Hot-Atom Chemistry of Halogens in Cobaltammine Complex Salts. I. Hot-Atom Chemistry of Bromine in Bromopentammine Cobalt Complex Salts

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Many attempts have already been made to study the hot-atom effect of central atoms in metal complex salts, while very little attention has so far been paid to the hot-atom effect of ligand atoms[1].

The present authors investigated the behavior of radiobromine in ligands of bromopentammine cobalt complex salts following (n, γ) process induced by neutron irradiation. The distribution of radiobromine was studied after the salts were irradiated in different phases and at varied temperatures. The authors were especially interested in the irradiation of the complex ion loaded on a cation exchange resin, because some results were already obtained in their laboratory with respect to the behavior of hot-atoms in ion exchange resins[2].

Experimental

Samples.—Five bromopentammine cobalt complex salts were prepared by methods already known:

1. $[Co(NH_3)_5Br](NO_3)_2$[3]
2. $[Co(NH_3)_5Br](C_2O_4)$[4]
3. $[Co(NH_3)_5Br]Cl_2$[5]
4. $[Co(NH_3)_5Br]Br_2$[6]
5. $[Co(NH_3)_5Br]I_2$[7]

Their composition was checked by the spectrophotometric method and by the determination of halogen contents.

For the irradiation in resin phase, $[Co(NH_3)_5Br]^{2+}$ was adsorbed on Dowex 50 W, cation exchange resin in the hydrogen form, 8% cross-linked, consisting of 100～200 mesh beads. As the bromopentammine cobalt complex salts are aquated in the presence of moisture, the resin loaded with complex ion was dried immediately after washing, by means of suction on a sintered-glass filter for a few hours, or by means of heating at 40～60°C under reduced pressure in an Abderhalden's desiccator with phosphorus pentoxide. However, prolonged procedure of drying, especially, of heating in the Abderhalden's desiccator, caused in the meantime considerable aquation. (The remaining moisture caused aquation even after it was reduced to a very small amount by drying.)

Thus, in the case of the complex ion on the resin, not the pure complex ion but the mixture of $[Co(NH_3)_5Br]^{2+}$ and the aquated products, $[Co(NH_3)_5H_2O]^{3+}$ and Br^-, was actually irradiated. The ratio of bromo- and aquo-pentammine complex salts was estimated by determining the amount of Br^- liberated in the aquation reaction 1;

$$[Co(NH_3)_5Br]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + Br^- \qquad (1)$$

and was shown in Table III. The procedure of determination was as follows: the dried resin with the mixture was washed with water, and Br^- which had been liberated was extracted and determined volumetrically.

Irradiation.—The neutrons produced by Be-D reaction in a cyclotron were thermalized. The flux was approximately 10^7 neutrons/cm^2 sec. The samples were irradiated for two to three hours at room temperature or at a lower temperature (−72°C). For the irradiation at room

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[1] A. W. Adamson and J. M. Grunland, *J. Am. Chem. Soc.*, **73**, 5508 (1951).

[2] N. Saito, M. Furukawa and I. Tomita, *J. Chem. Phys.*, **27**, 1432 (1957); N. Saito, I. Tomita and M. Furukawa, Presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

[3] S. M. Jörgensen, *J. prakt. Chem.*, [2] **19**, 62 (1879).

[4] S. M. Jörgensen, ibid., [2] **19**, 67 (1879).

[5] S. M. Jörgensen, ibid., [2] **19**, 55 (1879).

[6] H. S. Booth, "Inorganic Syntheses", Vol. I, McGraw-Hill Book Co., Inc., New York (1939), p. 186.

[7] F. Ephraim, *Ber.*, **56**, 1513 (1923).

temperature, the samples were placed in a paraffin block, while for the irradiation at $-72°C$, they were put in a test tube immersed in a mixture of dry ice and ethanol in a Dewar's vessel.

The complex salts as aqueous solutions or adsorbed on the resin and dipped in water were irradiated with their container immersed in a mixture of ice and water.

