On the Szilard-Chalmers Reaction with Potassium Bromate

Preparation of ^{82}Br , Hot-atom Chemistry, and Radiation Chemistry

ERIC BERNE

Laboratory of Nuclear Chemistry, Chalmers University of Technology,
Gothenburg, Sweden*

In a previous paper¹ the preparation of an ion-exchanger for the separation of halide and halate ions was described. The purpose of this paper is to investigate the use of this ion-exchanger in the preparation of ^{82}Br having a high specific radioactivity.

Irradiation of bromine in the nuclear reactor of the A.E.R.E.**, Harwell, yields a product of specific radioactivity between 22 and 60 mc/gram². For some purposes it is desirable to increase the specific radioactivity particularly because the half life of ^{82}Br is short (36 hours). The problems associated with the Szilard-Chalmers reaction used for the concentration of ^{82}Br are the following:

1. The development of a method for the separation of bromide and bromate suitable for further use of ^{82}Br , when the radioactivities involved are of the order 100 to 1000 mc.
2. The decomposition of the bromate target during irradiation in the reactor.
3. The retention of bromates irradiated in the reactor.

1. THE SEPARATION OF BROMIDE AND BROMATE

For the separation the ion-exchanger described in the previous paper¹ is used. The properties of the material are: capacity = 4×10^{-5} equiv./cm³ bed volume, volume fraction of liquid in the column $\approx 60\%$, possible flow rate = 0.6 ml per minute per cm² for halide concentrations of 0.01 to 0.02 *M*.

* Operated under the auspices of the Swedish Atomic Energy Committee.

** A.E.R.E. = Atomic Energy Research Establishment.

For purification of the eluate a small column containing the cation-exchanger Dowex 50 in hydrogen form is used.

For the checking of the operation of the column it is considered unsuitable to measure the radioactivity of the eluate. If quantities of 100 to 1 000 mc are handled, very thick radiation shields have to be used between the column and the instrument for the measurement of the radioactivity. This would require long tubes between the column and the outlet of the system. As will be shown later, this would lead to a very bad separation between bromide and the iodide used for the elution.

The eluate contains small amounts of silver ions of concentration depending on the composition of the eluate. The operation of the column may thus be checked by measurement of the silver ion concentration in the eluate. By use of the arrangement shown in Fig. 1 the E.M.F. of the cell

can be measured. If we neglect the activity coefficients, the E.M.F. is determined by:

$$E = e_{\text{Ag}}^0 - e_{\text{calomel}} + \frac{RT}{F} \ln [\text{Ag}^+]_{\text{eluate}} \quad (1)$$

i. e. at 25° C,

$$E = 553 + 59.21 \log [\text{Ag}^+]_{\text{eluate}} \quad (2)$$

where E is expressed in mV.

The appearance of bromate has no influence on the silver ion concentration in the eluate which before the halide ions appear is determined by the hydroxyl ion concentration. However, if the ion exchange column is treated prior to the separation with a solution of hydroxyl ion concentration different from that of the solution to be separated, the appearance of the bromate fraction can be approximately observed. When the bromide fraction appears in the eluate, the measured E.M.F. must suddenly drop due to the decrease in silver ion concentration. When the bromide fraction is finished, the E.M.F. must once more suddenly drop and the pure bromide fraction can thus be observed in the eluate.

Experimental

Experiment 1: A solution 0.1 M in potassium bromate and 0.01 M in sodium bromide was separated using the apparatus shown in Fig. 1. Bromide was eluted by 0.01 M

1. Apparatus for measurement of $[Ag^+]$ in the eluate, A = silver electrode, B = salt bridge containing 1.5 M ammonium nitrate solution, C = saturated calomel electrode.

2. Measured E.M.F. as a function of the volume of the eluate. — — — = calculated values.

sodium iodide solution. The E.M.F. measured during the separation is shown in figure 2 together with the calculated values. Before the separation the column was treated with a solution 1 M in sodium hydroxide.

Experiment 2: In order to demonstrate the importance of having short tubes, an experiment was performed in which the column was connected to a liquid flow counter by a rubber tube of about 15 cm in length. A solution equal to the one of experiment 1 and containing ^{82}Br as bromide and as bromate was treated. The silver ion concentration of the solution was measured immediately after it left the counter and compared to the radioactivity measured by the counter. In this case the column was treated before the separation with pure water. The results are shown in Fig. 3.

The yield of pure bromide in the separation is determined by the length of the bromide band on the column and by the volume in the column between the end of the ion-exchanger and the outlet of the system. This volume is called the "dead volume" (V_d) and is indicated in Fig. 1.

