Effects of Outer Anions on the Recoil Reactions in the Irradiated Nitropentamminecobalt(III) Complexes

By Nobufusa SAITO, Takeshi TOMINAGA, and Hirotoshi SANO

(Received December 4, 1962)

It was already reported that recoil reactions in the irradiated hexammine- and aquopentamminecobalt(III) complex salts were greatly influenced by the kind of outer anions in the target compound[1,2]. In this work, the investigation of the effects of outer anions has been extended to a group of nitropentamminecobalt-(III) complex salts.

Seven kinds of nitropentamminecobalt(III) complex salts (listed in Table I) were irradiated for one hour in the JRR-1 reactor at a thermal neutron flux of approximately 3×10^{11} n/cm² sec. All irradiations were made at pile temperature in the presence of air. After irradiation the ^{60}Co-labeled species present in aqueous solutions of the target salt were separated by means of ion exchange, precipitation, or paper electrophoresis[*1].

The results are summarized in Table I. For nitropentamminecobalt(III) nitrate, chloride, bromide and iodide (i. e., $X=NO_3$, Cl Br and I), however, $^{60}CoA_5X^{2+}$ fraction in Table I did not represent real retention but was composed of two divalent complex cations containing different acidic ligands. These two species were further separated by fractional precipitation (recrystallization to constant specific activity), or ion exchange after aquotization[*2]. Table II shows percentages of the two species: species a represents "retention", whereas species b is a substituted product formed through incorporation of outer anions.

In Fig. 1 are plotted percentages of the species a and b against the frequency of the maximum in the first absorption band of $Co(NH_3)_5X$, where X denotes the outer anion of the target salt[*3]. It will be seen that, as

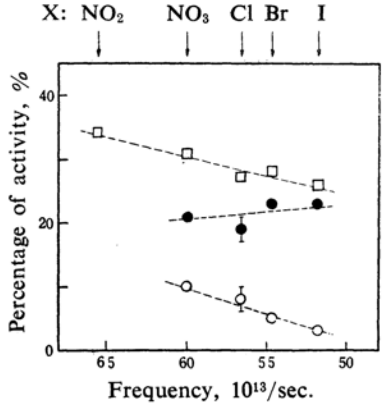

Fig. 1. Relationship between the percentage of $^{60}CoA_5X^{2+}$ fraction (species a and b) and the frequency of the maximum in the first absorption band of $Co(NH_3)_5X$.

● Species a (retention)
○ Species b ($^{60}CoA_5NO_3^{2+}$, $^{60}CoA_5Cl^{2+}$, etc.)
□ a+b

TABLE I. PERCENTAGE DISTRIBUTION OF ^{60}CO-LABELED SPECIES IN IRRADIATED NITROPENTAMMINECOBALT(III) COMPLEXES*

Target	^{60}Co-Labeled species, %**					
	CoA_6^{3+}	CoA_5X^{2+}	$CoA_4X_2^{+}$	Co^{2+}	CoA_3X_3	$CoA_2X_4^{-}$
$[Co(NH_3)_5NO_2](NO_2)_2$	<3.7	34.0	6.1	53.1	1.4	1.7
$[Co(NH_3)_5NO_2](NO_3)_2$	<4.7	30.9	10.0	50.3	2.0	1.9
$[Co(NH_3)_5NO_2]Cl_2$	<3.4	27.3	1.9	67.3	0.1	0.2
$[Co(NH_3)_5NO_2]Br_2$	<3.6	28.1	1.4	66.3	0.6	0.1
$[Co(NH_3)_5NO_2]I_2$	<6.5	25.9	5.9	59.5	1.0	1.2
$[Co(NH_3)_5NO_2]SO_4$	<4.4	25.1	2.3	67.4	0.5	0.4
$[Co(NH_3)_5NO_2]C_2O_4$	<1.9	17.9	2.1	77.8	0.4	0.1

* The irradiated salts were stored at dry-ice temperature for 1~3 days before separation.
** $A=NH_3$ (or partly H_2O) ; $X=NO_2$, NO_3, Cl, Br, I, etc.

---

1) N. Saito, T. Tominaga and H. Sano, This Bulletin, 35, 365 (1962).

2) N. Saito, T. Tominaga and H. Sano, ibid., 36, 231 (1963).

[*1] Sometimes, paper electrophoresis method gave slightly lower retentions than those obtained by ion exchange method. The latter values were used in the present paper.

[*2] For example, when the solution containing $CoA_5NO_2^{2+}$ and CoA_5Br^{2+} is warmed in adequate conditions, CoA_5Br^{2+} is rapidly aquotized to give $CoA_5H_2O^{3+}$ whereas $CoA_5NO_2^{2+}$ remains practically unchanged. Then the trivalent and divalent cations can be readily separated by ion exchange method.

[*3] Since the oxalate and sulfate containing divalent anions may be different from the other salts as to the crystal structure and the outer anion-to-cobalt ratio, they are not included in Fig. 1.

TABLE II. PERCENTAGES OF ^{60}Co-LABELED SPECIES IN THE FORM OF ^{60}CoA$_5$X^{2+}

Target	^{60}Co-Labeled species, %*	
$[Co(NH_3)_5NO_2](NO_3)_2$	a : $CoA_5NO_2^{2+}$	21±1
	b : $CoA_5NO_3^{2+}$	10±1
$[Co(NH_3)_5NO_2]Cl_2$	a : $CoA_5NO_2^{2+}$	19±2
	b : CoA_5Cl^{2+}	8±2
$[Co(NH_3)_5NO_2]Br_2$	a : $CoA_5NO_2^{2+}$	23±1
	b : CoA_5Br^{2+}	5±1
$[Co(NH_3)_5NO_2]I_2$	a : $CoA_5NO_2^{2+}$	23±1
	b : CoA_5I^{2+}	3±1

* Species a represents retention; species b represents a substituted product in each target salt.

the frequency of the maximum decreases, the percentage of species b decreases while the percentage of the parent species a (retention) remains almost unchanged or slightly increases.

As in the preceding works[1,2] the results may be presumably explained by assuming that fragmented NH_3 or NO_2 groups and outer anions compete with each other in the recoil reactions involving complex formation, upon which the stability of the outer anions as complexed with cobalt may be reflected, as indicating the facility of co-ordination.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo