BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1437—1438 (1969)

Hot-Atom Chemistry of Bromine. I. Distribution of Bromine-82 Recoiled by the Bromine-82m Isomeric Transition Process in Aqueous Potassium Bromate

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(Received July 4, 1968)

In spite of a number of investigations of the chemical state of recoil bromine atoms arising from radiative neutron capture in bromate,[1-3] the discovery of ^{82m}Br in independent studies[4,5] has prompted a re-evaluation of the ^{82}Br hot-atom data. Saito *et al.*,[2] in 1967, discussed isotope effects with regard to the isomeric transition-induced reaction of ^{82m}Br after (n, γ) reactions in various solid bromates.

To study the chemical state of radioactive bromine atoms after (n, γ) and (I. T.) reactions in aqueous media, the present authors irradiated an aqueous (0.1M) potassium bromate solution in a reactor for one minute (thermal neutron flux of 5×10^{12} n/cm^2/-sec and attendant γ-dose rate of 2.7×10^7 R/hr) and then investigated the distribution of ^{82}Br atoms arising from both (n, γ) and (I. T.) reactions by means of paper electrophoresis (on Toyoroshi No. 50 with a potential gradient of 50 V/cm and with 0.1M $NaClO_4$ as the electrolyte). It was found that most of the activities in the form of BrO_3^- and Br_2[6] at the end of irradiation decayed with a half-life of ^{82m}Br, while the activities in the form of Br^- grew simultaneously.

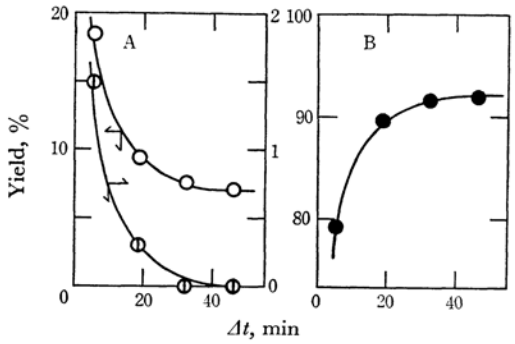

Fig. 1. Decays and growth of ^{82}Br-recoil species in irradiated aqueous BrO_3^-.
○: BrO_3^-, ◐: Br_2, ●: Br^-

Figures 1A and 1B show plots of the activities

1) The literature has been well surveyed by Saito *et al.* in Ref. 2.

2) N. Saito, F. Ambe and H. Sano, *Radiochim. Acta*, **7**, 131 (1967).

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

4) O. U. Anders, *Phys. Rev.*, **138**, B1 (1965).

5) J. F. Emery, *J. Inorg. Nucl. Chem.*, **27**, 903 (1965).

6) Activities remained on the point of origin on a paper strip. The neutral bromine species which could have been thought to be present in the solution after stabilization was Br_2.

of BrO_3^-, Br_2 and Br^- in percentages obtained from a neutron-irradiated aqueous potassium bromate solution which has been left to stand for various periods of time, Δt, after the end of irradiation. The curves of BrO_3^- and Br_2 decrease with an increase in the standing time, while that of Br^- increases.

About 91% of the initial radioactive bromine when the ^{81}Br atoms have been captured with neutrons is the 6.2 min ^{82m}Br isomer,[5] which decays primarily (*i.e.*, 99.8%) by means of a highly-converted transition from the 46 keV level (internal conversion coefficient $\alpha_k=268$) to the ^{82}Br ground state. This means that, in the process of the isomeric transition the ^{82}Br atom gains a highly positively-charged state as a result of the emission of a conversion electron and accompanying Auger electrons. The high positive charge results in a Coulomb repulsion. Bromine-82, which combines with oxygens to form the bromate ion, will then recoil into the aqueous medium. The chemical form in which the bromine finally remains will be the bromide ion. Early work by Libby and his co-worker[7] has shown that, if the bromate ion in solution is labeled with ^{80m}Br, the isomeric transition produces a disruption of the bromate molecule. Then the recoil ^{80}Br becomes a bromide ion.