If the boundary between bromide and iodide on the column were absolutely sharp the length of the bromide band could have any value. This is, however, not the case. There is always a small overlapping due to irregularities in the exchanger bed. The bromide in this fraction is not pure and cannot be used. The magnitude of this overlapping, in the experience of the author, is about 2 to 4 mm for areas of 0.2 to 1 cm^2 . Hence if the loss due to the diffuse region between iodide and bromide is to be kept below 10 to 20 %, a reasonable figure, the bromide band has to be at least 2 cm long.

The yield of the separation excluding the loss due to the diffuse section is determined by the dead volume. A comparison between the Figs. 2 and 3 shows that a considerable mixing of iodide and bromide through diffusion takes place after they leave the ion-exchanger bed. Hence, as soon as the

3. Measured E.M.F. ——— and radioactivity — — — as a function of the volume of the eluate.

4. Microtitration apparatus for the determination of bromide.

iodide band has left the ion-exchanger, the bromide fraction has to be cut off. The yield can thus be calculated from the equation

$$\eta = 1 - \frac{[I^-] V}{l'' A (C + \alpha [I^-])} - \frac{0,4}{l''} \quad (4)$$

where η = yield, l'' length of bromide band, C = capacity of ion exchanger, A = area of the column, and $[I^-]$ = concentration of the solution used for the elution and α = volume fraction of liquid.

For a calculation of the optimum conditions for the irradiation, separation, and yield, the decomposition during the irradiation and the retention must be known. The investigation of these factors is described in the following sections.

2. RADIATION CHEMISTRY AND HOT-ATOM CHEMISTRY

The best compound for the irradiation is potassium bromate. Ammonium bromate is not stable and sodium bromate would yield a very high disturbing radioactivity from sodium, which would increase the difficulties with the radiation shield.

Experimental

Decomposition: 500 mg of potassium bromate containing less than 0.01 % of bromide were irradiated in the pile of A.E.R.E. for five days, with a neutron flux of about $10^{11} \text{ cm}^{-2}\text{sec}^{-1}$. After the irradiation the preparation had a brownish colour, indicating that some decomposition had taken place. The potassium bromate was dissolved in 10 ml of 0.1 *M* sodium hydroxide solution and diluted to 50 ml. The bromide content of this solution was determined by potentiometric titration of 1 ml with 0.1 *M* silver nitrate solution using a micro titration apparatus as described in Fig. 4. The titration vessel A,

taking 2 ml, is connected to a saturated calomel electrode B via a salt bridge C containing agar gel 1.5 *M* in ammonium nitrate and a solution of ammonium nitrate D. The other electrode E consists of a silver wire. Silver nitrate is added by the micro burette F of the type "Aglar" constructed by the Wellcome Physiological Research Laboratories, England. The burette measures volumes down to 0.1 μ l. The solution was stirred by blowing air through the capillary G with the rubber balloon H. The equivalence point was found to be located at 8.5 μ l corresponding to 68 μ g of bromide, *i. e.* 3.4 mg in the whole of the solution.

Retention: The retention of ^{82}Br in bromate was determined in the following way. 1 ml of the solution containing the irradiated material was added to a solution 0.1 *M* in potassium bromate and 0.01 *M* in sodium bromide. The bromide and bromate were separated using an apparatus as described in Fig. 5. The ion-exchange column contained a layer of Dowex 50 in hydrogen form in order to absorb the radioactive potassium isotope ^{40}K present in the solution. The two fractions of the eluate indicated in Fig. 6 were collected, diluted to 100 ml, and 10 ml of each measured by a liquid counter.

Regardless of the mechanism, the decomposition is proportional to the time of irradiation, for constant neutron flux and γ -radiation. The rate of decomposition, *D*, expressed as moles of bromide per mole of bromate per hour, thus can be calculated:

$$D = 1.2 \cdot 10^{-4} \text{ hr}^{-1}$$

The decomposition is the sum of the effect due to neutrons and to γ -radiation:

$$D = D_{\gamma} + D_n \quad (5)$$

D_n can be roughly estimated. With a neutron flux of $10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ and a thermal activation cross section of about 2 barns [$\sigma(^{79}\text{Br}) + \sigma(^{80}\text{Br})$], there are $4.3 \cdot 10^{14}$ nuclear reactions per hour per mole in the target material. The magnitude of the decomposition following each nuclear reaction is rather uncertain and cannot be exactly calculated from the present knowledge of the hot-atom chemistry of bromates. However, if there is no chain reaction mechanism, the decomposition due to the very short range of the recoiling atom certainly can be assumed to be less than 10^{17} ions per mole per hour. This gives $D_n \leq 1.7 \cdot 10^{-7}$. As *D* was found to be $1.2 \cdot 10^{-4}$, the decomposition is almost completely due to γ -radiation. The retention of the radioactive isotope is defined by

$$R = \frac{I(\text{BrO}_3^-)}{I(\text{BrO}_3^-) + I(\text{Br}^-)} \quad (6)$$

where *I* = radioactivity. *R* was determined in two preparations irradiated under the same conditions, and was found to be 25 and 27 %.

