Decay of the 4.5-Hour Br^{80} Isomer

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Evidence of a limit of 85±4 percent to the chemical extractability of the 18-min. bromine from its 4.5-hr. parent isomer is presented. This is interpreted as the fraction of 4.5-hr. bromine which emits conversion electrons. In agreement with Grinberg and Roussinow gamma-rays of about 30 to 40 kev average energy were found coming from the 4.5-hr. bromine. It does not seem possible to make a unique interpretation yet. The presence of a gamma-ray accompanying the 18-min. period is confirmed, but its energy is placed above 0.6 Mev.

I. INTRODUCTION

CONSIDERABLE confusion surrounds the radiations emitted by both the 18-min. and the 4.5-hr. Br^{80}. The discovery that at least a large part of the 4.5-hr. bromine changes to the 18-min. form[1–3] has both cleared up some points and raised others. Snell[4] observed a gamma-ray of "less than 0.5 Mev" from the 18-min. form, but it becomes uncertain because he observed none from the 4.5-hr. period although it is now known that there must have been 18-min. bromine present in equilibrium with his 4.5-hr. sample. Buck[5] found a gamma-ray with the 4.5-hr. period but said that it must be softer than the 18-min. gamma-ray found by Snell. Abelson[6] and Roussinow and Yusephovich[7] observed Br x-rays associated with the 4.5-hr. period. Roussinow and Yusephovich found[1] and measured[8] conversion electrons of 34 and 47 kev from the 4.5-hr. period. Valley and McCreary[9] found and measured these and also a third line of conversion electrons of 24 kev from the 4.5-hr. period. The corresponding gamma-ray energies would be 48.9 and either 37.1 or 25.3 kev. Siday[10] from cloud-chamber work concluded that the conversion coefficient was about 0.3. As will be discussed later the finding of cases in which a much larger fraction of the isomeric transitions than this produce chemical reaction makes it necessary to conclude that the conversion coefficient must be much higher.

While this paper was in preparation the work of Grinberg and Roussinow[11] appeared in which they report unconverted 37-kev gamma-radiation from the 4.5-hr. bromine. Their measurements further exclude the possibility of any large proportion of gamma-rays of other energies. Section III of this paper may therefore be taken as a confirmation of their first finding.

II. CHEMICAL EVIDENCE FOR THE AMOUNT OF CONVERSION

A continuation of the study of the chemical effects induced by the isomeric transition has given data which seem to bear directly on the problem outlined above. It is intended to publish the details of the work and a discussion of the chemical effects in a chemical journal. However, the results of interest here are presented in the accompanying tables. They show the apparent existence of an upper limit of 85 ± 4 percent to the amount of activity which can be extracted chemically in 18-min. form from a compound containing 4.5-hr. Br^{80}.

The substances listed in the second column of Table I contained Br^{80} of 4.5-hr. half-life and were allowed to stand under the conditions listed in the next column long enough for the 18-min. Br^{80} present to reach equilibrium with its 4.5-hr. parent. A chemical extraction was then per-

[1] L. I. Roussinow and A. A. Yusephovich, Comptes rendus Acad. Sci. U.S.S.R. **20**, 645 (1938).
[2] E. Segrè, R. S. Halford and G. T. Seaborg, Phys. Rev. **55**, 321 (1939).
[3] D. DeVault and W. F. Libby, Phys. Rev. **55**, 322 (1939).
[4] A. H. Snell, Phys. Rev. **52**, 1007 (1937).
[5] J. H. Buck, Phys. Rev. **54**, 1025 (1938).
[6] P. Abelson, Phys. Rev. **55**, 424 (1939).
[7] L. I. Roussinow, and A. A. Yusephovich, Phys. Rev. **55**, 979 (1939).
[8] L. I. Roussinow, and A. A. Yusephovich, Comptes rendus Acad. Sci. U.S.S.R. **24**, 129 (1939).
[9] G. E. Valley and R. L. McCreary, Phys. Rev. **56**, 863 (1939).
[10] R. E. Siday, Nature **143**, 681 (1939).
[11] A. P. Grinberg and L. I. Roussinow, Phys. Rev. **58**, 181 (1940).

