperature in °K, is used. A plot of the fraction annealed *vs.* T/T_m revealed that the relative ease of annealing was $CsBrO_3 > KBrO_3 > {}^{7}LiBrO_3$. Detectable amounts of radiobromite were found to remain in the crystals up to temperatures of nearly 300°.

Thermal-Transfer Annealing. A conversion of radiobromide to bromate ion may be induced by heating $LiBrO_3$ or $KBrO_3$ crystals doped[21] with small amounts of LiBr or KBr (see Table III). No radiobromite or hypobromite was formed, however. This type of reaction, which has been termed "transfer annealing," did not proceed to the same extent nor as rapidly as the thermal-annealing reaction in neutron-irradiated bromates, although in many respects it was similar. In the "transfer anneal," of course, the reaction occurs in an undamaged lattice which differs from the case when the crystal has been irradiated; and, as noted above (*cf.* Figure 2), radiation damage to the crystal appears to facilitate the reaction leading to the reconstitution of bromate ion. Transfer-annealing reactions have been observed with radioiodide ion in crystalline $Ca(IO_3)_2$[22] and with radiochromic ion in K_2CrO_4.[23] However, studies with radiochloride ion in molten $NaClO_3$ have indicated that an exchange of ^{38}Cl between Cl^- and ClO_3^- ions does not occur to an appreciable extent.[24]

Table III. Thermal-Transfer Annealing of Radiobromine in Bromide-Doped Crystals[a]

Temp, °C	$R(BrO_3^-)$	System
200	34.4	$^{7}LiBr^* + {}^{7}LiBrO_3$
238[b]	80.1	$^{7}LiBr^* + {}^{7}LiBrO_3$
235	80.7	$LiBr^* + LiBrO_3$
150	0.0	$KBr^* + {}^{7}LiBrO_3$
204	9.1	$KBr^* + {}^{7}LiBrO_3$
237	81.3	$KBr^* + {}^{7}LiBrO_3$
250	0.0	$KBr^* + KBrO_3$
400	1.3	$KBr^* + KBrO_3$
425[b]	72.5[c]	$KBr^* + KBrO_3$

[a] Annealing period = 1 hr. [b] Melted. [c] Heated 7 min.

Radiation-Annealing Processes. Exposure of neutron-irradiated bromates to energetic ionizing radiations has been found[5,7] also to induce the transfer of recoil radiobromine to bromate. The ionizing radiations are effective either during the neutron bombardment or afterward. Results from a study of the changes of the distribution of radiobromine during bombardment of $^{7}LiBrO_3$ are summarized in Table IV.

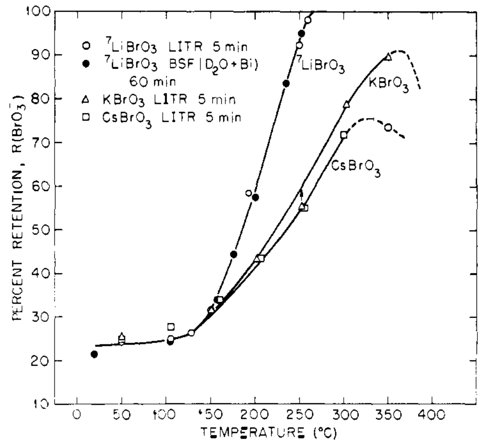

Figure 3. Increase in radiobromate yields (*i.e.*, "retention") caused by heating neutron-irradiated alkali metal bromates for 1 hr at various temperatures.

Table IV. Dependence of Relative Yields of Bromine Species on Time of Irradiation of $^{7}LiBrO_3$ at 35°

Irradiation time, min (LITR)	R (BrO_3^-)	R (BrO_2^-)	R (BrO^-)	R (Br^-)
1.0	20.2	3.4	2.1	73.4
5.0	22.6	6.2	3.8	67.6
10.0	23.9	8.3	2.2	65.2

The increase in the relative yield of radiobromite and the decrease in radiobromide with increasing time is noteworthy. The radiobromate also shows a small increase suggesting the reactor radiations form bromate from bromide possibly *via* hypobromite and bromite.

