Hot-Atom Chemistry of Halogens in Cobaltammine Complex Salts. II. Hot-Atom Chemistry of Radiobromine in Pentammine Cobalt(III) Bromides and Bisethylenediamine Cobalt(III) Bromides

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Among a number of studies of the hot-atom chemistry of complex compounds, only a few have contributed to elucidate the recoil reactions of ligand atoms or outer anions[1-6].

In the first paper of this series[2], the present authors reported on the behavior of radiobromine recoils in some neutron-irradiated bromopentammine cobalt(III) complex salts. They

1) A. W. Adamson and J. M. Grunland, *J. Am. Chem. Soc.*, **73**, 5508 (1951).
2) N. Saito, H. Sano and T. Tominaga, This Bulletin, **33**, 20 (1960).
3) N. Saito, T. Tominaga and H. Sano, ibid., **33**, 120 (1960).
4) H. Rauscher, N. Sutin and J. M. Miller, *J. Inorg. & Nuclear Chem.*, **12**, 378 (1960).
5) N. Ikeda, K. Yoshihara and S. Yamagishi, This Bulletin, **34**, 139 (1961).
6) G. Harbottle, Paper presented at the IAEA Symposium on the Chemical Effects of Nuclear Transformations, Prague, October, 1960.

found that radiobromine recoil atoms arising from thermal-neutron capture in outer anions of cobaltammine bromides could substitute in the cobalt co-ordination sphere to produce radiobromine-labeled complex cations[3].

In order to investigate the mechanism of such substitution of ligands by radiobromine recoil atoms, the present authors irradiated, with slow neutrons, solid complex salts of the formulas $[Co(NH_3)_5X]Br_{2,3}$ and $[Co(en)_2X_2]\cdot Br_{1,3}$, all of which contained different kinds of ligand (X), and bromine atoms outside the co-ordination sphere. It was found that the fraction of total radiobromine produced finally retained in ligands varied with the kind of ligand group, X, in each complex. A model has been proposed by the present authors to explain the experimental results.

Experimental

Sample.—Seventeen cobaltammine complex salts were prepared by well-known methods described in the literature:

1) $[Co(NH_3)_6]Br_3$[7]
2) $[Co(NH_3)_5NCS]Br_2$[8]
3) $[Co(NH_3)_5NO_2]Br_2$[9]
4) $[Co(NH_3)_5OH_2]Br_3$[10]
5) $[Co(NH_3)_5ONO]Br_2$[11]
6) $[Co(NH_3)_5ONO_2]Br_2$[12]
7) $[Co(NH_3)_5F]Br_2$[13]
8) $[Co(NH_3)_5Cl]Br_2$[14]
9) $[Co(NH_3)_5I]Br_2$[15]
10) $[Co(NH_3)_5Br]Br_2$[16]
11) $[Co(en)_3]Br_3\cdot 3H_2O$[17]
12) *trans*-$[Co(en)_2(NH_3)_2]Br_3\cdot H_2O$[18]
13) *trans*-$[Co(en)_2(NCS)_2]Br\cdot 1^1/_2\ H_2O$[19]
14) *cis*-$[Co(en)_2(NCS)_2]Br\cdot H_2O$[20]
15) *trans*-$[Co(en)_2Cl_2]Br$[21]
16) *cis*-$[Co(en)_2Cl_2]Br\cdot H_2O$[22]
17) *trans*-$[Co(en)_2Br_2]Br$[23]

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

Irradiation.—Bombardments were made under conditions previously described[2].

Procedures of Separation.—The procedures of separation were similar to those employed for solid samples in the previous paper[2]. Two fractions were separated by means of a procedure involving a cation-exchange resin after dissolution of the activated salt. The first fraction contained bromide ions in the sample solution and anionic radiobromine. The second fraction contained ligand bromine, including its radioisotopes, which had been aquotized through digestion on a warm-bath and then extracted with water.

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 to the bromine content. The methods of determination have all been described previouly[2]. Although the hot-atom effects of ^{80m}Br and ^{82}Br, both arising from (n, γ) reactions, were observed at the same time, the contribution of ^{82}Br to the gross activity was, practically, small.

For convenience of discussion, the authors have defined the quantity "ligand yield", which indicates the fraction of the total activity produced retained in ligands of complex ions. "Ligand yield" was calculated as follows:

$$\text{Ligand yield} = \frac{\left(\begin{array}{c}\text{the activity of the}\\ \text{2nd fraction}\end{array}\right)}{\left(\begin{array}{c}\text{sum of the activtiy of the}\\ \text{1st and the 2nd fraction}\end{array}\right)} \times 100$$

Results and Discussion

Ligand Yield.—It was found by the present authors that energetic radiobromine atoms arising from the outside of the co-ordination sphere could substitute for ligands in these cobaltammine complex salts. The fraction of the radiobromine atoms retained in the ligands, or the ligand yield, is shown in Tables I and II.