Procedures of Separation.—Solid samples were dissolved in water one to four hours after the end of irradiation. (The samples irradiated at a lower temperature were kept at room temperature after the irradiation was over.) The solution was poured into a $1.5\,\text{cm.}\times 0.8\,\text{cm}^2$ column of Dowex 50 W in the hydrogen form*, 8% cross-linked, 100∼200 mesh. The column was then washed with water until the total volume of the effluent amounted to 100 ml. The effluent yielded the first fraction containing anions of the sample solution and radiobromine leached out as anions**. The complex ions were adsorbed on the cation exchange resin so firmly that none of them could be detected spectrophotometrically in the first fraction.

The resin loaded with the complex ions was then immersed in water and digested on a bath at 70 to 85°C for about an hour. As the aquation of the bromopentammines was very rapid at elevated temperatures, ligand bromine including radioisotopes was almost completely aquated with this procedure and was extracted by water as the bromide ion. The extract was separated from the resin and aquo complex ion. The extract and the washing yielded the second fraction.

The complex salts irradiated as solutions were treated in the same way as the solids except that precautions were taken to prevent the aquation before the separation process.

The treatment of the complex ion in the resin phase was as follows. The irradiated resin and complex ion were put into a sintered-glass filter of 1 cm. in diameter containing from about a half to an equal volume of Dowex 50 W, 8% cross-linked, (hydrogen form), at the bottom. The size of the column was about $0.8\text{cm}^2\times 4\sim 5\text{cm}$. The column was immersed in water and then washed by suction with 250∼300 ml. of cold water. The washing yielded the first fraction. The resin and the complex ion were digested with water, and the extract yielded the second fraction. In this case, the resin with the aquo complex ion still contained considerable activity which could hardly be removed by further digestion with hot water, or by treatment with inorganic acids or with a reducing agent ($0.3\,\text{M}$ $NaHSO_3+0.2\,\text{M}$ H_2SO_4). This was the third fraction.

Measurements were made on each fraction with respect to the gross activity of ^{80m}Br (actually, of its daughter, ^{80}Br, in equilibrium) and ^{82}Br, and with respect to the content of bromine.

In order to eliminate the hot-atom effect of ^{80}Br ($T_{1/2}=18$ min.) following the isomeric transition from ^{80m}Br, measurements of activity were made more than three hours after the first fraction had been separated. Thus the gross hot-atom effect of ^{80m}Br and ^{82}Br was observed in this investigation. The ratio of activities of the two isotopes, ^{80m}Br and ^{82}Br, was about 15 : 1 at the end of irradiation, while 5.5 hr. after the end of irradiation it became 8 : 1. The distribution of activity was calculated for each sample by referring to a definite time (5.5 hr. after the end of irradiation).

Activity was measured with either an immersion-type G-M tube or an end-window G-M tube. Silver bromide precipitates were mounted on counting dishes in the latter case.

Bromide was determined volumetrically by Mohr's method or colorimetrically by the method of Stenger and Kolthoff[8]. The amounts of bromine retained in the resin were estimated by radioactivation analysis.

Results and Discussion

Hot-Atom Chemistry in Solids.—The results of measurements on the solid complex salts are shown in Table I. In any of the complex salts investigated, over eighty per cent of radiobromine atoms was leached out into water with an enrichment factor of at least 50. As the maximum recoil energy of radiobromine resulting from slow neutron capture was calculated to be 174 eV.[9], and this is large enough to break Co–Br bond, such a high extractability may not be unexpected.

The column F–2 in Table I is expected to denote the fraction of radiobromine retained in the ligands of the cobalt complex salts. When a bromine atom in $[Co(NH_3)_5Br]^{2+}$ recoils following the neutron capture, the bond between the metal and the bromine is broken and the resulting hot-atom may have several collisions with the surrounding molecules or atoms before it slows down. In the hot reactions with the recoiling bromine or in the recombination reactions which follow them, complex ions such as $[Co(NH_3)_4BrBr^*]^+$ may probably be produced*** as well as $[Co(NH_3)_5Br^*]^{2+}$ (Br^* denotes radiobromine). As

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* Potassium form was also used, but the results were not significantly different from those obtained with hydrogen form.

** It was reported by Saito, Tomita and Furukawa that most of radiobromine produced in the neutron irradiation of bromates was found in the form of bromide (presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958).