Results from measurements of the increase in the yield of radiobromate in neutron-bombarded $KBrO_3$ held at various temperatures during an irradiation with ^{60}Co γ rays are shown in Figure 4. The energetic, ionizing radiations produced no change in the retention of ^{82g}Br in crystals kept at $-78°$; however, a definite increase in $R(BrO_3^-)$ with absorbed dose[25] was observed at 0° and above. Measurements with neutron-irradiated $^{7}LiBrO_3$ and $NaBrO_3$ gave results nearly identical with those for $KBrO_3$.

Irradiations of the alkali metal bromates with ^{60}Co γ rays at *ca.* 105° (*i.e.*, the source temperature) to relatively large doses revealed significant differences in annealing rates dependent on the nature of the cation (Figure 5). Unexpectedly, $NaBrO_3$ showed the smallest and $KBrO_3$ the largest susceptibility to radiation annealing. The data in Figure 5 also show that an exponential dependence of the yield of unannealed radiobromine on dose held only for relatively small doses and that saturation was approached for large doses. At a dose of 10×10^{23} ev mole^{-1}, approximately 2% of the bromate ions have been decomposed by the γ radiation. The relative yield of radiobromite

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(21) Small amounts of neutron irradiated LiBr or KBr were added to an aqueous solution of alkali metal bromate, and the mixture was evaporated to dryness in a Pt dish. The solid residue was quickly melted and quenched to obtain a uniform distribution of the bromide in the bromate. Chromatographic analyses of these eutectics showed that no radiobromate had been formed and that all the ^{82g}Br remained as bromide ion.

(22) S. Kaučič and M. Vlatkovic, *Croat. Chem. Acta*, **35**, 305 (1963).

(23) (a) D. J. Apers, K. E. Collins, C. H. Collins, Y. F. Goos, and P. C. Capron, *Radiochem. Acta*, **3**, 18 (1964); (b) C. H. Collins, K. E. Collins, Y. F. Goos, and D. J. Apers, *ibid.*, **4**, 211 (1965).

(24) A. Vanden Bosch and A. H. W. Aten, Jr., *J. Am. Chem. Soc.*, **75**, 3835 (1953).

(25) The dose absorbed in a 15-hr irradiation was 2.3×10^{23} ev mole^{-1}.

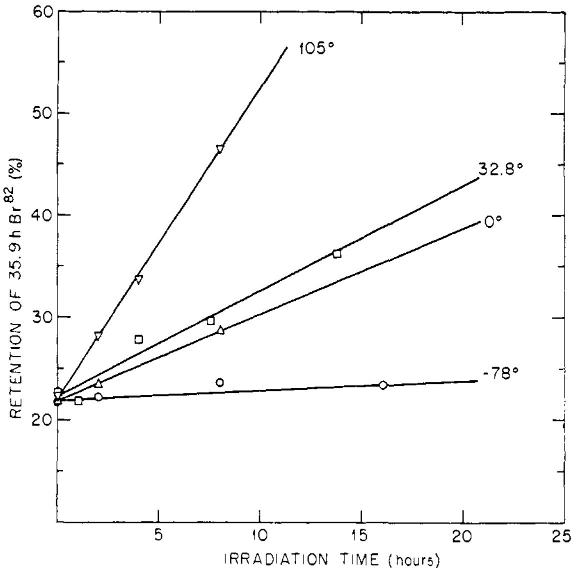

Figure 4. Temperature dependence of the increase in radiobromate yield caused by the irradiation of $KBrO_3$ with ^{60}Co γ rays.

in γ-irradiated $^7LiBrO_3$ increased from 2.4 to 7.1%, while that in $KBrO_3$ remained virtually constant at ~0.7%.

γ-Ray irradiations of radiobromide ion doped bromate crystals, in striking contrast to neutron-irradiated crystals, produced no radiobromate whatsoever within the limits of detection in the analyses.