As various complexes labeled with radiobromine (Br*) might be produced through reactions of hot radiobromine atoms with the target complex, the observed ligand yield was expected to be the sum of the fractions of radiobromine retained in ligands of such labeled complexes. Thus, on the irradiation of the complex salts of the formula $[Co(NH_3)_5X]Br_{2,3}$, some unstable radiobromine-labeled complexes ($[Co(NH_3)_4XBr^*]^{1,2+}$, etc.) of which the present authors have not yet confirmed the existence, might possibly be formed at first as

7) W. C. Fernelius, "Inorganic Syntheses", Vol. 2, McGraw-Hill Book Co., Inc., New York (1946), p. 216.
8) A. Werner and H. Müller, *Z. anorg. Chem.*, **22**, 108 (1900).
9) A. Werner and A. Miolati, *Z. physik. Chem.*, **12**, 43 (1893).
10) S. M. Jörgensen, *J. prakt. Chem.*, [2], **31**, 62 (1885).
11) The salt was precipitated by ammonium bromide from an aqueous solution of chloride prepared by the method of Jörgensen (*Z. anorg. Chem.*, **5**, 168 (1894).).
12) S. M. Jörgensen, *J. prakt. Chem.*, [2], **23**, 227 (1881).
13) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **266**, 49 (1951).
14) S. M. Jörgensen, *J. prakt. Chem.*, [2], **18**, 221 (1878).
15) R. G. Yalman, *J. Am. Chem. Soc.*, **77**, 3219 (1955).
16) H. S. Booth, "Inorganic Syntheses", Vol. 1, McGraw-Hill Book Co., Inc., New York (1939), p.186.
17) A. Werner, *Ber.*, **45**, 121 (1912).
18) A. Werner, *Ann.*, **386**, 194 (1912).
19) A. Werner and Braünlich, *Z. anorg. Chem.*, **22**, 139 (1900).
20) A. Werner and Braünlich, ibid., **22**, 147 (1900).
21) S. M. Jörgensen, *J. prakt. Chem.*, [2], **41**, 441 (1890); W. C. Fernelius, "Inorganic Syntheses", Vol. 2, McGraw-Hill Book Co., Inc., New York (1946), p. 222.
22) W. C. Fernelius, ibid., Vol. 2, p. 223; P. Larisch, Dissertation, Zürich (1904), p. 87.
23) A. Werner, L. Gerb, S. Lorie and J. Rapiport, *Ann.*, **386**, 111 (1912).

TABLE I. LIGAND YIELD OF IRRADIATED COMPLEX SALTS, $[Co(NH_3)_5X]Br_{2,3}$

No.	Irradiated salt	Ligand yield[a], %	Enrichment factor
1	$[Co(NH_3)_6]Br_3$	4.8±0.2	4×10^2
2	$[Co(NH_3)_5NCS]Br_2$	5.7±0.3	1.2×10^2
3	$[Co(NH_3)_5NO_2]Br_2$	8.0±0.3	4×10^2
4	$[Co(NH_3)_5OH_2]Br_3$	7.1±0.7	0.2×10^2
5	$[Co(NH_3)_5ONO]Br_2$	8.8±0.1	9×10^2
6	$[Co(NH_3)_5ONO_2]Br_2$	9.0±0.3	0.3×10^2
7	$[Co(NH_3)_5F]Br_2$	7.3±0.6	6×10^2
8	$[Co(NH_3)_5Cl]Br_2$	15.2±0.4	3×10^2
9	$[Co(NH_3)_5I]Br_2$	15.8±0.4	5×10^2
10	$[Co(NH_3)_5Br]Br_2$	17.3±0.6	—

a) The ligand yield is nearly identical with the fraction (%) of radiobromine in the form of $[Co(NH_3)_5Br^*]^{2+}$.

