in contact with the cell containing saturated sodium perchlorate and the other saturated sodium chloride.

Meites[10d] indicated that at high concentrations of arsenic the height of the limiting-current plateau became independent of arsenic concentration. He suggested that at these concentrations the electrode surface became completely coated with a non-conducting layer of elemental arsenic and that the current then became limited by the electrode area rather than by diffusion. These observations were qualitatively confirmed in the present study. To avoid anomalous results due to this behavior, all experiments were performed with 0.1 mM solutions. Calculations indicated that at this concentration the electrode should not have a coating on more than 5% of its area at any time during drop life. Experimentally, the current was found to be proportional to arsenic(III) concentration in this concentration region.

Appendix (by W. H. R.)

Relations of Derivative Polarography.—By rearranging

$$E = E_{0.5} + \frac{RT}{\alpha n_a F}\ln (i_l - i)/i \qquad (16)$$

it can be shown that for an electron-transfer-controlled wave the current at any point can be written as

$$i = \frac{i_l}{i + \sigma} \qquad (17)$$

where

$$\sigma = \exp\left(\frac{\alpha n_a F}{RT}(E - E_{0.5})\right)$$

Differentiation yields

$$\frac{di}{dE} = \left(\frac{\alpha n_a F}{RT}\right)\frac{i_l \sigma}{(1 + \sigma)^2} \qquad (18)$$

Substituting the equality $i_d/(1 + \sigma)^2 = i^2/i_d$ into the above equation gives

$$\frac{di}{dE} = \frac{\alpha n_a F}{RT}\frac{i^2\sigma}{i_l} \qquad (19)$$

Rearranging and taking logarithms of both sides shows that

$$E = E_{0.5} + \frac{RT}{\alpha n_a F}\ln\left(\frac{1}{i^2}\frac{di}{dE}\right) + \frac{RT}{\alpha n_a F}\ln\frac{RTi_l}{\alpha n_a F} \qquad (20)$$

Since the first and third terms on the right-hand side are independent of potential, plotting ln $(di/dE)/i^2$ *versus* E should give the slope $RT/\alpha n_a F$. However, in contrast to the usual procedure of plotting ln $(i_l - i)/i$, it is possible to obtain this slope without the necessity of obtaining an accurate measure of i_l. Since the current–potential relation has the same form in the Nernst-controlled (reversible) case, similar equations hold. The only difference is that for αn_a should be substituted n.

Equivalent relations can be derived for the case in which not the plateau current but the residual current level is uncertain. This can be done by assuming that $(i_l - i)$ rather than i is the easily measurable quantity.

It should be pointed out that this method is much more tedious than the conventional procedure of plotting ln $(i_l - i)/i$ and is subject to much greater inherent inaccuracy because of the error in estimating the finite difference $\Delta i/\Delta E$ which is substituted for the derivative di/dE in practical applications. In addition, the method cannot be used when the interfering wave contributes significantly to the measured i. However, for cases such as the one discussed in the text, it is useful. It may find further application in the analysis of Tafel-type plots where curvature is found due to concentration polarization but limiting-current plateaus often are not reached because of experimental limitations.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Hot-Atom Chemistry of Bromine Atoms in Crystalline Potassium Bromate[1]

BY GARMAN HARBOTTLE

RECEIVED JULY 27, 1959

The reactions of recoil bromine atoms in potassium bromate have been further investigated. The retention (yield of bromate) has been determined as a function of the bombardment time, flux of neutrons, conditions of dissolution and the particular isotope investigated. The yield of bromate from the isomeric transition process in Br^{80m}-labelled potassium bromate also has been measured as a function of the ambient temperature. The results of these experiments are compared with previous work and significant differences are found.

Introduction

A number of investigators[2-8] have studied the reactions of recoil bromine atoms in crystalline bromates, and the factors which influence the yields of the several oxidation states.[4,6-8] Despite these studies, one cannot yet be sure as to the nature of the primary fragments formed by recoil in the crystal, or the reactions of these fragments on dissolution in aqueous media, although a promising beginning has been made on this problem.[8] The experiments reported in this paper were undertaken (a) to extend our knowledge of this system both on lines suggested by previous work and in other directions, (b) to clear up some discrepancies in the published literature and (c) to examine in detail a particular aspect in which the recoil reaction in po-

---

[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] E. Amaldi, O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti and E. Segrè, *Proc. Roy. Soc.* (*London*), **A149**, 522 (1935).

