BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2835—2839 (1970)

The Thermal Annealing Behavior of ^{80}Br Recoils Produced by the Nuclear Isomeric Transitions in Alkali Metal Bromates*[1]

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(Received April 8, 1970)

The transient annealing behavior of bromine recoils produced by isomeric transition was studied in five alkali metal bromates. In the case of ^{80m}Br-labelled potassium bromate, the isothermal annealing curves were characterized by maximum and minimum points. A numerical treatment of them indicated that, at the earlier stage of the thermal treatment, the annealing processes proceeded very fast, which was ascribed to the characteristics of the isomeric transition recoils. A remarkable effect of the cationic components on the thermal annealing was observed and interpreted in terms of their ionization potentials.

Several investigations have been reported into the thermal annealing behavior of bromine recoils produced by the radiative neutron capture.[1-5] However, no detailed work has been made on the thermal annealing effect of isomeric transitions.

Jones[6] found that the retention for ^{80}Br recoils in the ^{80m}Br-labelled sodium bromate increased rapidly for a few minutes and then decreased over a longer period on thermal annealing. Shiokawa and his co-workers[7] have also studied the transient

*1 Presented at The 5th International Hot-Atom Chemistry Meeting, Cambridge, July, 1969.

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1) J. E. Boyd, J. W. Cobble and S. Wexler, *J. Amer. Chem. Soc.*, **74**, 237 (1952); J. W. Cobble and G. E. Boyd, *ibid.*, **74**, 1282 (1952).

2) J. Jach and G. Harbottle, *Trans. Faraday Soc.*, **54**, 520 (1958).

3) I. G. Campbell and C. H. W. Jones, *Radiochim. Acta*, **9**, 7 (1968).

4) G. E. Boyd and Q. V. Larson, *J. Amer. Chem. Soc.*, **90**, 254 (1968).

5) T. Andersen, H. B. L. Marsen and K. Olesen, *Trans. Faraday Soc.*, **62**, 2409 (1966).

6) C. H. W. Jones, *Inorg. Nucl. Chem. Lett.*, **3**, 363 (1967).

annealing of the recoils in the ^{80m}Br-labelled potassium bromate. They observed that the annealing curves had maximum and minimum points and that the increase in the retention continued even after the radioactive equilibrium had been reached. The thermal annealing behavior of the recoils produced by isomeric transition depends only on the annealing temperature, while that of the recoils produced by neutron capture is complicated with the secondary effects of gamma radiation during a pile irradiation, for this radiation inevitably produces vacancies, color centers, various defects, etc. Therefore, the transient annealing of ^{80}Br recoils seems to provide us with direct information about the effects of the inherent crystal defects on the thermal annealing.

This paper will describe the annealing behaviors of ^{80}Br recoils produced by the nuclear isomeric transition. A numerical treatment will be given to explain the role of the inherent crystal defects. The effects of the cations, which supports the previous assumptions regarding the thermal annealing of manganese recoils[8], will also be described.

Experimental

Samples. The potassium bromate labelled with ^{80m}Br atoms was prepared by a previously-described method.[7] The other labelled alkali metal bromates were prepared from the potassium bromate by usnig cationic exchange resin. All the samples except for lithium salt were dried at 160°C for 1 hr, while the latter was dried at 110°C for 1 hr.

Thermal Annealing Procedure. After drying, all the samples were stored at the temperature of liquid nitrogen until the radioactive equilibrium was attained. The thermal annealing procedure in the temperature region above 100°C was usually carried out by using an oil bath whose temperature was controlled within ±1°C.

Chemical Separation and Radioactivity Measurements. Although most of the samples were dissolved in redistilled water, in some cases aqueous solutions of methanol or solutions whose pH had been adjusted with nitric acid or sodium hydroxide were used as the solvents. The chemical separations were performed by the extraction method described by Saito *et al.*[9] The radioactive measurements were carried out by means of a multi-channel pulse-height analyser connected with a well-type NaI(Tl) scintillation detector. The 0.62 MeV gamma rays of ^{80}Br were counted for aliquots of the organic and the inorganic fractions. The retention—the yield of the inorganic fraction—was calculated in a manner reported before.[7]

Results and Discussion

Thermal Annealing Processes. The recoil species detected were the bromide and bromate ions, but no evidence for the presence of $^{80}BrO_2^+$ ions found in the ^{80m}Br-labelled bromate solution by Campbell[10,11] was obtained.

The transient annealing curves of ^{80}Br recoils in the labelled potassium bromate are shown in Fig. 1. In these experiments, samples were stored for 3 hr at −196°C to ensure the radioactive equilibrium and were then quickly heated to 184 or 264°C. While the annealing curves have maximum and minimum points in the early stage of the heating, the retentions increase slowly even after the radioactive equilibrium has been attained. In Fig. 2, the retentions for the samples annealed for 3—4 hr are plotted against the annealing temperatures. The retentions are constant for all the bromates in the temperature region below room temperature, while they increase slowly at higher temperatures. All the alkali bromates show different rates of thermal annealing.

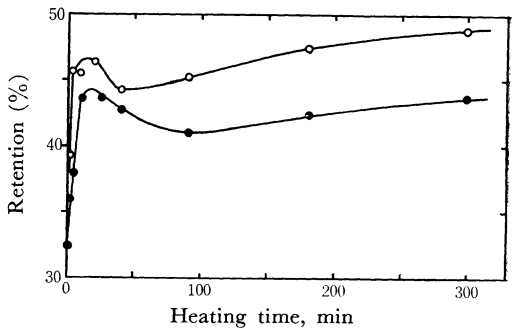


Fig. 1. Isothermal annealing curves for the retention in the labelled potassium bromate.
●: 184°C ○: 264°C

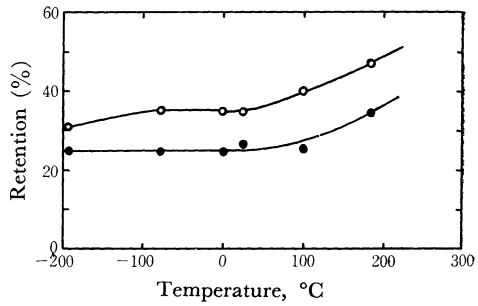


Fig. 2a. The relationships between the retention and the annealing temperature for sodium and rubidium salts.
○: $NaBrO_3$(^{80m}Br) ●: $RbBrO_3$(^{80m}Br)

7) T. Shiokawa, T. Sasaki and S. Takahashi, *Radiochem. Radioanal. Lett.*, **1**, 31 (1969).
8) T. Shiokawa, M. Yagi and T. Sasaki, *Radiochim. Acta*, **12**, 54 (1969); T. Shiokawa and T. Sasaki, This Bulletin, **43**, 801 (1970).
9) N. Saito, F. Ambe and H. Sano, *Radiochim. Acta*, **7**, 131 (1967).
10) I. G. Campbell, *J. Chim. Phys.*, **56**, 480, 665 (1959).
11) I. G. Campbell, *J. Inorg. Nucl. Chem.*, **15**, 46 (1960).

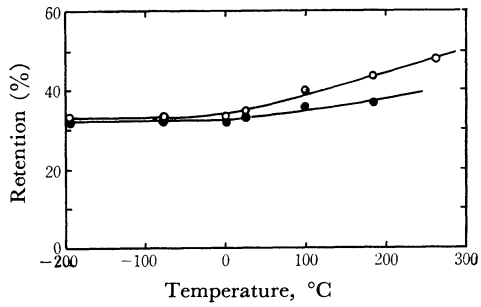
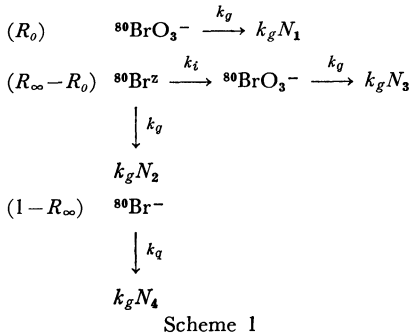


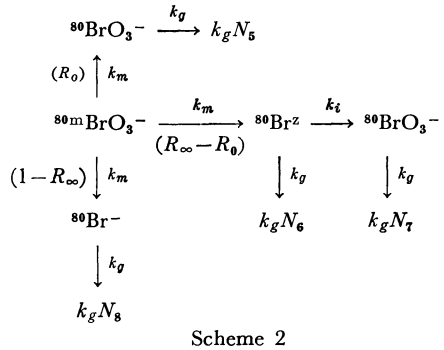
Fig. 2b. The relationships between the retention and the annealing temperature for potassium and cesium salts.