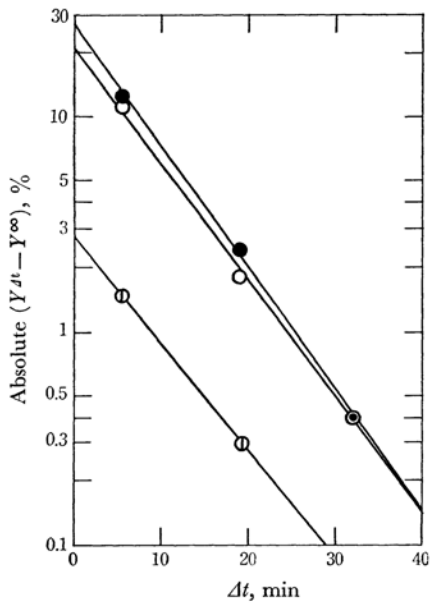

Fig. 2. ^{82}Br-recoil species as a result of isomeric transition in aqueous BrO_3^-.
○: BrO_3^-, ◐: Br_2, ●: Br^-

If the observed decrease or increase in the ^{82}Br yields of subjecting species were a result of chemical excitation by the isomeric transition alone, the rate of the decay or growth of the yield should be dependent only on the decay of ^{82m}Br and should be related to the half-life of the ^{82m}Br. Therefore, if Y^{∞} represents the yield of a species reached in the solution after all the ^{82m}Br has decayed to the ^{82}Br ground state, and if Y^0 represents the yield produced at the end of neutron irradiation, the yield, $Y^{\Delta t}$, at any time before the ^{82m}Br has completely decayed minus Y^0 would be $(Y^{\infty}-Y^0)$ multiplied by the fraction of ^{82m}Br atoms, present when the sample was separated, which had decayed to ^{82}Br. The fraction remaining would be $\exp(-\lambda\Delta t)$, where λ is the decay constant of ^{82m}Br. The decay of ^{82m}Br in BrO_3^- or Br_2 is then given by $Y^{\Delta t}-Y^{\infty}=(Y^0-Y^{\infty})\cdot\exp(-\lambda\Delta t)$. A plot of $Y^{\Delta t}-Y^{\infty}$ *vs.* Δt on a semilogarithmic scale should yield a straight line with a slope of $-0.693/2.303T_{1/2}$ (Fig. 2). The fraction which had decayed is $1-\exp(-\lambda\Delta t)$. Similarly, the growth of ^{82}Br in Br^- will be given by $Y^{\Delta t}-Y^0=(Y^{\infty}-Y^0)(1-\exp(-\lambda\Delta t))$. By rearranging the equation, we can see also that a plot of $Y^{\infty}-Y^{\Delta t}$ *vs.* Δt on the same scale should yield a straight line (Fig. 2). The ^{82m}Br half-life values were determined to be 5.53, 5.57 and 5.29 min using the yields of BrO_3^-, Br_2, and Br^- respectively. These values are in fairly close agreement with the values of 363 sec and 6.2 min reported in Refs. 4 and 5 respectively. The agreed relative rates of decrease or increase in the BrO_3^-, Br_2, or Br^- yields can be attributed to ^{82m}Br isomeric transition-excited reactions.

The Y^{∞} values in BrO_3^-, Br_2, and Br^- were 7.7%, 0%, and 92.1%, and the (Y^0-Y^{∞}) values in them were 21.3%, 2.9%, and 27.3% respectively. By adding; $(Y^0-Y^{\infty})(BrO_3^-)+Y^{\infty}(BrO_3^-)$; here, the latter term must be due, for the most part, to the direct formation of ^{82g}Br from the (n, γ) process; the experimentally-determined retention in BrO_3^- at the end of neutron irradiation was 29.0%, the 21.3/29.0=0.78 fraction of which was estimated to be $BrO_3^-(^{82m}Br)$. The yields of ground- and metastable-state bromine-82 in bromate at the end of irradiation arising directly from the (n, γ) reaction were distinguished.

The authors wish to express their appreciation to Dr. Shiro Iwata, Dr. Yoshiyuki Kiso, and the personnel of the Research Reactor Institute, Kyoto University, for their assistance in the irradiation. Thanks are also due to Mr. Shin'ichi Toyama for helping with the experimental work.

7) D. C. DeVault and W. F. Libby, *Phys. Rev.*, **55**, 322 (1939).