[3] W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

[4] (a) G. E. Boyd, J. W. Cobble and Sol Wexler, *ibid.*, **74**, 237 (1952); (b) J. W. Cobble and G. E. Boyd, *ibid.*, **74**, 1282 (1952).

[5] (a) E. Berne, *J. Chem. Soc.*, Suppl. 2, S338 (1949); (b) E. Berne, *Acta Chem. Scand.*, **6**, 1106 (1952).

[6] R. Henry, C. Aubertin and E. de la Gueronniere, *J. phys. radium*, **18**, 320 (1957).

[7] J. Jach and G. Harbottle, *Trans. Farad. Soc.*, **54**, 520 (1958).

[8] (a) I. G. Campbell, *J. chim. phys.*, **56**, 480 (1959); (b) I. G. Campbell, *ibid.*, in press. This material is available in English translation as Report 79/V Polish Academy of Sciences, Institute of Nuclear Research, Warsaw, April (1959).

tassium bromate had been reported to differ from that in other crystals which had been investigated.[9,10]

Experimental

a. **Preparation of Samples and Bombardments.**—The potassium bromate was Reagent Grade which had been recrystallized three times, dried and stored *in vacuo* over Drierite.

For bombardment, samples usually were enclosed in polythene vials, in the presence of air. In one experiment, samples of $KBrO_3$ were sealed off *in vacuo* in quartz ampoules after having been outgassed at 100° and pressure $<10^{-5}$ mm. for 2 hr. These samples already had been pumped at room temperature and the same pressure for a week. Since these samples gave the same results as those irradiated in the presence of air, the latter procedure was used routinely.

Bombardments were carried out in the Brookhaven reactor. For convenience of reference, characteristics of the various bombardment sites are summarized in Table I. No attempt was made to control the temperature during bombardment, but it was probably no higher than 35° since (a) the times of exposure were short and (b) the sample carrier was made of an insulating material.

TABLE I

CHARACTERISTICS OF BOMBARDMENT SITES IN BROOKHAVEN REACTOR

Site design.	Neutron flux, *n*/cm.^{2} sec.	Cd ratio[a]	Radiat. level, *R*/hr.[b]	Ambient temp., °C.
Thermal column	6.9×10^8	~4000	100	Room
PN 4	2×10^{12}	~300	$\sim 10^7$	35–40
PN 3	1.1×10^{13}	38		85
PN 10	1.6×10^{13}	35		130 (est.)

[a] Ratio of counting rate of a manganese foil irradiated bare at the site shown to that of a similar foil irradiated wrapped in cadmium. [b] Approximate radiation flux in roentgens/hr.

Following bombardment, samples in which Br^{80m} or Br^{80} were to be determined were worked up immediately while samples for Br^{82} analysis were stored for five days to allow the decay of interfering activities.

b. **Chemical Procedures.** 1. **Boyd Method of Analysis.**—Following the method of Boyd, *et al.*,[4] many of the irradiated samples were analyzed by dissolution of a 20 to 100 mg. portion in 35 ml. of bromine water (one-fourth saturated in Br_2). An aliquot portion was removed to be counted for total activity, and the remaining solution was extracted twice with an equal volume of CCl_4. An identical aliquot portion then was removed to be counted for non-extractable activity. The apparent "retention"[11] was then the ratio of the latter to the former counting rates, after correction for decay, background and the presence of interfering activities.

2. **Recrystallization Technique.**—In an attempt to find alternative methods of analysis, a recrystallization procedure was used. A somewhat larger sample (*ca.* 5 g.) of potassium bromate was bombarded. After "cooling" for five days, the sample was mixed carefully to ensure uniformity, a weighed sample was withdrawn and dissolved in a known volume of water. An aliquot portion of this solution was counted to determine the over-all specific activity of the irradiated salt. The remainder of the salt was recrystallized, in the presence of inactive bromide ion, to constant specific activity (determined in the same way as for the over-all irradiated salt). The retention, or yield of radiobromate, was then simply the ratio of the two specific activities.