○: $KBrO_3(^{80m}Br)$ ●: $CsBrO_3(^{80m}Br)$

In order to discuss quantitatively the mechanism of the thermal annealing of ^{80}Br recoils, corrections must be made for the radioactive growth and decay of ^{80}Br atoms during the thermal annealing. Their schematic processes and the thermal annealing of ^{80}Br recoils are shown in Fig. 3.



Scheme 1



Scheme 2

Fig. 3. Schemes for the radioactive growth and decay of ^{80}Br and for the thermal annealing processes.

In these schemes, k_m and k_g are the decay constants of the metastable and ground states, while k_gN_{2i-1} and $k_gN_{2i}(i=1, 2, 3, 4)$ are the radioactive intensities corresponding to the bromate ions and the bromide ions respectively. R_0 is the initial yield of the recoil species which become precursors of the bromate ion in consequence of the isomeric transition at −196°C, while R_∞ is the plateau or the asymptotic value of the retention in the annealing curve.

Scheme I shows the changes in the initial yield of the recoil species; these species are, respectively, R_0, $(R_\infty-R_0)$, and $(1-R_\infty)$ at the beginning of the thermal treatment. An intermediate species, Br^z, which may be converted by the thermal annealing to a precursor of the bromate ion with a rate constant, k_i, is assumed. Scheme 2 shows the annealing and the decay processes of the recoils which are produced during the thermal treatment of the sample. Thus, considering the radioactive growth and decay of ^{80}Br, the retention, R, is related to the annealing time, t, as follows (see also the Appendix):

$$R=R_0+[k_i(R_\infty-R_0)\{1-\exp(-kt)\}]/k$$

where $k=k_g+k_i-k_m$. Since the values of R and R_0 are determined experimentally k_i can be calculated by varying the value of R_∞ as a parameter.

Some of the calculated results are shown in Fig. 4. The constant values of k_i are obtained after the initial rapid decrease in both the annealing temperatures. The changes in k_i show similar trends regardless of the changes in R_∞ at the same annealing temperature.

The results from the transient annealing seem to offer direct information about the role of the inherent crystal defects in the thermal annealing processes of bromine recoils. Campbell[3] has found that the thermal annealing of the ^{82}Br recoils produced by the (n, γ) reaction in the sodium bromate could be prevented by heating the samples prior to the neutron irradiation. This phenomenon was ascribed to the removal of the crystal defects, which might otherwise participate in the annealing processes of the recoils in the non-heated sample. The observations about k_i may, then, be interpreted as follows. The concentration of crystal defects is higher in the early stage of the thermal treatment, and the thermal annealing proceeds very fast. Since it becomes lower after a few hours' heating, the processes of the ^{80}Br recoils produced during the thermal treatment are

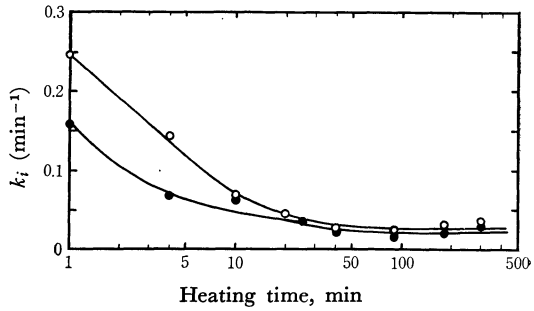


Fig. 4. Variations of k_i calculated from the results in Fig. 1.

●: 184°C, $R_\infty=0.60$ ○: 264°C, $R_\infty=0.65$

Table 1. The annealed fractions in the alkali metal bromates

Compound	R (%)		ΔY(%)	ΔR(%)*
	−196°C	184°C		
$LiBrO_3$	25.7±1.3	40.5±1.1	14.8	24.0
$NaBrO_3$	31.4±1.0	47.2±0.8	15.8	—
$KBrO_3$	32.5±1.2	43.6±1.3	11.1	19.5
$RbBrO_3$	25.3±1.2	34.2±1.0	8.9	—
$CsBrO_3$	32.2±1.0	35.5±0.8	3.3	17.8

* The values of ΔR were estimated from the work by Boyd and Larson[4] as follows:
$\Delta R = R$(200°C, 1 hr) − R(room temperature)

suppressed; this corresponds to the rapid decrease in the value of k_i with the lapse of the annealing time.