TABLE II. LIGAND YIELD OF IRRADIATED COMPLEX SALTS, $[Co(en)_2X_2]Br_{1,3}$

No.	Irradiated salt	Ligand yield[b], %	Enrichment factor
11	$[Co(en)_3]Br_3\cdot 3H_2O$	0.0±0.1	—
12	*trans*-$[Co(en)_2(NH_3)_2]\cdot Br_3\cdot H_2O$	0.8±0.1	0.8×10^2
13	*trans*-$[Co(en)_2(NCS)_2]\cdot Br\cdot 1^1/_2H_2O$	4.5±0.2	6×10^2
14	*cis*-$[Co(en)_2(NCS)_2]Br\cdot H_2O$	5.0±0.1	4×10^2
15	*trans*-$[Co(en)_2Cl_2]Br$	16.6±0.3	5×10^3
16	*cis*-$[Co(en)_2Cl_2]Br\cdot H_2O$	17.9±0.3	4×10^3
17	*trans*-$[Co(en)_2Br_2]Br$	37 ±2	—

b) The ligand yield denotes the fraction (%) of radiobromine in the form of $[Co(en)_2XBr^*]^{1,2+}$

well as the complex $[Co(NH_3)_5Br^*]^{2+}$. However, almost all radiobromine-labeled complexes other than $[Co(NH_3)_5Br^*]^{2+}$ were extremely unstable in aquotization, and adequate procedures of separation made it possible to determine the ligand yield as nearly entirely due to the stable complex $[Co(NH_3)_5Br^*]^{2+}$, without any appreciable contribution from unstable complexes.

In this investigation, the irradiated complex salts had been kept standing in aqueous solutions at room temperature for a sufficiently long time before the completion of the separation of the first fraction. By this treatment, most of the unstable radiobromine-labeled complexes, if they did exist at all, were aquotized and the labile radiobromine atoms extracted as anions into the first fraction, whereas the complex $[Co(NH_3)_5Br^*]^{2+}$ was not aquotized practically, keeping the radiobromine in ligands (i. e., in the second fraction). Therefore, the ligand yield shown in Table I may be considered to be nearly identical with the fraction of radiobromine in the form of $[Co(NH_3)_5Br^*]^{2+}$, which might be synthesized through replacement of X in $[Co(NH_3)_5X]^{2,3+}$ by Br*.

On the irradiation of the salts of the formula $[Co(en)_2X_2]Br_{1,3}$, the probability of the replacement of ethylenediamine molecules with radiobromine seemed to be very small (Table II). Thus, the ligand yield shown in Table II may be taken as indicating the fraction of radiobromine in the form of $[Co(en)_2XBr^*]^{1,2+}$.

Mechanism of Substitution of Ligands by Hot Radiobromine Atoms.—For both groups of complex salts shown in Tables I and II, the ligand yield was found to vary with the kind of ligand, X. Attempts to find the relationship between the ligand yield and the chemical or physical properties of the ligand X, might contribute to clarifying the mechanism by which radiobromine atoms substitute for ligands of the complex salts.

If radioactive complexes, $[Co(NH_3)_5Br^*]^{2+}$ and $[Co(en)_2XBr^*]^{1,2+}$, were produced through substitution of X in the target complex by a hot radiobromine atom (Br*), the ligand yields in the forms of such labeled complexes might be related to the stability of the ligand, X. With the cobalt complex salts studied in the present work, the relationship between their stability and the wavelength of the maximum in their optical absorption bands has been known as the spectrochemical series. In Fig. 1, the ligand yield was plotted against the frequency

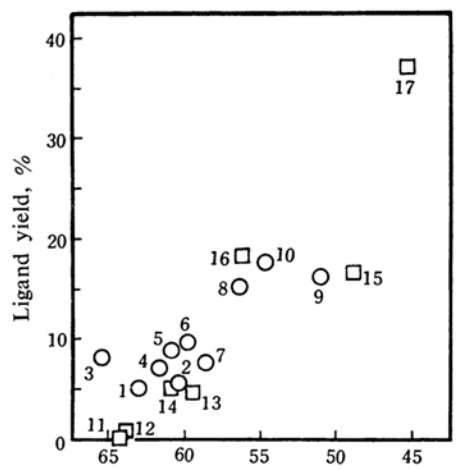

Fig. 1. The relationship between the ligand yield and the frequency of the maximum in the first absorption band.
○ $[Co(NH_3)_5X]Br_{2,3}$
□ $[Co(en)_2X_2]Br_{1,3}$
Numbers in Figs. 1 and 2 correspond to those in Tables I and II.

of the maximum in the first absorption band of the target complex. Fig. 1 shows that the ligand yield roughly tends to increase with the decrease in the frequency of the maximum in the first absorption band or with the decrease in the stability of the ligand, X: the less stable the ligand X is, the more easily it is substituted for by hot radiobromine. However, the ligand yield in some complex salts was incompatible with the general tendency. For example, the ligand yield in $[Co(NH_3)_5 \cdot NO_2]Br_2$, which contained a very stable ligand NO_2, was considerably high, and the ligand yield in $[Co(NH_3)_5F]Br_2$, $[Co(NH_3)_5Cl]Br_2$, $[Co(NH_3)_5Br]Br_2$ and $[Co(NH_3)_5I]Br_2$, all of which contained halogen atoms (F, Cl, Br, I), did not increase in the order of the spectrochemical series.