3. **Paper Electrophoresis.**—This method of analysis has been described elsewhere.[7,12] In the present experiments, both Whatman 3 MM and Reeve Angel glass fiber paper were employed.

4. **Potassium Bromate Labelling Procedure.**—In the experiments on the yield of radiobromate following the isomeric transition $Br^{80m} \xrightarrow[\text{I.T.}]{\text{4.6 hr.}} Br^{80}$, it was desired to label potassium bromate with Br^{80m} (4.6 hr.). This was done in two ways: the first being simply the recrystallization of the neutron-activated salt. This method had the disadvantage that radioactive potassium (K^{42}, 12.5 hr.) is also incorporated. A cleaner method made use of the exchange between bromine and bromate in strongly acid solutions. Ammonium bromide was irradiated to provide a source of Br^{80m}, and this material was warmed on a steam-bath with potassium bromate in 1 *N* nitric acid, in a closed flask. After one hour, the labelled potassium bromate was purified by recrystallization.

c. **Counting Procedure.**—Samples in which Br^{82} (35.8 hr.) was to be determined were counted in a well-type scintillation counter. The isotope Br^{80} was determined by counting solutions in shallow counting cells closed by thin plastic windows. These cells were placed under end-window proportional counters and were inter-calibrated for Br^{80} radiation. Paper electrophoresis runs were counted as described elsewhere[7]; in these analyses both Br^{82} and Br^{80m} (4.58 hr.) were determined. All counts were corrected where necessary for background, decay, resolution loss and interfering activities.

Results

1. **Dependence of Retentions of Bromine 80 and 82 on Duration and Intensity of Bombardment.**—One of the interesting results in the work of Boyd, *et al.*,[4] was the observation that the retention of Br^{80} (18 min.) in potassium bromate increased sharply with time of irradiation for short exposures in the Oak Ridge reactor, rising from an extrapolated, zero-time value of about 9% to 15% for a bombardment time of only twenty seconds (Ref. 4b, Fig. 1, inset graph). Such behavior is in direct contrast to that observed for chromium recoils in potassium chromate[9]; for this reason it was felt that experiments should be done to check and extend the existing data on potassium bromate.

In the same paper Cobble and Boyd[4b] presented data in which, on a single curve, points representing yields of Br^{80} (for bombardments up to 20 minutes duration) and Br^{82} (for bombardment times longer than 20 minutes) were plotted. Such a presentation implies that there should be no isotopic difference in retention. At the time of their work the existence of isotopic differences in the behavior of recoil atoms was not suspected, however, several have been observed[13-15] recently and in particular in crystalline bromates.[7]

In the experiments reported here, in an attempt to check the behavior of potassium bromate as reported by Cobble and Boyd,[4b] samples of the salt were bombarded different times in several positions in the reactor (PN 4, eight times of exposure ranging from 1 second to 3 minutes, PN 3, 10 seconds, PN 10, 5 and 10 seconds; see Table I). No dependence of the retention of Br^{82} on time of exposure or flux was found, and the average retention found in 27 experiments was 22.1 ± 1.1%. No effect was found when a sample was outgassed (see "Experimental, a") before bombardment. Ordinary stock-bottle $KBrO_3$ as received gave the same retention as the purified, dried product.

---

(9) G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954).

(10) R. R. Williams, *J. Phys. & Colloid Chem.*, **52**, 603 (1948).

(11) "Retention" is a term first used by Libby[8] and may be taken to denote the yield of recoil atoms in the form of the parent species, *i.e.*, the species taken for bombardment; in this case, bromate.

(12) J. Jach, H. Kawahara and G. Harbottle, *J. Chromatography*, **1**, 501 (1958).

(13) A. G. Maddock and N. Sutin, *Trans. Farad. Soc.*, **51**, 184 (1955).

(14) K. J. McCallum and O. G. Holmes, *Can. J. Chem.*, **29**, 691 (1951).

(15) R. M. S. Hall and N. Sutin, *J. Inorg. & Nuclear Chem.*, **2**, 184 (1956).