Effect of the Cations. A remarkable effect of the cations was observed in the thermal annealing behavior of the recoils. Table 1 shows the retentions for the samples stored at −196 and 184°C for 5 hr and the values of ΔY, which are the fractions annealed between these two temperatures. The tabulated values are the means of three determinations. The values of ΔR are the annealed fractions of ^{82g}Br recoils estimated from the work by Boyd and Larson.[4] The values become smaller in the order of the atomic number of the cation, and the tendencies are independent of the type of nuclear transformation.

In a study of the radiolytic decomposition of the alkali metal bromates, Boyd and his co-workers[12] found the relationship between the G-value and the crystal free space. The latter term was introduced by Saito and his co-workers[9] in order to interpret the amount of the retention for bromine recoils produced by the (n,γ) reactions. However, the electrostatic factor seems to influence the annealing behaviors of the recoils more strongly. The relationship between ΔY and the first ionization potential of the alkali metal is shown in Fig. 5.

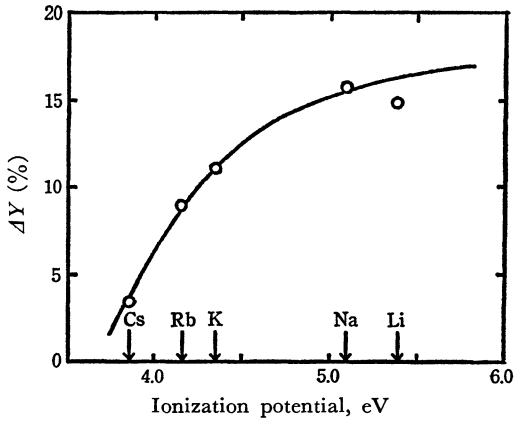


Fig. 5. Relationship between the retention and the ionization potential of alkali metals.

Although the trend is similar to that observed for the annealing behavior of bromine recoils in alkaline earth metal bromates,[13] it is entirely the reverse of the results for the permanganates salts.[8] These observations suggest that the thermal annealing is the more promoted as the polarization of the lattice constituents is larger, or as the electron density of the inactive bromate ion is higher, and that it proceeds through a direct interaction between the bromate ion and the reduced species of bromine recoil. The present conclusions also support the previous considerations regarding the annealing behavior of manganese recoils.[8]

Comparison with the Results for Other Nuclear Transformations. The thermal annealing of bromine recoils produced by the isomeric transition proceeds more rapidly than that of those produced by the (n,γ) reactions.[1-5] Furthermore, the retention for the former nuclear process is higher than those for the other nuclear transformations at room temperature, as Table 2 shows.

Table 2. Retentions for the various nuclear transformations in potassium bromate crystals

Nuclear transformation	Retention (%)	Reference
$^{80m}Br \xrightarrow{IT} {}^{80}Br$	35.5±1.2	present work
$^{79}Br(n,2n)^{78}Br$	12.4±0.4	14)
$^{79}Br(n,\gamma)^{80m}Br$	12±1	9)
$^{81}Br(n,\gamma)^{82m}Br \xrightarrow{IT} {}^{82}Br$	14.6±0.2	9)

A similar effect of the different nuclear processes on the retention was also observed in the case of aqueous solutions of labelled potassium bromate; the retention was 24.6±2.3% for the $^{80m}Br \xrightarrow{IT} {}^{80}Br$ process, whereas it was lower than 5% for the

12) G. E. Boyd, E. W. Graham and Q. V. Larson, *J. Phys. Chem.*, **66**, 300 (1962).

13) T. Shiokawa, T. Sasaki and S. Takahashi, to be published in *Radiochem. Radioanal. Lett.*

14) N. Saito, F. Ambe and H. Sano, *Nature*, **205**, 688 (1965).