TABLE I. *Amount of 18-min. activity extracted from various* Br^{80} *compounds under various conditions. Methods of extraction: (1) by pure water, (a) by shaking either gas or liquid with water, (b) by spraying water into gas, (c) by adding water and* CCl_4 *or benzene to get a separation of layers. (2) By adding inactive* Br_2 *(except when already present) and immediately (a) shaking with* Na_2SO_3 *solution or (b) spraying* Na_2SO_3 *solution in, (c) shaking with* KI *solution. (3a) By adding* Br^- *and then* $Ag(NH_3)_2^+$, *(b) by adding* Br^-, $Ag(NH_3)_2^+$ *already present in the* BrO_3^- *solution.*

Expt. No.	Compound	Conditions	Method of Ext'n	Amt. 18-min. Ext'd (±4% for most of these)
		Present experiments		
1	C_2H_5Br	gas, 21 mm	1*a*	95%
2	C_2H_5Br	gas, 94 mm	2*b*	90[c]
3	C_6H_5Br[b]	solution in EtOH	1*c*	89
4	C_2H_5Br	solution in EtOH	1*c*	89
5	C_2H_5Br	gas, 9 mm	2*b*	86[c]
6	C_2H_5Br	80% gas (459 mm)+20% liquid	1*a*	85
7	C_2H_5Br	gas, 318 mm	1*a*	84
8	C_2H_5Br	gas, 9 mm+400 mm argon	2*b*	84[c]
9	C_2H_5Br	gas, 9 mm+100 mm argon	2*b*	83[c]
10	BrO_3^-	solution in H_2O	3*b*	82
11	BrO_3^-	solution in H_2O	3*a*	80
12	C_2H_5Br	80% gas (459 mm+)20% liquid	1*a*	80[a]
13	$CHBr_3$	gas, 3 mm	2*b*	79[c]
14	BrO_3^-	solution in H_2O	3*b*	79
15	BrO_3^-	solution in H_2O	3*b*	79
16	C_2H_5Br	gas, 12 mm+380 mm argon	2*b*	77[c]
17	BrO_3^-	solution in H_2O	3*b*	75
18	C_2H_5Br	gas, 0.5 mm	2*b*	73[c]
19	$(CH_2Br)_2$	gas, 10 mm	2*b*	69[c]
20	C_2H_5Br	gas, 21 mm+20 mm H_2O vap.	1*b*	63[c]
21	C_2H_5Br	liquid at 0°C	2*a*	58
22*	$CH_3CHBrCHBrC_2H_5$	solution in CCl_4+Br_2	2*a*	52
23	C_2H_5Br	gas, 21 mm+500 mm argon	1*b*	51[c]
24	C_2H_5Br	gas, 21 mm+700 mm argon	1*a*	50
25*	$CH_3CHBrCHBrC_2H_5$	solution in CCl_4	2*a*	45
26	C_2H_5Br	liquid at 0°C	1*a*	43
27*	$(CH_3)_3CBr$	solution in CCl_4	1*a*	38
28	$CHBr_3$	solution in CCl_4	1*a*	36
29	C_2H_5Br	solution in *n*-pentane	1*a*	33
30	C_2H_5Br	solution in CCl_4	1*a*	21
31	C_2H_5Br	solution in C_6H_5Br	1*a*	18
32*	$CH_3CHBrCHBrC_2H_5$	solution in $CCl_4+CH_3CH=CHC_2H_5$	2*a*	2.6
Ref.		*Previously published results*		
2	$(CH_3)_3CBr$	solution in CH_3OH+H_2O	1*c*	90
12	$(CH_2Br)_2$	liquid+5% of $C_6H_5NH_2$	1*a*	90
3	BrO_3^-	solution in water	3	75
13	Br_2	solution in CCl_4	2*c*	8 to 34

* Unpublished experiments by Charles H. Klute and Edward L. Wagner.

[a] These values are corrected for incomplete attainment of equilibrium before extraction.

[b] This was C_6H_5Br that was irradiated with neutrons and used directly. Much of the 4.5-hr. activity may have been in other forms [E. Glückauf and J. W. J. Fay, J. Chem. Soc. 390 (1936)] such as $C_6H_4Br_2$, etc. 4.5-hr. activity extractable by Br_2 and Na_2SO_3 solution was previously removed.

[c] These are the sums of several successive extracts corrected for small new amounts of 18-min. Br formed between extracts.

formed by the method indicated in the next to the last column. In experiments 3 and 11 (and in those of DeVault and Libby[3] and le Roux, Lu and Sugden, Table I[12]) the growth of the activity of the parent compound after extraction was measured. In the other cases the 18-min. activity of the extract was measured, and the total amount present at the time of separation was determined by direct measurement on some of the parent substance in experiments 10, 14, 15 and 17 and by calculation from the measured specific activity of the bromine used in preparing the parent compound in the other experiments. The last column tells the percent of the total activity (minus 34-hr. Br^{82} activity) present at the time of extraction which was removed in 18-min. form by the extraction. The second part of Table I gives the previously published results in similar form.