Annealing in Mixed Crystals. Observations were made with mixed crystals of $NaBrO_3$ in $NaClO_3$ prepared by "flash melting" of an intimate mixture of the two compounds. These salts are known to form solid solutions with as much as 60-65 mole % $NaBrO_3$ in $NaClO_3$.[26] X-Ray diffraction powder patterns taken on the compositions listed in Table V confirmed this report. The increase in the yield of radiobromate as the $NaBrO_3$ was diluted with $NaClO_3$ was striking (Table V); moreover, this increase also was reflected in the decrease of the relative yield of radiobromide. Recently, a similar increase in $R(BrO_3^-)$ has been reported[27] for neutron irradiations at 37.5° of $NaBrO_3$–$NaClO_3$ mixtures prepared by a freeze-drying technique. Interestingly, irradiations at −77° of the same mixtures produced only a slight increase in $R(BrO_3^-)$. These authors did not measure $R(BrO_2^-)$, $R(BrO^-)$, or $R(Br^-)$, however.

Table V. Yields in Mixed Crystals: $NaBrO_3 + NaClO_3$[a]

Compn, wt % $NaBrO_3$	R (BrO_3^-)	R (BrO_2^-)	R (BrO^-)	R (Br^-)
1.0	49.5	1.4	1.3	45.9
5.0	35.3	1.6	0.5	59.8
25.0	30.0	2.6	0.3	65.4
100	23.8	3.5	0.5	69.8

[a] LITR, 15 min, 35°.

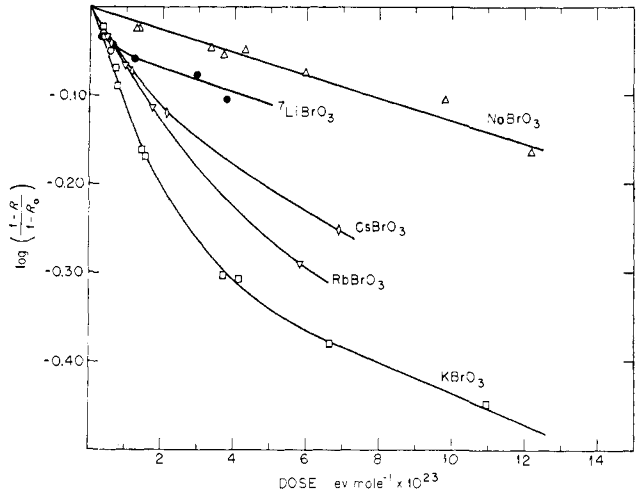

Figure 5. Dose dependence of the fraction of nonbromate radiobromine for irradiations of the alkali metal bromates at 105° with ^{60}Co γ rays (note log scale on ordinate).

Discussion

Chemical Identity of Recoil Radiobromine in Irradiated Crystals. The method employed in the analysis of the neutron-irradiated bromates involved a chromatographic analysis of alkaline aqueous solutions in which the crystals were dissolved. The question therefore arises as to the identity of the precursors in the crystal of the radiobromide, hypobromite, bromite, and bromate ions observed in solution. No direct evidence on the identities of these precursors was obtained in this research; however, certain inferences may be drawn from measurements made in the experiments reported in Figure 1 (see Table VI). Sodium arsenite in 0.1 *M* bicarbonate solutions rapidly and quantitatively reduces BrO^- ion but reacts only slowly with BrO_2^- ion and not all with BrO_3^- ion; in the presence of OsO_4 catalyst, AsO_2^- in bicarbonate rapidly and quantitatively reduces both BrO^- and BrO_2^-, but BrO_3^- is unaffected.[28] The changes in the relative yields of radiohypobromite, bromite, and bromate given in Table VI may be understood in terms of the reactions[29,30]

Table VI. Dependence of Relative Yields of the Chemical Forms of Radiobromine Produced in $LiBrO_3$ on the Composition of Aqueous 0.1 *M* $KHCO_3$ in Which Crystals Were Dissolved