The retention of Br^{80} was likewise found to be virtually independent of the conditions (PN 4, 1 second and 1 minute, PN 3, 1 second and thermal column, 10 minutes) of bombardment. However, an average value of 16.2 ± 0.6% (9 experiments) was obtained, in contrast to the higher figure for Br^{82} reported above.

2. **Separation of Bromate and Bromide by Paper Electrophoresis.**—In recent research Jach and this author[7] employed paper electrophoresis in basic media for the separation of species formed in recoil in various alkali bromates. In the work mentioned samples were bombarded at Dry-Ice temperature, dissolved in 0.1 *N* NaOH and separated electrophoretically on Whatman 3 MM paper. In the present research, samples were bombarded at room temperature but other conditions were the same, except that in some separations a glass fiber paper was employed. The results of the present experiments may be summarized as follows: the average retentions were Br^{80m} 13.5 ± 0.5% and Br^{82} 16.4 ± 0.8. For bombardments at Dry-Ice temperature Jach and this author[7] found retentions of 10 and 11%, respectively.

3. **Determination of the Retention by Recrystallization of Irradiated Potassium Bromate.**—When the data obtained by paper electrophoresis were compared with those from the Boyd (extraction) method, it was evident that a serious discrepancy existed in the results for the room temperature bombardments. As was mentioned in the paper of Jach and the author,[7] a small percentage of the activity in the paper electrophoretic separation "smears out" between the origin and the bromate peak. Even if this activity is included with bromate, the average retention of Br^{82} is increased to only about 18.0%. If the only fragments present in the irradiated crystal were bromate, bromide, bromine and hypobromite, it was difficult to see how dissolution in an alkaline medium could give a retentive lower than dissolution in bromine water with subsequent carbon tetrachloride extraction.

Therefore a new method of analysis, as described in "Recrystallization Technique" above, was applied to irradiated potassium bromate. It was found that a retention of 17.7 ± 0.2% was obtained regardless of whether the irradiated crystals were dissolved in pure water, 0.1 *M* potassium hydroxide or bromine water.

4. **Efficiency of the Single Bromine Extraction into Carbon Tetrachloride.**—A comparison of the results obtained by the recrystallization method with those from paper electrophoresis and the bromine–CCl_4 extraction procedures suggested that the latter was not removing all the non-bromate radioactive bromine species from the aqueous layer. Such an effect was very hard to understand, since Boyd, *et al.*,[4] found (and the present author has verified) that two extractions with an equal volume of CCl_4 suffices to remove bromine (as Br_2) quantitatively. However, it was found that if 10 microliters of pure bromine were mixed with the twice-extracted aqueous phase, and this bromine extracted with carbon tetrachloride, an additional 2.5 to 5% of the bromine activity could be removed. Repetition of this step ceased to remove activity after the second time, and extraction with benzene gave the same results as carbon tetrachloride.

5. **Miscellaneous Experiments on the Chemical Behavior of Recoil Bromine Atoms in Potassium Bromate.**—In the course of these studies a number of experiments were performed in an attempt to understand the nature of the non-extractable, non-bromate bromine species present in neutron-irradiated $KBrO_3$. These experiments are reported in Table II below.

6. **Determination of the Yield of the Isomeric Transition Process in Potassium Bromate.**—In the decay of the isomer Br^{80m} (4.6 hr.) to the ground-state Br^{80} (18 min.), the gamma rays are internally converted, electrons are emitted and a highly charged atom is, on the average, the end result. The recoil energy *per se* from the electron emission is small; however, the presence of a momentary large positive charge on an atom or group normally negatively charged could cause ion displacement. Such a process has been described in detail by Varley.[16] The chemical implications of this type of charge-displacement process have been mentioned by Levey and Willard.[17] In any case, chemical effects resulting from this type of nuclear decay have been observed repeatedly,[17–21] and the author felt that it would be interesting to determine the yield of Br^{80} (18 min.) labelled bromate ions (or species producing them) on decay of Br^{80m} (4.6 hr.) labelled potassium bromate in the solid state. In solution, the yield is about 35%.[8a]

Unknown to the author, and at the time this work was being carried out, similar experiments were sent in for publication by Campbell.[8b] The measure of agreement will be discussed in the final section, below.

