Effects of Outer Anions on the Recoil Reactions in the Irradiated Hexammine-cobalt(III) Complex Compounds

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It was previously reported by the present authors that various ^{60}Co-labeled species were formed through recoil reactions in the irradiated cobalt complex compounds and that among these labeled species were found such substituted products as might be produced by incorporation of outer anions of the target complex into ligands[1]. Though the mechanism of formation of these recoil species has not been fully clarified, such outer anions of the target complex must no doubt play an impotant role during the recoil reactions. In the present work, they have investigated the distribution of recoil species in various hexamminecobalt(III) complex salts containing different kinds of outer anions in order to elucidate the role of the outer anions in recoil reactions.

Nine kinds of hexamminecobalt(III) complex salts listed in Table I were irradiated in an experimental hole in JRR-1 reactor for one or five hours at ambient temperature. Thermal neutron flux was approximately 3×10^{11} n/cm^2 sec. After bombardments, the ^{60}Co-labeled species present in aqueous solutions of the

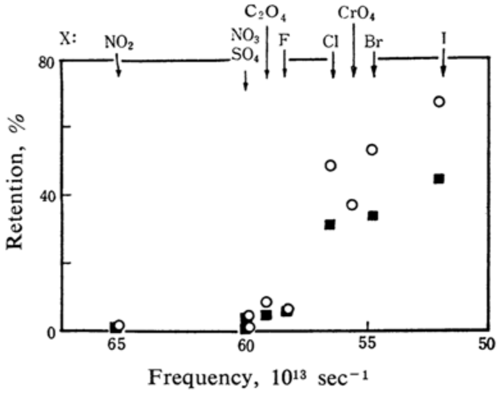

Fig. 1. The relationship between retention and frequency of the maximum in the first absorption band of $Co(NH_3)_5X$.
■ : Irradiated for one hour
○ : Irradiated for five hours

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[1] N. Saito, T. Tominaga and H. Sano, This Bulletin, 33, 1621 (1960).

TABLE I. PERCENTAGE DISTRIBUTION OF ^{60}Co-LABELED SPECIES IN IRRADIATED HEXAMMINECOBALT(III) COMPLEX SALTS

Target	Time of irradiation hr.	^{60}Co-labeled species, %*)					
		CoA_6^{3+}	CoA_5X^{2+}	$CoA_4X_2^+$	Co^{2+}	CoA_3X_3	$CoA_2X_4^-$
$[Co(NH_3)_6](NO_2)_3$	1	0.8	5.9	20.3	53.2	15.6	4.2
	5	1.4	15.5	34.5	24.7	11.1	12.4
$[Co(NH_3)_6](NO_3)_3$	1	2.8	8.5	20.9	66.7	0.7	0.3
	5	4.4	12.1	25.4	57.8	1.7	0.3
$[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$	1	0.2		2.1	96.0	1.4	0.3
	5	0.3		0.5	98.2	0.6	0.4
$[Co(NH_3)_6]_2(C_2O_4)_3$	1	3.6			96.4		
	5	$\leq$10			$\geq$90		
$[Co(NH_3)_6]F_3$	1	6.1	0.6	3.1	87.5	1.8	0.9
	5	6.8		2.4	88.2	1.9	0.5
$[Co(NH_3)_6]Cl_3$	1	33.4	5.2	3	57.5	2.3	—
	5	51.3	4.6	2.9	40.1	1.0	0.1
$[Co(NH_3)_6]_2(CrO_4)_3$	5	$\leq$36.8			$\geq$63.2		
$[Co(NH_3)_6]Br_3$	1	34.6	3.7	3	54.0	1.5	—
	5	54.2	2.8	1.3	41.0	0.7	—
$[Co(NH_3)_6]I_3$	1	45.0	5.7	5	37.4	1.3	1.2
	5	66.4	4.8	5	21.4	1.1	0.5

* $A=NH_3$ (or partly H_2O) ; $X=NO_2$, NO_3, F, Cl, Br, I, etc.

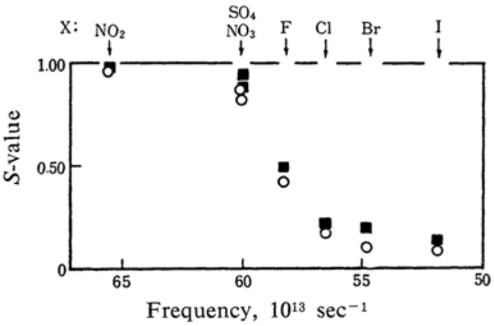

Fig. 2. The relationship between S-value and frequency of the maximum in the first absorption band of $Co(NH_3)_5X$.
■ : Irradiated for one hour
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target salt were separated by procedures involving paper electrophoresis, ion exchange, precipitation, or recrystallization. The results are summarized in Table I.

For the salts shown in Table I, the distribution of ^{60}Co-labeled recoil species was found to vary with the kind of outer anion in the target. The retention (or the percentage of activity as CoA_6^{3+}) tends to increase with the decrease in frequency of the maximum in the first absorption band of CoA_5X (X denotes the outer anion in CoA_6X_3), or the decrease in stability of the outer anion X complexed with cobalt. This relationship is shown in Fig. 1.

For the convenience of discussion on the relative yield of substituted recoil products, a factor, S, was calculated as in the following:

$$S=\frac{\left(\begin{array}{c}\text{Sum of percentages of }^{60}\text{Co-labeled com-}\\ \text{plexes containing more anionic ligands}\\ \text{than the target complex}\end{array}\right)}{\left(\begin{array}{c}\text{Sum of percentages of all}\\ ^{60}\text{Co-labeled complexes}\end{array}\right)}$$

As seen in Fig. 2, the relative yield of substituted products (S) seems to decrease with the decrease in frequency of the maximum in the first absorption band of CoA_5X, or the decrease in stability of the outer anion X complexed with cobalt.

The above relationships indicate together that the facility of incorporation of outer anions into ligands around the hot cobalt atom might mainly depend on the stability of such anions as ligands in cobalt(III) complexes.

It was presumed from these results that chemical processes might mainly contribute to determine the fate of hot cobalt atoms at such stages in recoil reactions as involved energies low enough to distinguish the difference in stabilities of these anions as ligands.

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