Species	No reductants added	AsO_2^-	AsO_2^- + OsO_4
Br^-	62.1	76.4	80.1
BrO^-	4.9	0.2	0.1
BrO_2^-	10.5	2.5	0.0
BrO_3^-	22.4	20.9	19.8

$$2BrO^- \xrightarrow{k_1} BrO_2^- + Br^- \qquad (1)$$

$$BrO_2^- + BrO^- \xrightarrow{k_2} Br^- + BrO_3^- \qquad (2)$$

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where $k_2 \gg k_1$. A comparison of the second and fourth columns of Table VI indicates that a small amount of radiobromate (*i.e.*, *ca.* 10%) was formed *via* reactions 1 and 2. However, the precursor of most of the radiobromate found in aqueous solution was not reduced by $AsO_2^- + OsO_4$; therefore, the precursor in the crystal probably was bromate ion. A comparison of column 2 with columns 3 and 4, Table VI, shows that the precursors of BrO^- and BrO_2^- and these species themselves are reduced by $AsO_2^- + OsO_4$. The thermal annealing results given above have shown that these precursors are unstable at elevated temperatures as also are solid lithium hypobromite and bromite. The simplest, *ad hoc* hypothesis which fits these observations is that radiohypobromite and bromite ions are present in the solid. A comparison of the relative yields of radiobromite given in columns 2 and 3 of Table VI appears to suggest that BrO_2^- was reduced by AsO_2^- ion. This inference must be invalid, however, in the light of the established chemistry of bromite ion in aqueous solutions. Therefore, it is suggested that the yield of radiobromite in column 2 was abnormally large because of reaction 1 above.

A significant yield of *neutral* radiobromine has been reported[8] in neutron-irradiated $LiBrO_3$ and $KBrO_3$ based on the observed extraction of ^{82g}Br by CCl_4 from aqueous solutions, and on the disappearance of a peak in the electrophoresis separations when the crystals were dissolved in NaOH solutions rather than in pure water. The extraction of 2–4% of the ^{82}Br in $KBrO_3$ by CCl_4 was confirmed in this research. It was further shown that heating the crystals 30 min at 350° eliminated the CCl_4 extractable activity, as also did the addition of Br^- ion or AsO_2^- ion to the aqueous solution before extraction. All of these observations can be explained if BrO_2^- is the species involved. In view of the ease of hydrolysis of bromine and the ultramicro amounts of it in the systems studied, it seems unlikely that Br_2 molecules or Br atoms could have been present.

Genesis of the Radiobromine Valence States in Neutron-Irradiated Crystals. If it may be assumed that recoil radiobromine is stabilized in neutron-irradiated bromate crystals as Br^-, BrO^-, BrO_2^-, and BrO_3^- ions, the next question is how were they formed? Recoil ^{82g}Br is produced by a two-step nuclear process. The capture of a neutron by stable ^{81}Br leads almost exclusively to the formation of 6.20-min ^{82m}Br together with the release of the binding energy of the neutron (7.6 Mev) in a complex capture γ-ray spectrum; γ rays of high energy, up to 7.6 Mev, are emitted and the mechanical recoil from them is sufficient to break all the oxygen to bromine chemical bonds in the bromate ion and give an interstitial bromine atom. Recent work has demonstrated that numerous low-energy transitions occur in the capture γ-ray cascade;[31] these will undergo internal conversion and ultimately will cause chemical-bond rupture. The decay of the 6.20-min ^{82m}Br takes place *via* a highly converted, low-energy γ ray (46 kev) to form 35.3-hr ^{82g}Br. An electron vacancy cascade is established with the rapid loss of valence electrons from the bromine and with the buildup of large positive charges which cause a "Coulomb explosion"[32] of the molecular ion in which the bromine is combined. Positively charged bromine and oxygen atoms from the Coulomb explosion will recoil into the crystal lattice, although with less energy than when energetic capture γ rays are emitted. Since the Auger electrons will also lose their kinetic energy in the vicinity, the entire 46-kev of primary ionization energy will have been expended locally in electronic excitation.[33] Further, both the Auger transitions and the dissipation of Auger electron kinetic energy are so rapid (*i.e.*, *ca.* 10^{-15} sec) that they may be considered as a part of the primary event. The likelihood that the initially highly charged bromine and oxygen atom recoils will be stable in the crystal lattice is small. Electron capture from the immediate surroundings during the slowing down will cause further excitation and chemical damage within a highly localized region. These damage centers surrounding a radiobromine atom will be widely spaced in the crystal and will extend over only a few lattice distances. The chemical forms into which the bromine finally combines therefore will be determined by the reactions within these centers. Almost certainly all of the ^{82g}Br produced will have broken away from the original BrO_3^- ion in which the target ^{81}Br was combined; therefore, the species in which radiobromine appears (*i.e.*, BrO^-, BrO_2^-, and BrO_3^-) must be the result of recombination reactions. The observed independence of the radiobromate ion yield on the nature of the cation in the crystal lattice is consistent with the model of widely separated damage centers wherein rapid reactions between correlated fragments can take place.