The technique of preparing Br^{80m}-labelled potassium bromate is described under "Experimental, b" above. The experiment is to allow some of this material to stand for 2–2.5 hr. at a particular temperature while Br^{80} grows into equilibrium. Then the salt is dissolved in bromine water and extracted twice with an equal volume of CCl_4. Aliquot portions of the unextracted and extracted phases are then placed in cells for counting. The radioactivity of the unextracted portion decays with the 4.6 hr. half-life while that of the extracted portion grows into equilibrium. From these counting data one can calculate the yield of the reaction producing non-extractable bromine. As we have seen, this may be bromate, or species which transform to bromate on aqueous dissolution, or "anomalous" bromine activity. The results were as follows: when the Br^{80m}-labeled potassium bromate was held at Dry-Ice temperature (−78°) bromate yields of 48 and 46% were found in two experiments. At room temperature, yields were 36, 37 and 34%, while at 98° they were 49 and 51%. All experiments have an error of about ±2%.

---

[16] J. H. O. Varley, *J. Nuclear Energy*, **1**, 130 (1954).

[17] G. Levey and J. E. Willard, THIS JOURNAL, **78**, 2351 (1956).

[18] R. R. Williams, Jr., *J. Chem. Phys.*, **16**, 513 (1948).

[19] A. W. Adamson and J. M. Grunland, THIS JOURNAL, **73**, 5508 (1951).

[20] C. C. Coffin and W. D. Jamieson, *J. Chem. Phys.*, **20**, 1324 (1952).

[21] T. A. Carlson and W. S. Koski, *ibid.*, **23**, 2410 (1955).

TABLE II

MISCELLANEOUS EXPERIMENTS ON THE BEHAVIOR OF RECOIL BROMINE ATOMS (Br^{82} EXCEPT WHERE NOTED) IN POTASSIUM BROMATE

Exp. no.	Description of experiment		Retention,[a] %
10	Salt dissolved in Br_2 water, stood 1.5–2 hr. in the dark, extracted twice with equal volume CCl_4		23.2, 22.5
11	Salt dissolved in 25 ml. of water containing 50λ 2% $NaAsO_2$, stood 2 hr. in dark, then excess Br_2 added and extracted twice with equal volume CCl_4		31.6, 30.9
12	Salt dissolved in 0.1 *M* NaOH, then just acidified with acetic acid, bromine added and extracted twice with equal volume CCl_4		31.6, 32.4
13	Same as 12; no Br_2 added until after acidification		27.0
		B	20.2
		C	19.8
14	Salt dissolved in Br_2 water which had been made alkaline, then acetic acid added until just acid, extracted twice with CCl_4 as usual		24.5
		B	19.8
		C	19.5
15	Sample dissolved in Br_2 water. One sample removed for counting, and a known volume placed in an open dish overnight (became colorless). More Br_2 water added and again stood 7 hr. (until colorless). Final solution made up to known volume and counted to determine retention		20.6
16	Samples dissolved in 0.1 *M* NaOH, stood in room light 2 hr. then just acidified with acetic acid, 10λ Br_2 added and extracted twice with CCl_4		35.2, 34.4
		B	21.3, 21.4
17	Same as 16, except that NaOH solution stood in dark 2 hr.		36.1
		B	20.7
		C	18.5
18	Salt irradiated, PN 4, 1 sec., then treatment A, B and C[a]; Br^{80} isotope (18 min.) counted		13.0
19	Salt bombarded, 1 min. PN 4. Annealed 5 hr. at 200°, Br^{82} counted	A	51.8
		B	51.5
20	Duplicate sample of No. 19	A	50.4

[a] Key to letters: A—Sample dissolved in Br_2 water and extracted twice with an equal volume of CCl_4. B—Ten microliters of bromine mixed with the aqueous phase and extracted with two successive portions of CCl_4. C—Repetition of step B.