5. Separation column connected to liquid flow counter (B). A = lead shields.

6. Radioactivity of eluate as a function of volume. Fractions used for the determination of R .

This value of the retention is not in agreement with that found by Libby³, who determined R as $(4 \pm 4) \%$ if solid sodium bromate is irradiated and dissolved in pure water, and $R = (10 \pm 8) \%$ if a solution of sodium bromate 3 M in sodium hydroxide is irradiated. In Libby's work the reaction $^{79}\text{Br}(n, \gamma)^{80}\text{Br}$ was studied. The use of this reaction instead of $^{81}\text{Br}(n, \gamma)^{82}\text{Br}$ should, however, be of no importance since it can be assumed that the excitation energy given to the recoiling bromine atom is about the same for ^{80}Br as for ^{82}Br ; neither should it be of any importance that sodium bromate instead of potassium bromate was irradiated. The difference may be explained in the following way:

The brownish colour of the potassium bromate after the irradiation indicates that the decomposition product is, at least partly, free bromine. When dissolved in sodium hydroxide solution, this bromine reacts as follows:

The radioactivity is immediately evenly distributed between Br_2 and Br^- through the equilibrium

Hence, if the amount of bromine is much larger than that of bromide, the retention according to (7) must be 16.7 % if the reaction is allowed to proceed to completeness. The lower value found by Libby can be explained by bromide impurities in the bromate irradiated. Libby's irradiation was carried out with a 200 mc Ra-Be source. In this case the decomposition is certainly very small

compared to the bromide impurities in usual analytical reagents. Furthermore, when dissolved in pure water of $\text{pH} = 7$, the reaction (7) at room temperature is a rather slow process.

The higher values of the retention found in this investigation must be due to the fact that R is a sum of two terms:

$$R = R_p + R_s \quad (9)$$

where R_p = primary retention, and R_s = secondary retention. Here the primary retention is that part of ^{82}Br which either recombines with oxygen atoms during the cooling of the hot recoiling atom, or is not liberated from the bromate ion as a consequence of the nuclear reaction. The secondary retention is that part of ^{82}Br which reacts to form bromate during the separation. As the isotopic exchange between bromate and bromine has a measurable rate only in acid solution the secondary retention is due only to reaction (7), and is determined by the ratio Br^-/Br_2 after the irradiation and by the completeness of reaction (7). From the experimental results available up to the present, nothing can be said with certainty about the chemical state of the decomposition products, *i. e.* the ratio Br^-/Br_2 ; hence it can only be stated that $R_s \leq 16.7$ and $9 \leq R_p \leq 26$. Libby's results, in spite of the large errors stated, support the view that R_p is rather small. It is therefore probable that the decomposition product due to the γ -radiation is mainly free bromine and that the primary retention is 9 %. Nothing can be said about the chemical state which results as a consequence of the (n, γ)-reaction.

The question whether the primary retention is due to recombination during the cooling process or to the fact that the bromate ion in some cases is not decomposed is impossible to answer so long as the number and energy of the γ -quanta emitted from the intermediate nucleus are not known.

3. GENERAL CALCULATION OF THE SEPARATION PROCESS

The success of the preparation method outlined in part 1 depends on the concentration factor and the yield which can be obtained. The concentration factor F is defined as the ratio between the specific radioactivity obtained with the use of a Szilard-Chalmers reaction and that obtained without this process. F is determined by the following factors: 1) the initial bromide content of the irradiated bromate, 2) the decomposition during the irradiation, 3) the retention, and 4) the time necessary for the separation. The initial bromide content of the irradiated bromate can be made practically zero by purifying the bromate with the ion exchanger used for the separation. If the retention is assumed

to be independent of the length of the irradiation the specific radioactivity obtained is determined by the equation

$$I_s = \frac{100-R}{100} \frac{kx(1-e^{-\lambda t_i})}{Dxt_i} e^{-\lambda t_i} \quad (10)$$

where I_s = specific radioactivity of bromide, R = retention, k = saturation specific radioactivity of bromate, x = irradiated amount of bromate, D = rate of decomposition, λ = decay constant of ^{82}Br , t_i = time of irradiation, and t_s = time of separation. The time of separation is determined by the equation

$$t_s = \frac{x}{bvA} + t' \quad (11)$$

where b = solubility of potassium bromate, v = flow rate during the separation, and t' = time for elution of the bromide band and for purification in the cation-exchanger. For the ratios between bromide and bromate which usually appear, t' can be neglected in comparison with the other term.