Because of their large electron affinities, the strongly positively charged atoms from the "Coulomb explosion" of a bromate ion will be neutralized during their collisions in the crystal lattice, and the final reactions might be expected to occur between a neutral bromine atom and the fragments within the disordered region.[34] An important consideration is whether Br^+ and O^+ are neutralized before they react. The electron affinities of these and several other possible species in the crystal are given in Table VII from which it is seen that the acquisition of electrons by Br^+ and O^+ is so favored energeti-

Table VII. Electron Affinities of Selected Bromine and Oxygen Species[a]

Species	Electron affinity, ev	Type of measurement
Br^+	11.8	IP
Br	3.54	EA
Br_2	2.6	EA
O^+	13.6	IP
O	1.465	EA
O_2	0.87 ± 0.13	Calcd
O_3	2.89	Calcd
BrO_3	<3.9	EA

[a] Data from V. I. Vedeneev, *et al.*, "Bond Dissociation Energies, Ionization Potentials and Electron Affinities," Academy of Science Publishers, Moscow, 1962.

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(31) R. C. Greenwood and J. H. Reed, "Prompt Gamma Rays from Radiative Capture of Thermal Neutrons," Report USAEC 11TRI-1193-53, 1965, p 295H.

(32) T. A. Carlson and R. M. White, Proceedings of the IAEA Symposium on Chemical Effects of Nuclear Transformations, Vol. I, 1965, p 23.

(33) P. R. Geissler and J. E. Willard, *J. Phys. Chem.*, **67**, 1675 (1963).

(34) Recent Mössbauer effect measurements appear to give support to the hypothesis that highly positively charged species in condensed phases must be neutralized extremely rapidly (*i.e.*, $<10^{-8}$ sec); *cf.* Proceedings of the IAEA Symposium on Chemical Effects of Nuclear Transformations, Vol. II, 1965, p 439.

cally that neutralization may be expected during the slowing down. The recombination of an electron and a positive ion usually gives an excited atom, and this is likely to persist for a time quite long enough for "chemical" interactions with neighboring atoms. If the bromine atom deexcites before reacting, it may capture an additional electron. Because of its relatively large electron affinity, a bromine atom is much more likely to capture an electron to form Br^- than will an oxygen atom to form an O^- ion. The electron affinities of the free-radical species, BrO, BrO_2, and BrO_3, are also likely to be sufficiently large to compete with oxygen atoms for electrons. Finally, the reaction of oxygen atoms with each other to give molecules is quite favored energetically. Thus, the tendency of the recoil ^{82g}Br atom to appear in the lowest valence state of bromine can be understood.