Discussion

The work reported here supports the view that the retention of bromine isotopes in neutron-irradiated $KBrO_3$ is of the order of 15–23%, depending on the particular isotope and method of analysis. No evidence was found over a wide range of bombardment conditions for values of only 2–20% in the CCl_4 fraction (extractable portion of the activity) as had been reported in one paper.[6]

The measurements of the retention of Br^{82} (R(82)), determined by the Boyd method[4] (a single extraction of Br_2 with two portions of CCl_4), show that there is no effect of bombardment time, or of neutron dose rate, on the retention, for exposures of 1 second to 3 minutes in the reactor. The range of integrated dose covered in the experiments was from 2×10^{12} to 4×10^{14} neutrons/cm.^{2} and in dose rate from 7×10^{8} to 1.6×10^{13} n./cm.^{2}/sec. These measurements show that the curve given by Cobble and Boyd[4b] for the yield $(1 - R(82))$ for bombardments >20 minutes extrapolates smoothly, through the values found in this research, to a value of about 78% for time $t = 0$, and does not show a sudden rise.

In the determination of the retention of Br^{80} for short bombardments at room temperature, a substantial isotopic difference is found, with $R(82)/R(80) \approx 1.40$. This difference remains when the more efficient extraction process is employed. The author feels that the difference may be in part due to a difference in annealing rates of Br^{80} and Br^{82} and that bombardments at Dry-Ice temperature would reveal a much smaller intrinsic difference. The retention of Br^{80} found for short bombardments (1 second) is substantially larger than that obtained by Cobble and Boyd[4b]; 16% *versus* their figure of about 9%.

If the results by the different methods be now compared, it will be found that the paper electrophoresis results agree fairly well with the recrystallization method, while the more efficient multiple-extraction of bromine is still slightly higher. The numbers are 16.4 ± 0.8, 17.7 ± 0.2 and 18.7 ± 1.5, respectively, compared to 22.1 ± 1.1% for a single extraction.

When one attempts to interpret the unusual behavior of the non-bromate portion of the recoil bromine atoms, as evidenced for example by the data in Table II, it may be noted that the reactions which take place do not seem to affect the yield of authentic bromate ion in any serious way. For example, estimation of the yield of bromate by recrystallization gave concordant results regardless of the conditions of dissolution. It seems likely, therefore, that exchange reactions involving bromate are not influencing the results.

It was likewise shown that adsorption on the glass containers, from the alkaline solutions, was unimportant: less than 1/5000 of the bromine activity was found to be adsorbed after such solutions had stood for 3 hr.

One knows that through the hydrolysis equilibrium

$$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HBrO \qquad (1)$$

the specific activity of bromine in the three lowest oxidation states is the same, and since Br_2 is the only bulk constituent, its removal should remove all the activity of bromine in those three forms. The fact that the reaction

$$2Br_2 + HBrO_3 + 2H_2O \longrightarrow 5HOBr \qquad (2)$$

proceeds in acid solutions[22] does not affect our results; its rate is far too slow.

Taking all the evidence, it seems that one is almost compelled to invoke the recoil formation of bromite, or fragments which produce radiobromite on dissolution. For this explanation to be reasonable, one must say that (1) bromite does not exchange rapidly with hypobromite or bromate, (2) bromite is very slow to disproportionate and (3) the equilibrium

---

(22) R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, **29**, 666 (1951).

$$H_2O + Br_2 + HBrO_2 \rightleftharpoons 3HOBr \qquad (3)$$

is attained only slowly. In defense of these requirements it can be said with some assurance that (2) is true, particularly, in alkaline solutions[23] and that (3) may well also be true, in view of the very slow rate of disproportionation of HOBr.[22] Assumption (1) can be said to be plausible, although it is difficult to test experimentally. Attempts to locate a peak, which could be assigned to bromite, through paper electrophoresis on glass fiber paper gave no positive result. The possibility remains that bromite, although present, might be masked by the larger bromide peak.

Three points remain, which do not admit ready explanation. The first is the apparently larger fraction of "anomalous" bromine (*i.e.* non-bromate, non-exchangeable with Br_2–Br^-–BrO^-) when the irradiated bromate is dissolved in alkaline solution. The second is the fact that this material is not reduced by the presence of arsenite, in alkaline media, in contrast to the expected behavior of bromite, a powerful oxidizing agent. The third is that the simple act of addition of Br_2 transfers this anomalous bromine activity into the extractable fraction, while standing with Br_2 does not seem to increase the fraction so transferred (Table II).

It is interesting that in thermally annealed irradiated $KBrO_3$ the anomalous bromine seems to have largely disappeared (Experiment 19, Table II).