$^{79}Br(n,\gamma)^{80m}Br$ reaction. By an approximate calculation, the initial kinetic energy is estimated to be less than 50 eV for the isomeric transition, while it is 220 eV for the (n,γ) reaction and 260 keV for the $(n,2n)$ reaction. Therefore, the disordered region of the ^{80}Br recoil sites may be smaller than those of the recoils produced by the (n,γ) and $(n,2n)$ reactions, and the recovery process for the former may proceed faster than those for the latter in the condensed phase. These properties caused by the isomeric transition account for the characteristic annealing curves shown in Fig. 1.

The authors wish to thank Dr. K. Yoshihara and Dr. T. Omori for their useful discussions. They are also indebted to Dr. K. Kondo for arranging the bremsstrahlung irradiation in the Laboratory of Nuclear Science of Tohoku University.

Appendix

In order to obtain information about the processes of the thermal annealing of ^{80}Br recoils, corrections of the measured radioactivities must be made for the growth and the decay of ^{80}Br atoms. According to the schemes shown in Fig. 3, $^{80m}BrO_3^-$ ions are converted to $^{80}BrO_3^-$, ^{80}BrZ, and $^{80}Br^-$ ions in consequence of the isometic transition at the ratio of R_0, $(R_\infty - R_0)$, and $(1-R_\infty)$ respectively. If these values are taken to be constant regardless of the annealing time, Scheme I under the state of radioactive equilibrium may be expressed as follows:

$$\frac{dN_2}{dt} = -k_gN_2 - k_iN_2 \tag{1}$$

$$\frac{dN_4}{dt} = -k_gN_4 \tag{2}$$

where N_2 and N_4 are, respectively, the numbers of Br^z and bromide ions after the lapse of annealing time, t. Thus, the values of N_2 and N_4 are given by the following equations:

$$\ln N_2 = -(k_g+k_i)t + \ln(R_\infty - R_0)N_g^\circ \tag{3a}$$

or:

$$k_gN_2 = k_g(R_\infty - R_0)N_g^\circ \exp\{-(k_g+k_i)t\} \tag{3b}$$

and:

$$\ln N_4 = -k_gt + \ln(1-R_\infty)N_g^\circ \tag{4a}$$

or:

$$k_gN_4 = k_g(1-R_\infty)N_g^\circ \exp(-k_gt) \tag{4b}$$

Equations for Scheme II are given with the same considerations as for Scheme I:

$$\frac{dN_6}{dt} = k_mN_m - k_iN_6 - k_gN_6 \tag{5}$$

$$\frac{dN_8}{dt} = k_mN_m - k_gN_8 \tag{6}$$

The values of N_6 and N_8 are evaluated from the equations for a transient equilibrium:[15]

$$k_gN_6 = \frac{k_gk_m(R_\infty - R_0)N_m^\circ}{k_g+k_i-k_m} \times [\exp(-k_mt) - \exp\{-(k_g+k_i)t\}] \tag{7}$$

$$k_gN_8 = \frac{k_gk_m(1-R_\infty)N_m^\circ}{k_g-k_m} \times \{\exp(-k_mt) - \exp(-k_gt)\} \tag{8}$$

and:

$$N_g^\circ = \frac{k_m}{k_g-k_m}N_m^\circ \tag{9}$$

In the above equations, N_m° and N_g° denote the total numbers of ^{80}Br and ^{80m}Br atoms at $t=0$. The sum of Eqs. (3b), (4b), (7), and (8) gives the radioactive intensity of the bromide fraction. Therefore, the retention can be related with the annealing time as follows:

$$\begin{aligned} R &= 1 - \frac{\sum_{i=1}^{4}(k_gN_{2i})}{k_gN_g} \\ &= 1 - \frac{(k_g-k_m)(N_2+N_4+N_6+N_8)}{k_mN_m^\circ \exp(-k_mt)} \\ &= R_0 + \frac{k_i(R_\infty - R_0)}{k_g+k_i-k_m}[1-\exp\{-(k_g+k_i-k_m)t\}] \end{aligned} \tag{10}$$

15) G. Friedlander and J. W. Kennedy "Nuclear and Radiochemistry," 4th Ed., John Wiley and Sons, Inc., New York (1960), pp. 129—137.