Although the amount of 18-min. bromine activity left ultimately in extractable form by various chemical conditions ranges from 0 to

[12] L. J. le Roux, C. S. Lu and S. Sugden, Nature **143**, 517 (1939).

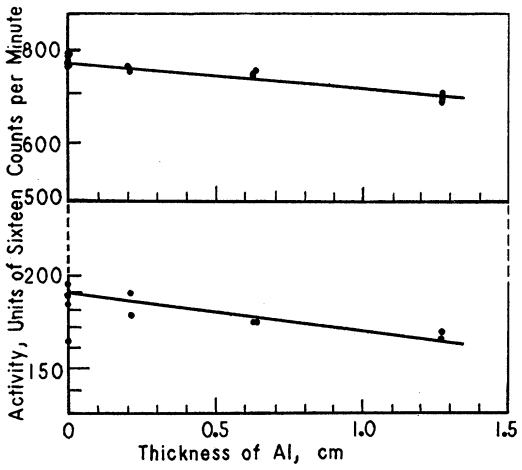

FIG. 1. Aluminum absorption of gamma-rays. Upper curve: 34-hr. Br^{80}. Lower curve: 18-min. Br^{80} purified by isomer separation technique, a small amount of 4.5-hr. and 34-hr. activities still present being corrected for. All points are corrected for decay. The similarly corrected counts without paraffin were: Upper curve, 1300; lower curve 3.0×10^5 sixteens per minute.

95 percent of the total activity (many results below 75 percent are omitted to save space), *the range of values from 79 to 90 percent (all within experimental error of about 85 percent) is reached under widely different conditions such as: with gaseous ethyl bromide and bromoform and with aqueous or alcoholic solutions of bromate, ethyl bromide and bromobenzene, and is obtained by measurements on both extract and residue. Yet only one value, probably high, was found between 91 and 100 percent.*

It seems worth while therefore to consider this apparent limitation to the amount that can be extracted as imposed by the nuclear or other processes that would not be appreciably influenced by neighboring atoms.

85 ± 4 percent of the decay of the 4.5-hr. bromine must be by conversion electron emission since it does not seem that any other process could break the bonds.[13,14] The other 15 percent could be by (1) gamma-ray emission, (2) beta-ray emission, in which the 4.5-hr. bromine goes directly to krypton, (3) conversion electron emission which occurs in another way so as practically never to lead to chemical reaction, or (4) mixtures of these. For (3) some sort of deactivation of the atom after the emission which can proceed nearly independently of neighboring atoms may be suggested. There is probably not enough difference between K- and L-electron emission either with or without Auger electrons to make the difference between possibility and impossibility of causing decomposition. (1) affords the simplest interpretation. In case of (2) the 15 percent of unextractable activity comes from 4.5-hr. bromine itself rather than from 18-min. bromine in equilibrium with it and may introduce some error into the determination of the relative amounts if it is not counted with the same efficiency as the 18-min. beta-rays.

III. DETECTION OF UNCONVERTED GAMMA-RAYS

Detection of unconverted gamma-rays should aid in interpreting the above results. Evidence for these radiations has been obtained by absorption measurements on the radiations from 4.5-hr. Br^{80}.

The detector was an aluminum-walled (60 mg per cm^2 wall thickness), argon-alcohol-filled counter coupled to a high speed scaling and counting circuit. The counter tube was surrounded by an inch or more of lead, in which was cut a window to admit the radiations. The radiations were taken from 2-mg samples of AgBr spread out on 15-mm diameter pieces of filter paper and covered with Cellophane. They were placed about 3 cm from the window in the lead, or 12 cm from the counter tube. The absorbers were placed next to the samples.

The 18-min. Br^{80} was not removed but allowed to reach equilibrium with the 4.5-hr. mother activity, and its 2-Mev beta-rays were removed by filling the window in the lead shield with paraffin 2.6 cm thick. (This amount of parafin should transmit about 11 percent of the 12-kev Br K x-rays, about 54 percent of any 25-kev gamma-rays, and about 68 percent of any 50-kev gammas.) Unfortunately, a certain amount of 34-hr. Br^{82} activity is produced with the 4.5-hr. in the neutron bombardments. For these reasons it was necessary to determine the absorption curves for both the 18-min. and the 34-hr. activities separately and to subtract them from the 4.5-hr. curve.