[8] V. A Stenger and I. M. Kolthoff, *J. Am. Chem. Soc.*, 57, 831 (1935).

[9] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry", John Wiley & Sons, Inc., New York (1951), p. 247.

*** The replacement of an ammine group by hot bromine was proved by the fact that ligand yield as $[Co(NH_3)_5Br]^{2+}$ of about 5% was obtained in the irradiation of $[Co(NH_3)_6]Br_3$ with slow neutrons. Details will be published elsewhere.

TABLE I. DISTRIBUTION OF ^{80m}Br AND ^{82}Br ACTIVITY AND ENRICHMENT FACTOR IN SOLIDS

Complex salt	Irradiation at room temp. F-1 %	F-2* %	Irradiation at −72°C F-1 %	F-2* %	Enrichment factor of F-1
$[Co(NH_3)_5Br](NO_3)_2$	83.9	16.1	87.3	12.7	1×10^2
$[Co(NH_3)_5Br](C_2O_4)$	82.6	17.4	—	—	0.5×10^2
$[Co(NH_3)_5Br]Cl_2$	82.2	17.8	84.2	15.8	0.5×10^2
$[Co(NH_3)_5Br]Br_2$	82.7	17.3	82.6	17.4	—
$[Co(NH_3)_5Br]I_2$	87.6	12.4	—	—	2×10^2

* Ligand yield as $[Co(NH_3)_5Br^*]^{2+}$. These values were reproducible in at least three runs within 0.4∼0.7% standard deviation.

both complex ions are cationic, the second fraction essentially includes the activity in the form of $[Co(NH_3)_4BrBr^*]^+$ besides $[Co(NH_3)_5Br^*]^{2+}$. The probability of the formation of complex ions containing more than two bromine atoms in ligands may be negligibly small.

For the convenience of discussion, the authors defined a quantity $(L.Y.)_A$, "ligand yield in the form of A", which indicated the fraction of total produced activity retained in the form of the complex ion, A. The value in the second fraction is then the summation of ligand yields of all the complex cations; $(L.Y.)_{[Co(NH_3)_5Br^*]^{2+}}$ and $(L.Y.)_{[Co(NH_3)_4BrBr^*]^+}$ (*cis*- and *trans*-isomers).

In this case, however, all the tetrammine complex salts containing radiobromine are much more unstable and are much more rapidly aquated with liberation of bromine than the pentammine complex salts are. The aquation reactions are

$$[Co(NH_3)_4Br_2]^+ + H_2O \rightarrow [Co(NH_3)_4BrH_2O]^{2+} + Br^- \qquad (2)$$

$$[Co(NH_3)_4BrH_2O]^{2+} + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + Br^- \qquad (3)$$

Radiobromine in the tetrammine complex salts is liberated and enters the first fraction, through either of these reactions. Half time of the aquation reactions in nearly neutral aqueous solutions were estimated to be a few minutes at 15∼20°C, while that of reaction 1 was estimated to be about a hundred hours[10].

In this investigation, the irradiated complex salts were dissolved in water (pH 5∼6) at room temperature and kept in solutions for a sufficiently long time in order to eliminate $(L.Y.)_{[Co(NH_3)_4BrBr^*]^+}$ from the second fraction. When all the unstable complex ions were aquated and only the pentammine remained, the curve for the observed activity of the second fraction vs. the period of separation (period of standing in water) leveled off****. Therefore the distribution of activity in the second fraction in Table I may be taken as almost identical with the ligand yield in the form of $[Co(NH_3)_5Br^*]^{2+}$, or so-called "retention".

As seen in Table I, ligand yield as $[Co(NH_3)_5Br^*]^{2+}$ of the complex salts does not vary appreciably as the anionic component is replaced, except that the iodide shows considerably low yield. The irradiation at a lower temperature decreases the yield in some salts, while in the bromide the yield remains almost unchanged. It is interesting to note that the bromide shows almost the same yield as other salts in the irradiation at room temperature: the hot-atoms resulting from the anions may behave in the same way as those from ligands of the complex salts.

Hot-Atom Chemistry in Aqueous Solutions.— The results of measurements of aqueous solutions of the complex salts are shown in Table II. In this case, practically all radiobromine was leached out into the first fraction.

