Recoil Reactions in the Irradiated Aquopentamminecobalt(III) Complexes

By Nobufusa Saito, Takeshi Tominaga
and Hirotoshi Sano

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The present authors previously studied recoil chemistry of various hexamminecobalt(III) complexes and found that outer anions of the

TABLE I. PERCENTAGE DISTRIBUTION OF ^{60}Co-LABELED SPECIES IN IRRADIATED AQUOPENTAMMINECOBALT(III) COMPLEXES

Target	^{60}Co-Labeled species, %*					
	$CoA_5H_2O^{3+}$	CoA_5X^{2+}	$CoA_4X_2^+$	Co^{2+}	CoA_3X_3	$CoA_2X_4^-$
$[Co(NH_3)_5H_2O](NO_3)_3$	18.6	22.3	5.0	51.1	0.9	0.8
$[Co(NH_3)_5H_2O]_2(SO_4)_3\cdot 3H_2O$	25.7	3.7	1.9	66.5	0.7	1.5
$[Co(NH_3)_5H_2O]_2(C_2O_4)_3\cdot 4H_2O$	12.4	2.2	2.4	82.9	0.3	0.0
$[Co(NH_3)_5H_2O]Cl_3$	32.0	9.5	1.5	56.5	0.3	0.1
$[Co(NH_3)_5H_2O]Br_3$	32.9	12.4	2.0	52.3	0.3	0.1
$[Co(NH_3)_5H_2O]I_3$	32.4	7.4	1.8	58.3	0.2	0.0

* $A=NH_3$ (or partly H_2O) ; $X=NO_3$, Cl, Br, I, etc.
Percentage of $^{60}Co(NH_3)_6^{3+}$ was less than 0.4% and therefore was negligible.

target compound might play an important role in the recoil reactions$^{1)}$. In the present work, they have investigated the effects of outer anions on the recoil reactions in the irradiated aquopentamminecobalt(III) complexes.

Six kinds of aquopentamminecobalt(III) complexes listed in Table I were irradiated for one hour at pile temperature in the JRR-1 reactor, at a thermal neutron flux of approximately 3×10^{11} n/cm^2 sec. All irradiations were made in the presence of air. After the bombardments the target salt was stored at dry-ice temperature for one to five days. Then it was dissolved in distilled water and the percentages of ^{60}Co-labeled species present in the aqueous solution were determined by means of separation procedures involving ion exchange, precipitation, or paper electrophoresis (in the acetate buffer)*.

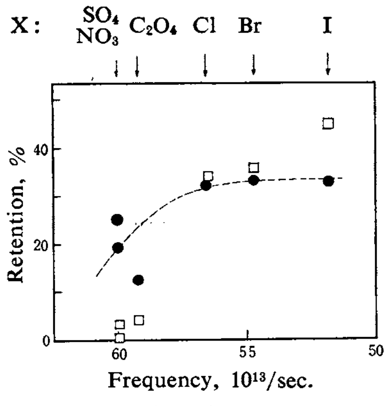

Fig. 1. The relationship between retention and frequency of the maximum in the first absorption band of $Co(NH_3)_5X$.

● Retention of $[Co(NH_3)_5H_2O]X_3$
□ Retention of $[Co(NH_3)_6]X_3$

The results summarized in Table I indicate that the distribution of recoil species in these salts was largely influenced by the kind of outer anions in the target. In Fig. 1 is plotted the retention (percentage of $^{60}CoA_5H_2O^{3+}$) of aquopentamminecobalt(III) complex salts against the frequency of the maximum in the first absorption band of $Co(NH_3)_5X$ (X denotes the outer anion in the target). It appears that the retention is generally increased with the decrease in the frequency of the maximum, or the decrease in stability of the outer anion X as complexed with cobalt. It will be seen that this retention-stability relationship is essentially similar to that already observed for the corresponding hexamminecobalt(III) complexes$^{1)}$, which are shown together in Fig. 1. Since the corresponding salts in the both series containing the same kind of outer anion may be rather alike in chemical composition except that a ligand NH_3 is replaced by H_2O, and vice versa, such a similarity in the recoil reactions may not be surprising.

In explanation of the results it may be presumed that the recombination process involving NH_3 and H_2O molecules to restore the parent form competes with the substitution processes involving outer anions where the facility of their incorporation into ligands may mainly depend upon the stability of such anions as complexed with cobalt.

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

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

* Retentions obtained by paper electrophoresis were somewhat lower than those obtained by ion exchange. The latter values were used in Table I.