[13] J. E. Willard, J. Am. Chem. Soc. **62**, 256 (1940).
[14] This point has already been discussed in the literature. F. Fairbrother, Nature **145**, 307 (1940); and G. T. Seaborg, G. Friedlaender and J. W. Kennedy, J. Am. Chem. Soc. **62**, 1309 (1940).

Figure 1 shows the absorption curves in Al for the pure 18-min. and 34-hr. activities, while Fig. 2, curve *A*, shows the 4.5-hr. curve after subtraction of the 34-hr. activity (obtained by allowing the sample to stand and measuring the intensity of the 34-hr. activity after the 4.5-hr. had decayed). It is obvious from these data that there is soft radiation present in the 4.5-hr. case not present in the others.

Just how much of the gamma-radiation in the 4.5-hr. case is made up of the hard 18-min. radiation cannot be determined from Fig. 2 alone, because the measurements were not carried to a large enough thickness of aluminum. However, the absorption of these radiations by 1.73 mm of lead was also determined. The transmission through this in the 4.5-hr. case was 0.26 of the paraffin transmissible (also 0.90 for the 34-hr. and 0.9 for the 18-min.). The slope of curve *A*, Fig. 2, for the total 4.5-hr. even without correction for any of the hard component is steep enough to show that none of the soft gamma-rays would be transmitted by the lead. Curve *B*, Fig. 2, is the amount of 18-min. activity corresponding to the lead transmissible radiation. If one compares the ratio of this amount of 18-min. gamma-ray counts to the amount of beta-ray counts associated with the 4.5-hr. period (see legend under Fig. 2) with the similar ratio for the pure 18-min. (Fig. 1), there appear to be about 25 percent more beta-rays present in the 4.5-hr. sample than would correspond to the amount of 18-min. activity chosen. There is some possibility, however, that the errors in measuring the large beta-ray activities are as great as this.

Curve *C*, Fig. 2, is the difference between curves *A* and *B*. Its slope corresponds to radiation of 30 to 40 kev. It was expected that this would be a mixture of 49-kev and softer gamma-rays, but the work of Grinberg and Roussinow[11] already mentioned has shown by means of selective absorbers that it is mostly, if not entirely, 37-kev.

Grinberg and Roussinow estimated the "yield" of these rays by comparison of their intensity with the Br x-ray activity. An attempt to estimate the yield has been made here by comparison with the number of beta-rays counted from the 18-min. Br^{80} in equilibrium with the 4.5-hr. RaD was used to calibrate the counter for these gamma-rays because it is known[15] to emit about 3.5 quanta of 47-kev energy and about 22 to 30 quanta of *L* radiation (16 kev) for each 100 disintegrations. The beta-radiation from the RaE in equilibrium with the RaD was used to determine the total number of RaD disintegrations.

Using paraffin as before to cut out the beta-rays, and aluminum absorption to distinguish the electromagnetic radiations, we found the ratio of beta-counts to x-ray counts was 2760 and that of x-ray to gamma-ray counts was 2.0. If the gamma- and x-ray counts are corrected for absorption of the rays in the paraffin and the beta-rays for the fraction (approx. 25 percent)

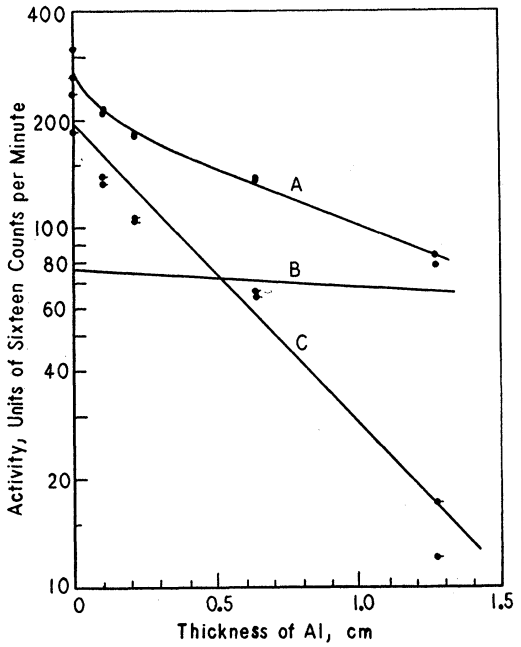

FIG. 2. Absorption by aluminum of 4.5-hr.+equilibrium 18-min. gamma-radiation. The count without paraffin was 1.6×10^5 sixteens per min. All measurements corrected for decay and 34-hr. activity present.

which would not penetrate the counter walls the efficiency of counting the x-rays becomes 0.4 percent and for the gamma-rays 0.6 percent. The fraction of Br^{80} beta-rays absorbed by the counter wall would probably be much less than for the RaE because their upper limit of energy is twice as high and the relative distribution should also be shifted toward the higher energies.