Hot-Atom Chemistry in Resin Phase. — As shown in Table III, about 80% of the total activity was extracted into the first fraction with enrichment factors of 3∼40 when the irradiated resin and complex ion was washed with water. Nine to thirteen per cent of the activity was retained in the ligands (F-2). More than 9% of the total activity remained in the resin even after the aquation of the complex ion on the resin had been brought to completion (F-3).

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[10] A. B. Lamb and J. W. Marden, *J. Am. Chem. Soc.*, **33**, 1873 (1911); J. N. Bronsted and R. Livingston, ibid., **49**, 435 (1927).

**** By means of extrapolation of the curves to the separation time zero, approximate values of unstable ligand yields (i. e. as $[Co(NH_3)_4BrBr^*]^+$) were roughly estimated to be about 2∼5%.

TABLE II. DISTRIBUTION OF ^{80m}Br AND ^{82}Br ACTIVITY AND ENRICHMENT FACTOR IN SOLUTIONS

Complex salt	Concentration	Irradiation at 0~3°C F-1 %	Irradiation at 0~3°C F-2 %	Enrichment factor of F-1
$[Co(NH_3)_5Br](NO_3)_2$	7×10^{-3} M	99.2	0.8±0.6	0.4×10^2
$[Co(NH_3)_5Br](NO_3)_2$	8×10^{-4} M	nearly 100	nearly 0	0.4×10^2

TABLE III. DISTRIBUTION OF ^{80m}Br AND ^{82}Br ACTIVITY AND PERCENTAGE OF AQUATION IN RESIN PHASE

Condition of drying	Temp. of irradiation	Distribution of activity F-1 %	Distribution of activity F-2 %	Distribution of activity F-3 %	Percentage of aquation (aquo-complex %)
Suction	room temp.	80.0	10.7	9.3	11~20
	−72°C	81.1	9.3	9.6	5~ 9
Abderhalden	room temp.	80.2	10.7	9.1	15~42
	−72°C	80.5	8.9	10.6	9~21
Without drying	0~13°C (dipped in water)	76.5	13.0	10.5	2~ 4

As mentioned above, the mixture of bromo- and aquo-pentammine complex ions and the liberated bromine was irradiated on the cation exchange resin. The "percentage of aquation" is shown in Table III. Therefore, the interpretation of the activity in the second fraction is more complicated in the resin phase than in solids. The complex cations possibly produced through the hot-atom effect in the irradiation of the mixture are as follows:

a) from $[Co(NH_3)_5Br]^{2+}$,

$$\begin{cases}[Co(NH_3)_5Br^*]^{2+}\\ [Co(NH_3)_4BrBr^*]^{+}\end{cases}$$

b) from $[Co(NH_3)_5H_2O]^{3+}$,

$$\begin{cases}[Co(NH_3)_5Br^*]^{2+}\\ [Co(NH_3)_4Br^*H_2O]^{2+}\end{cases}$$

Radiobromine in ligands of the unstable complex ions other than the bromopentammine may be considerably aquated during the separation process and eluted into the first fraction. However, these aquation reactions do not proceed as rapidly in the resin in the hydrogen form as in the solutions of the irradiated solids, because the rate of reaction 3 is dependent on the pH of solution and it becomes much slower in acid solutions[11].

In the cation exchange resin in the hydrogen form, the pH of the effluent was measured and found to be less than 3, where half time of reaction 3 was several hundred minutes. Therefore, as far as the products of reactions a) are concerned, only about 50% of $(L.Y.)_{[Co(NH_3)_4BrBr^*]^+}$ may be eliminated from the second fraction through the aquation reaction 2 which is almost completed during the period of separation in this investigation, but reaction 3 may not proceed appreciably in the meantime. Similarly, the products of reactions b) may remain without being aquated during the period of separation.