Thermal-Annealing Mechanisms. The annealing observed on heating neutron-irradiated alkali metal bromate crystals is essentially a solid-state reaction which converts radiobromide to radiobromate ions. The much smaller quantities of radiohypobromite and bromite in the crystals rapidly disappear at the same time largely by thermal decomposition. Thus, no sequence of products is established during the annealing (*i.e.*, $Br^- \rightarrow BrO^- \rightarrow BrO_2^- \rightarrow BrO_3^-$) as might be expected if the long-range movement of O atoms were involved in the oxidation. Evidently, trapped bromide and oxygen atoms present in a disorder center combine to yield BrO_3^- ion. The reduction in crystal lattice strain energy resulting from the annealing of the center would favor bromate ion formation. However, oxygen atom recombination to give stable oxygen molecules will compete with bromate ion formation so that the complete conversion of radiobromide should not be observed unless neighboring bromate ions, or radiolytically produced inactive bromite or hypobromite, also are decomposed to give oxygen atoms which combine with bromide ions to produce radiobromate. The observations of the "transfer annealing" of bromide ion doped bromate crystals suggests that the latter process may occur. The oxidation of bromide ion is all the more remarkable when it is realized that BrO_3^- ion is thermodynamically unstable with respect to decomposition to Br^- ion plus oxygen gas.[10] The rate of this decomposition in unirradiated alkali metal bromates is slow; however, it appears to be speeded when these solids are exposed to energetic ionizing radiations.[35] The alkali metal bromides form eutectics with their bromates and lower the melting points of the latter. In the molten state slightly above the melting point, the conversion of radiobromide to bromate is rapid and quantitative unless extensive decomposition occurs. The decomposition reactions may in fact give a pathway whereby a thermal exchange reaction may occur between bromide and bromate. For example, Duke and Shute[36] report that bromide ion catalyzes the decomposition of bromate ion in molten salts and propose the slow, rate-controlling reaction

$$BrO_3^- + Br^- \longrightarrow BrO_2^- + BrO^- \qquad (3)$$

where an oxide ion presumably is transferred to the bromide ion, followed by the rapid reactions

$$BrO_2^- \longrightarrow Br^- + O_2 \qquad (4)$$

$$BrO_3^- + BrO^- \longrightarrow 2BrO_2^- \qquad (5)$$

to give bromide ion and oxygen gas. By analogy with eq 5, the transfer of an oxide ion from BrO_3^- ion to BrO_2^- should also occur rapidly

$$BrO_3^- + BrO_2^- \rightleftharpoons BrO_2^- + BrO_3^- \qquad (6)$$

Hence, the conversion of labeled bromide to bromate ion may be quantitative so long as the concentration of Br^- ion is small. It is proposed that thermal exchange reactions [*i.e.*, (3), (5), and (6)] mediated by oxide ion transfer occur in bromate crystals, particularly in the damage centers where there must be appreciable disorder.

Radiation-Annealing Mechanisms. The process in the crystal causing an increase in the fraction of bromine combined as radiobromate appears to be different qualitatively from that for thermal annealing. A pronounced dependence of the rate of annealing on the nature of the cation in the crystal is observed; moreover, a tendency toward saturation occurs so that only part of the total radiobromine can be recombined to bromate even by a large radiation dose. The radiation annealing is a thermally activated process as no increase in the yield of radiobromate occurs on exposure to energetic ionizing radiations when the crystal is held at −78° or lower. There is no dependence of the rate of annealing at 10° on the dose rate over the range studied.[5] The defect theory of Maddock and co-workers,[37] which assumes that radiation annealing is the consequence of the interaction of an exciton with the disorder center containing the recoil radiobromine, gives a plausible explanation for the cessation of radiobromate formation at large doses. As the irradiation with ^{60}Co γ rays proceeds, additional radiolytic damage centers are created which can compete for the excitons until eventually the centers containing the radiorecoil atoms become relatively ineffective and annealing becomes quite slow. In the initial stages of the irradiation the radiobromine-containing centers trap the excitons effectively and the annealing is a first-order process. The annealing mechanism may involve electron–hole pairs rather than excitons.

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