As the maximum recoil energy of radiobromine resulting from slow neutron capture was calculated to be 174 eV.[24], most radiobromine atoms would recoil with energies larger than those which were involved in ordinary thermal reactions. Therefore, the present authors assumed a model in which collisions of a hot bromine atom with the donor atom in ligand X played an important role. When the masses of the donor atom in ligand X and of a bromine atom are M and M′ respectively, the fraction of the maximum possible loss in the recoiling energy of a hot bromine atom in an elastic collision with the donor atom is given as:

$$\gamma = 4MM'/(M+M')^2. \quad (1)$$

The calculated values of γ for donor atoms in different ligands, X, are shown in Table III. Fig. 2 shows the relationship between the ligand yield and the γ value for the complex salts listed in Tables I and II. As each complex molecule of the salts of the formula $[Co(en)_2X_2]Br_{1,3}$ contains more X's in ligands than that of $[Co(NH_3)_5X]Br_{2,3}$, the probability of the collision of a hot radiobromine atom with X may be somewhat larger for the salts

TABLE III. CALCULATED VALUES OF γ FOR THE DONOR ATOM IN LIGAND X IN A COLLISION WITH A HOT BROMINE ATOM

X	Donor atom	$\gamma=4MM'/(M+M')^2$
NH_3, NCS, NO_2	N	0.50
OH_2, ONO, ONO_2	O	0.56
F	F	0.64
Cl	Cl	0.85
I	I	0.95
Br	Br	1.00

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

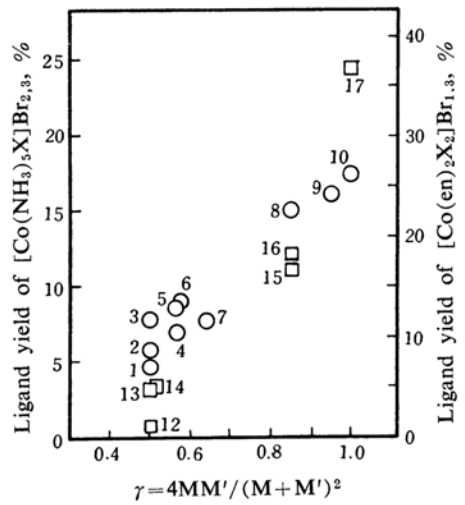

Fig. 2. The relationship between the ligand yield and the value of γ.

○ $[Co(NH_3)_5X]Br_{2,3}$
□ $[Co(en)_2X_2]Br_{1,3}$

of the former series*. Based on the available crystallochemical data, the ratio of relative collision cross sections of a bromine atom with X in ligands was estimated as about 1.5 : 1 for $[Co(en)_2X_2]Br$ and $[Co(NH_3)_5X]Br_2$. For convenience of comparison, these two series of complex salts, which did not seem much alike in crystal structure, are both shown in Fig. 2. Different ligand yield scales were used in Fig. 2 for the two series, considering the ratio of collision cross sections shown above. It is seen in Fig. 2 that the ligand yield tends to increase as the value of γ of the donor atom in ligands increases: the efficiency of replacement of X by a hot radiobromine atom depends mainly on γ.

It can be predicted on the collision model that a ligand group with the donor atom of a larger γ-value is more readily replaced by a hot radiobromine atom. As the experimental results are well explained by this model, the present authors presume that the kinetic processes might play an important role in determining the fate of hot radiobromine atoms, at least in the above solid complex salts. In addition to the kinetic processes, some chemical processes might contribute to determine the ligand yield at some stages in recoil reactions. However, it has not been unequivocally shown in the present work how much contribution such chemical processes make to the recoil reaction.

* Though the presence of crystalline water in some of the salts of the $[Co(en)_2X_2]Br_{1,2}$ series might possibly have more or less influence upon recoil reactions, the effect is not fully investigated in the present work.

Summary

The fate of energetic radiobromine atoms arising from the (n, γ) reaction on bromine in solid complex salts of the formulas $[Co(NH_3)_5X]Br_{2,3}$ and $[Co(en)_2X_2]Br_{1,3}$, was investigated. The fraction of the total radiobromine produced finally retained in ligands (ligand yield) was found to increase with a function of the mass of the donor atom in ligand X. Therefore, it was suggested that the kinetic processes might play an important role in recoil reaction in the solid complex salts.

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