By making suitable assumptions, the authors estimated ligand yields of the above complex ions separately. According to the investigations now being made in their laboratory[12] a considerable fraction of hot bromine resulting from anionic sphere was enriched in ligands of pentammine cobalt complex salts, $[Co(NH_3)_5Y]Br_{(2\text{ or }3)}$, when they were irradiated with slow neutrons. The value of $(L.Y.)_{[Co(NH_3)_5Br^*]^{2+}}$ for $[Co(NH_3)_5H_2O]Br_3$ sample was 7~8%, which was about a half of that in $[Co(NH_3)_5Br]Br_2$. By assuming that $(L.Y.)_{[Co(NH_3)_5Br^*]^{2+}}$ due to aquo- and bromo- pentammine complex ions in the mixture adsorbed on the resin are in the same ratio (i.e. about 1/2) as those separately obtained in the irradiation of solids of these complex salts, the ligand yields in bromopentammine cobalt complex ion corrected for aquation were calculated and are listed in Table IV. These values, however, may be larger than $(L.Y.)_{[Co(NH_3)_5Br^*]^{2+}}$ by about 50% of $(L.Y.)_{[Co(NH_3)_4BrBr^*]^+}$ (i.e. 1~2%)[13].

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[11] J. N. Brönsted, *Z. physik. Chem.*, **122**, 383 (1926).

[12] Results were partly reported at the 12th Annual Meeting of the Chemical Society of Japan, April, Kyoto, 1959. Details will be published elsewhere.

[13] Ligand yields of the tetrammine complex salts were estimated as about 1~4%.

TABLE IV. LIGAND YIELDS IN BROMOPENTAMMINE COBALT COMPLEX ION ON THE RESIN CORRECTED FOR AQUATION

Condition of drying	Temp. of irradiation	Ligand yields* %
Suction	room temp.	12.0
	−72°C	10.4
Abderhalden	room temp.	13.4
	−72°C	10.7
Without drying	0∼13°C (dipped in water)	13.0

* Ligand yields may include $(\mathrm{L.Y.})_{[\mathrm{Co(NH_3)_5Br^*}]^{2+}}$ and about 1/2 of $(\mathrm{L.Y.})_{[\mathrm{Co(NH_3)_4BrBr^*}]^{+}}$.

As seen in Table IV, the ligand yields in bromopentammine on the cation exchange resin are 10∼13% and lower than those obtained in solids. The yields decreased slightly when the samples were irradiated at a lower temperature. It is interesting to note that the presence of water in the samples did not influence the yields appreciably. Even in the case where the complex and the resin were dipped in water during the irradiation, the yields were not greatly different from those for the samples dried in the Abderhalden's desiccator. This may be understood as indicating that the rate of exchange of ligand bromine of bromopentammine with bromide ion in aqueous solutions is very slow and that the aquation reaction 1 does not disturb the mechanism of recombination from which some portion of the ligand yield may result.

Nearly 10% of the total activity was retained in the irradiated resin after the treatments described above. The enrichment factor of radiobromine in this fraction (F-3) was estimated as at least 100. The exchange reaction between the bromine remaining in the resin and bromide ion in water was regarded as being very slow even at elevated temperatures (70∼85°C). The reducing agent decreased the activity in the resin only slightly. The irradiation at a lower temperature increased the activity in the resin slightly.

It was presumed from these observations that most of the radiobromine remaining in the leached resin would be organically combined with the resin matrix: some results in favor of this conclusion were reported by Carlson and Koski[14].

Summary

The hot-atom effect was investigated on ^{80m}Br and ^{82}Br resulting from (n, γ) processes in ligand bromine of bromopentammine cobalt complex salts. The fraction of radiobromine retained in ligand (ligand yield) was compared for samples irradiated in different phases, and it increased in the following order: solution, resin, solid. It is interesting to note that in the irradiation of solids of bromopentammines $[\mathrm{Co(NH_3)_5Br}]\mathrm{Br_2}$ showed almost the same ligand yield as other salts. The hot-atoms resulting from the anions may behave in the same way as those from ligands of the complex salts. The exchange of ligand bromine in these complex salts with bromide in water was regarded as being very slow at room temperature.

In the irradiation of the complex ion adsorbed on a cation exchange resin, a considerable fraction of radiobromine was trapped in the resin matrix. Treatments with either inorganic acids or a reducing agent did not remove the activity appreciably. Most of the radiobromine remaining in resin was presumed to be organically combined with the matrix.

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[14] T. A. Carlson and W. S. Koski, *J. Chem. Phys.*, **23**, 2410 (1955).