Behavior of Energetic Radiobromine Atoms Arising from (n, γ) Reaction in Cobalt Complex Salts

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In the course of the investigation on the behavior of hot radiobromine atoms (^{80m}Br and ^{82}Br) in bromopentammine cobalt complex salts[1], the present authors found that some of such energetic radiobromine atoms arising from (n, γ) reaction either in ligand bromine or in anionic bromine eventually entered ligands of the complexes through formation of chemical bond with the cobalt atom. When solid complex salts, $[Co(NH_3)_5Y]Br_{2,3}$ and $[Co(en)_2Y_2]Br_{1,3}$, were irradiated, the fraction of total produced radiobromine finally retained in ligands (hereafter defined as "ligand yield") was found to vary with changing ligand group, Y. In order to clarify the mechanism of hot-atom behavior of radiobromine in these systems, the present authors investigated the effects of various ligands on the ligand yields in these complex salts.

Experimental procedures were similar to those described in the previous paper[1]. Distribution of radiobromine was determined by a procedure involving separation with a cation exchange resin.

As shown in Tables I and II, enrichment of radiobromine in ligands was observed with these complex salts. On the irradiation of the salts $[Co(NH_3)_5Y]\cdot Br_{2,3}$, several complexes labeled with Br* ($[Co(NH_3)_5Br^*]^{2+}$, $[Co(NH_3)_4YBr^*]^{1,2+}$, etc.) might possibly be produced through reactions of hot radiobromine atoms with the target complex. However, almost all labeled complexes other than $[Co(NH_3)_5\cdot Br^*]^{2+}$ were extremely unstable to aquotization in aqueous solutions, and it was possible with adequate procedures of separation to obtain the ligand yield without appreciable contribution of yields in the forms of unstable labeled complexes, $[Co(NH_3)_4YBr^*]^{1,2+}$ etc. Therefore, the ligand yield in Table I may be taken as almost identical with the fraction of radiobromine stabilized in the form of $[Co\cdot(NH_3)_5Br^*]^{2+}$, or that obtained through replacement of Y by Br*. On the irradiation of the salts $[Co(en)_2Y_2]Br_{1,3}$, the probability of replacement of ethylenediamine in ligands seemed to be very small. Thus, the ligand yield in Table II may be taken as indicating the fraction of radiobromine in the form of $[Co(en)_2YBr^*]^{1,2+}$. It is interesting that no significant differences were observed between the ligand yields of *cis*- and *trans*-isomers of both $[Co(en)_2(NCS)_2]Br$ and $[Co(en)_2Cl_2]Br$.

To explain the relationship between ligand yield and Y, the present authors proposed a model in which collisions of

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[1] N. Saito, H. Sano and T. Tominaga, This Bulletin, 33, 20 (1960).

Table I. Ligand yield of solid $[Co(NH_3)_5Y]Br_{2,3}$

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) $\text{Ligand yield}=\dfrac{\text{Activity of Br* retained in ligands}}{\text{Total activity of Br* produced}}\times100$

Table II. Ligand yield of solid $[Co(en)_2Y_2]Br_{1,3}$

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

Table III. Calculated values of γ for the donor atom in Y in a collision with a hot bromine atom

Y	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

hot bromine atom with the donor atom in Y played an important role. When the masses of the donor atom in ligand Y, and of bromine atom are M and M', respectively, the fraction of the maximum possible loss in the recoiling energy of a hot bromine atom for an elastic collision with the donor atom is given by $\gamma=4MM'/(M+M')^2$. Calculated values of γ for donor atoms in different ligands, Y, are shown in Table III. Fig. 1 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 $[Co(en)_2Y_2]Br_{1,3}$ contains more Y's in ligands than that of $[Co(NH_3)_5Y]Br_{2,3}$, the probability of the collision of a hot bromine atom with Y may be somewhat larger for the former

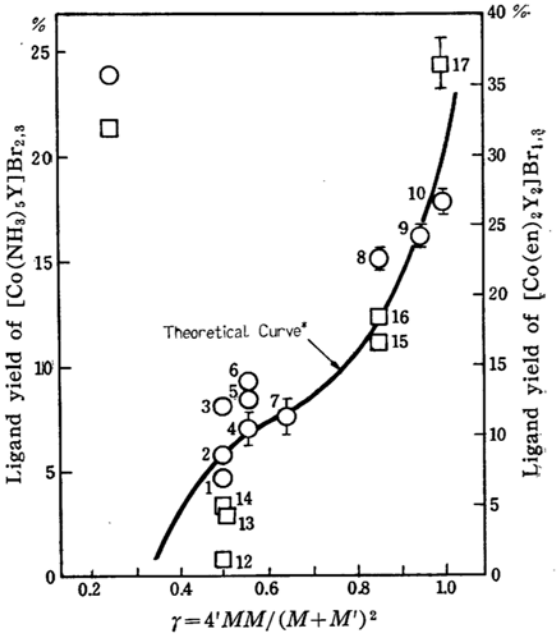

Fig. 1. The relationship between the ligand yield and the value of γ.
○ $[Co(NH_3)_5Y]Br_{2,3}$
□ $[Co(en)_2Y_2]Br_{1,3}$
* The shape of this curve was theoretically predicated on the basis of the model proposed by the present authors. Details will be published elsewhere.

salts. Based on the crystallochemical data, the ratio of relative collision cross sections of a bromine atom with Y in ligands was estimated as about 1.5 : 1 for $[Co(en)_2Y_2]Br$ and $[Co(NH_3)_5Y]Br_2$. Therefore, different ligand yield scales were used for the two series in Fig. 1 where both are shown together. It is seen in Fig. 1 that the ligand yield seems to increase as the value of γ of the donor atom in ligand Y increases: the efficiency of replacement of Y by hot bromine depends mainly on γ. Therefore, it may be presumed that the kinetic processes play an important role to determine the fate of hot bromine atoms in these systems.

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