The area of the column is determined by the equation

$$Al'(C + \alpha[\text{I}^-]) = Dxt_i \quad (12a)$$

where C = capacity of ion-exchanger, l' = minimum length of the bromide band for the yield intended, α = volume fraction of liquid in the column, and $[\text{I}^-]$ = concentration of the iodide used for the elution. Usually $\alpha[\text{I}^-]$ can be neglected in comparison with C . (For $[\text{I}^-] \leq 0.01 M$). Hence

$$Al'C = Dxt_i \quad (12)$$

From equations (11) and (12) t_s is found to be determined by

$$t_s = \frac{Cl'}{bDvt_i} \quad (13)$$

Hence

$$I_s = \frac{100-R}{100} \frac{k}{D} \frac{1-e^{-\lambda t_i}}{t_i} \cdot e^{-\frac{\lambda k_1}{\lambda t_i}} \quad (14)$$

where $k_1 = \frac{Cl'}{b v D}$

Hence

$$F = \frac{100-R}{100} \frac{1-e^{-\lambda t_i}}{t_i} \cdot e^{-\frac{\lambda k_1}{\lambda t_i}} \quad (15)$$

In order to find the time of irradiation which results in the best concentration factor, the derivative dF/dt is calculated and set equal to zero. This gives the equation for the optimum irradiation time t :

$$e^{-\lambda t} = \frac{t - \lambda k_1}{t - \lambda k_1 + \lambda t^2} \quad (16)$$

The following numerical values are used: $C = 4 \times 10^{-2}$ mmole/cm³; $l' = 2$ cm; $b = 0.43$ mmole/cm³; $v = 0.6$ ml/min cm²; $\lambda = 0.01925$ hr⁻¹; and $R = 26$ %. Then k_1 is found to be 44.1 hr² and $\lambda k_1 = 0.85$ hr. Then from (16) t by approximate methods is found to be 9.5 hours. With this optimum time of irradiation the concentration factor according to (15) is 102. If the usual time of irradiation in the pile of A.E.R.E., viz. 5 days is used, F decreases to 46.

The diameter of the column is determined by the amount of potassium bromate irradiated. From equation (12) and the numerical values found for optimum time of irradiation,

$$A = 0.0143 \ x \quad (17)$$

The yield of the separation process can now be calculated as a function of x from equations (4) and (17):

$$\eta = 0.8 - \frac{[I^-] V_d}{0.11 \ x} \quad (18)$$

DISCUSSION

The maximum concentration factor of about 100 considerably increases the specific radioactivity of the preparations, but for a Szilard-Chalmers reaction it is a rather low value. The concentration factor is limited by the rate of decomposition and by the time of separation. A gain in separation time is possible if sodium bromate, which is more soluble than potassium bromate, is irradiated. For the optimum time of irradiation, however, the decrease in F due to the time of separation is only 9 %. Hence there is no reason for using sodium bromate if the rate of decomposition cannot be decreased. Since the decomposition is due in the main to γ -irradiation, it should be possible to decrease the rate without any appreciable decrease in neutron flux. The absorption coefficients in lead for thermal neutrons and γ -radiation are $\mu_\gamma \leq 0.45$ cm⁻¹, $\mu_n = 3.3 \times 10^{-5}$ cm⁻¹. Hence if the material is surrounded by about 5 cm of lead during the irradiation, the rate of decomposition should be reduced by a factor 10. The possibility of having such a lead container in the reactor was not able to be investigated by the author, but if it were possible, it would lead to a considerable improvement in the concentration factor.

SUMMARY

An ion-exchanger containing silver oxide and capable of exchanging halide ions for hydroxyl ions has been used for the preparation of ^{82}Br by Szilard-Chalmers reaction on pile-irradiated potassium bromate. The checking of the separation column by E.M.F. measurements in the column is described.

The radiation chemistry and hot-atom chemistry for pile-irradiated potassium bromate have been investigated, and the results applied to a calculation of the maximum concentration factor and yield obtainable if the irradiation is carried out in the reactor of the Atomic Energy Research Establishment, Harwell, England, and if use is made of the ion-exchange column described. It has been found that a specific radioactivity of about 5 c per gram can be produced. Possible improvements yielding about 50 c per gram are discussed.

My thanks are due to Dr. W. J. Arrol, A.E.R.E. for arranging the irradiation of potassium bromate in the reactor.

LITERATURE

1. Berne, E. *Acta Chem. Scand.* **6** (1952) 1260.
2. *Isotope Catalogue*. A.E.R.E. Harwell, England.
3. Libby, W. F. *J. Am. Chem. Soc.* **62** (1940) 1930.

Received October 5, 1951.