Campbell,[8] on the basis of other evidence, has also postulated the presence of bromite as a possible recoil product, in irradiated solutions of bromates. He does not however believe that bromite is an important fragment in irradiated crystalline bromates.

The isomeric transition process in Br^{80m}-labelled $KBrO_3$ has also been studied recently by Campbell,[8b] who finds a value of around 30% for the retention, in reasonable agreement with the ~35% found here. However, Campbell finds no annealing effect for storage at 175°, in contrast to the increased retention (~50% for 98°) reported here. A possible reason for the discrepancy may be the difference in analytical procedures (Campbell employed precipitation of the Br^- fraction with AgBr). If there is an increase on storage at elevated temperatures, it can be understood in terms of the ordinary thermal annealing of recoil atoms.[4,7] It is more difficult to understand the high value for storage at Dry-Ice temperature. It is interesting that Willard, *et al.*,[24] found a similar increase in the retention of Br^{80} activated by isomeric transition in solid CCl_3Br as the temperature decreased. It is evident that some other process, possibly involving electronic rearrangements around the charged bromine atom, is operating and is outweighed by the annealing reaction only when the latter becomes rapid by virtue of the rise in temperature.

---

[23] P. Engel, A. Oplatka and B. Perlmutter-Hayman, THIS JOURNAL, **76**, 2010 (1954).

[24] S. Goldhaber, R. S. H. Chiang and J. Willard, *ibid.*, **73**, 2271 (1951).

UPTON, NEW YORK

[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY]

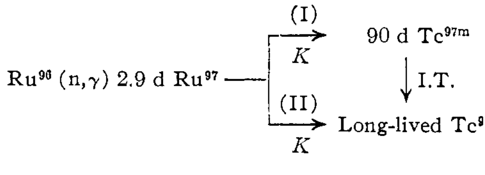
Isolation of Milligram Quantities of Long-lived Technetium from Neutron Irradiated Molybdenum

BY G. E. BOYD, Q. V. LARSON AND E. E. MOTTA

RECEIVED JUNE 29, 1959

The method employed for the isolation of milligram quantities of long-lived Tc^{99} formed in molybdenum metal by prolonged neutron irradiation in the Oak Ridge graphite-natural uranium pile is described. The identity of the element isolated was established by measurements of its X-ray and its optical emission spectra. Careful specific activity determinations using 4π beta counting techniques yielded a value of $2.15 \pm 0.05 \times 10^5$ years for the half-life of Tc^{99g}, while measurements of the absorption of its radiations in aluminum gave 0.29 ± 0.01 Mev. as its maximum β-ray energy. Collateral observations on the wet volatility, solvent extraction, reduction by metals in acid and alkaline solutions and on the coprecipitation of tracer quantities of technetium were made also. A convenient method for the preparation of high specific activity technetium tracer from cyclotron irradiated molybdenum metal targets is outlined.

The possibility that weighable quantities of the "missing element" technetium could be synthesized by neutron capture reactions was recognized soon after the first successful operation of the neutron chain reacting pile in the United States. It was not possible, however, to conduct such an effort until early 1946 when gram quantities of purified ruthenium hydroxide were irradiated in the Oak Ridge graphite natural uranium reactor[1] in an attempt to produce a long-lived technetium isotope of mass 97 by the sequence of nuclear events as indicated. Evidence for the production of microgram quantities of long-lived technetium *via* route II was not obtained, although during the course of this work route I was established so that it could be concluded that the radioactive tracer of 90 day half-life employed by Perrier and Segré[2] in their chemical studies with unweighable quantities of technetium was to be assigned[3] to mass number 97 (*i.e.*, 90 d Tc^{97m}).



---

[1] G. E. Boyd, E. E. Motta and A. R. Brosi, "Production and Mass Assignment of a 90 d Activity in Element 43," Oak Ridge National Laboratory Report MonC-132, July 23, 1946, Declassified January 31, 1956.

[2] C. Perrier and E. Segré, *J. Chem. Phys.*, **5**, 712 (1937); **7**, 155 (1939).

[3] E. E. Motta, G. E. Boyd and A. R. Brosi, *Phys. Rev.*, **71**, 210 (1947).