[15] The data on this are reviewed by D. D. Lee and W. F. Libby, Phys. Rev. **55**, 252 (1939).

From the data in Fig. 2 the number of counts per minute of the soft component was 3100 while the beta-radiation amounted to 2.6×10^6 counts per minute (determined after decaying about five half-lives). If the counting efficiency of the gamma-rays is 0.5 percent this gives about 37 percent as the yield of soft gamma-radiation from the 4.5-hr. transitions, after correcting for absorption in the paraffin. The determination is obviously rough. The "yield" obtained by Grinberg and Roussinow was apparently about 67 percent.

IV. Discussion

Grinberg and Roussinow[11] suggest that all of the 4.5-hr. Br^{80} decays through a completely converted 49-kev gamma-ray to an intermediate level. From this it goes to the 18-min. ground state of Br^{80} by emission of a 37-kev gamma-ray which is $\frac{1}{3}$ converted. Unless something like case (3) discussed at the end of Section II occurs, this scheme would predict the possibility of obtaining complete chemical extractions and would therefore be contrary to the evidence presented in Section II.

Several ways are still open for correlating the chemical and the physical data without invoking case (3). One is that the scheme of Grinberg and Roussinow holds for about 85 percent of the 4.5-hr. bromine and that the remainder gives beta-rays directly. If these beta-rays are not accompanied by a hard gamma-ray as are the 18-min. beta-rays, this idea finds some support in the observation that the beta-ray count from the sample analyzed in Fig. 2 seems to be too high to correspond to the number of hard gamma-rays found there. (It would be possible for example, that the 18-min. gamma-rays follow an undiscovered soft group of beta-rays so those beta-rays belonging to the 2-Mev group are not followed by gamma-rays. The proposed 4.5-hr. beta-rays would all be of the latter type.)

A second possibility would assure essentially the same scheme as Grinberg and Roussinow, but would suggest that the 49-kev transition is only about 85 percent converted. The small amount of unconverted 49-kev gamma-rays could possibly have escaped detection because of the preponderance of 37-kev radiation.

A third suggestion is that the total separation between the 4.5-hr. and the 18-min. levels of Br^{80} is 49 kev. It might then be that the one step transition is totally converted, but that the change to a level 37 kev below the 4.5-hr. (involving smaller spin change, although, also, smaller energy) is more than 15 percent unconverted. This scheme avoids the necessity of explaining why no transitions corresponding to an 86-kev jump have been found, although looked for by Valley and McCreary.[9] However, it also says that the "yield" of 37-kev gamma-rays should not be more than about 15 percent of the number of 4.5-hr. bromine atoms decaying, in contradiction to the yield found by Grinberg and Roussinow.

The present data do not seem to allow further distinction between these possibilities.

Calculations of the percentages of 18-min. bromine extracted have so far depended on the assumption that any radiations directly from the 4.5-hr. bromine do not affect the detector. The effect of the 4.5-hr. gamma-rays found here is still too small compared to the beta-ray effects to introduce appreciable error into this assumption.

It is interesting to note that the absorption data obtained on the 18-min. and 34-hr. gamma-rays, although not carried to great enough thicknesses to give much accuracy, do tend to set lower limits of 0.6 and 0.8 Mev for the energies of the two, respectively. These conclusions differ from some of the previous work[4,16] but confirm the value of 1.39 ± 0.09 Mev given by Blanc[17] for the energy of the 34-hr. gamma-ray. Blanc used coincidence counters to measure the absorption in aluminum of photoelectrons ejected by the gamma-ray.

The authors are much indebted to the staff of the Radiation Laboratory for the irradiations of many of the bromine samples on the cyclotron, and to numerous colleagues for suggestions and criticisms.

[16] B. Kourtchatow, I. Kourtchatow, L. Myssowsky, and L. Roussinow, Comptes rendus **200**, 1201 (1935).
[17] L. A. Blanc, Thesis, University of California (1937).