*Hot-atom Reaction in cis- and trans-Dinitrotetrammine Cobalt(III) Nitrate**

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Several models have been proposed to account for the mechanism of the hot-atom reaction in solids[1-4]. It should be possible to check the validity of these models by investigating the hot-atom reaction in compounds exhibiting optical and geometrical specificity. Zuber[5] irradiated dextro-tris(ethylenediamine)cobalt(III) nitrate and found the yield of ^{60}Co to be 4.5 per cent in the dextro form and 0.5 per cent in the laevo form. Recently, Rausher, Sutin and Miller[6] have studied the Szilard-Chalmers reaction in *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III) nitrate and have found that the yield of ^{60}Co is 3～7 per cent in the parent isomer and 0.1～0.2 per cent in the other isomer, while the corresponding yields of ^{38}Cl in that order are 12～16 per cent and 0.4～0.7 per cent respectively.

We have investigated the chemical effects of the ^{59}Co(n, γ)^{60}Co reaction in the cis and trans isomers of crystalline dinitrotetrammine cobalt(III) nitrate, which show a greater stability to aquation than do the dichloro complex salts. Furthermore, the retentions of nitroammine cobalt(III) complex salts are higher than those of the complex salts cited above.

Experimental

Materials.—The complex salts were prepared by the method of Jorgensen[7]. The salts were purified by recrystallization. The purity of the complex salts was checked by taking the absorption spectra of their solutions in distilled water and comparing the molar extinction coefficients and the maximum wavelengths with those reported by Basolo[8].

Neutron Irradiation.—Samples of *cis*-$[Co(NH_3)_4 \cdot (NO_2)_2]NO_3$ and *trans*-$[Co(NH_3)_4(NO_2)_2]NO_3 \cdot H_2O$ were irradiated at reactor temperature for one to five hours in the thermal column of the JRR-1 reactor. All bombardments were made in the presence of air. The neutron flux at the bombardment site was (3～5)×10^{11} n/cm^2 sec., and the gamma ray flux, approximately 5×10^5 r/hr.

Separation Procedure.—*Ion Exchange Separation.* —Two to five milligrams of the irradiated sample were dissolved in 10 ml. of water. (In preliminary tests, cobalt(II) nitrate, *cis*- or *trans*-dinitrotetrammine nitrate and nitropentammine nitrate were added prior to the dissolution of the sample, but

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1) W. F. Libby, *J. Am. Chem. Soc.*, **69**, 2523 (1947); L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949).

2) J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 865 (1950).

3) J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953).

4) G. Harbottle and N. Sutin, *J. Phys. Chem.*, **62**, 1344 (1958).

5) A. V. Zuber, NYO-6142 (1954).

6) H. E. Rauscher, N. Sutin, J. M. Miller, *J. Inorg. & Nuclear Chem.*, **12**, 378 (1960); ibid., **17**, 31 (1961).

7) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 470, 473 (1898).

8) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

no effect on the distribution of ^{60}Co was found.) The solution was passed through a resin column (0.8×17 cm. of Dowex 50W X-8, H-form 100∼200 mesh beads). The column was then washed with about 100 ml. of water. The effluent contained anionic and neutral species. Subsequently, 300 to 400 ml. of 1 M sodium chloride solution was passed through the column. Firstly, *trans*-$[Co(NH_3)_4 \cdot (NO_2)_2]^+$ ions were eluted, and then a mixture of *cis*-$[Co(NH_3)_4(NO_2)_2]^+$ ions and Co(II) species in the next fraction[9]. To the latter fraction were added 10 mg. of cobalt(II) nitrate as a carrier and 10 mg. of *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$ as a hold-back carrier. The cobalt(II) species were precipitated as hydroxide with a diluted sodium hydroxide solution. After reprecipitation, the precipitates were dissolved in diluted hydrochloric acid.

In another series of experiments, ammonium malonate was used as an eluent instead of sodium chloride. After the sample solution had been passed through a cation exchanger column (under the same condition as mentioned above but kept in ammonium form), the column was washed with about 100 ml. of water. The adsorbed cations were eluted with 300 to 400 ml. of 1/2 M ammonium malonate solution. Anionic and neutral species were collected in the first fraction. The cobalt(II) species was eluted in the second fraction as cobalt(II) malonate*. The *trans*- and *cis*-dinitrotetrammine, and nitropentammine species were eluted in the third, fourth, and fifth fractions respectively.

The non-cationic fraction was poured into an anion exchanger column (Dowex 1 X-8, NO_3-form, 100∼200 mesh beads, 0.8×10 cm.). The column was then washed with about 100 ml. of 0.1 M sodium chloride solution. Neutral species were collected in the effluent. The adsorbed anions were eluted with 1 M sodium chloride solution.

All samples were counted as liquids, in a well-type scintillation counter.

Paper Electrophoresis. — Samples of the irradiated compounds were dissolved in a 0.1 M ammonium oxalate solution at a concentration of 1∼2 mg./ml. Portions of 20∼50 λ were pipetted and placed at a zero-line on electrophoresis paper (Toyo Roshi No. 50). Potentials of the order of 400∼600 V. were applied, the useful length of the strips being about 30 cm. The strips were cooled during electrophoresis by immersion in monochlorobenzene. After one to two hours, the voltage was interrupted, the paper dried and cut transversely in 1 cm. strips. These were scintillation-counted in a standard way. It has been known that cis species move faster than trans species toward the cathode[10]. The preliminary tests showed that cobalt(II) species moved toward the anode.

Determination of Cobalt.—Each fraction obtained in the ion exchange separation was dried on a steam bath. After concentrated sulfuric acid and concentrated nitric acid were added, the solution was evaporated almost to dryness. This procedure was repeated until the complexes or malonates were completely decomposed. Then, the amount of cobalt in each fraction was determined spectrophotometrically, using the nitroso-R salt method[11].

Results

It was found that the ion exchange separation using ammonium malonate as an eluting agent was most suitable for our purpose, because those cationic species adsorbed on the resin were eluted chromatographically and, therefore, the precise distribution pattern of ^{60}Co could be obtained. The elution curve of ^{60}Co activity from the cation exchange column is shown in Figs. 1 and 2. Paper electrophoresis was not very effective in the separation of the irradiated cis salts, because the peaks of the trans salt were not sufficiently well-resolved to permit determination.

The percentage distributions of the ^{60}Co activity are summarized in Tables I and II. The most significant result is that there is a considerable amount of ^{60}Co which appears in

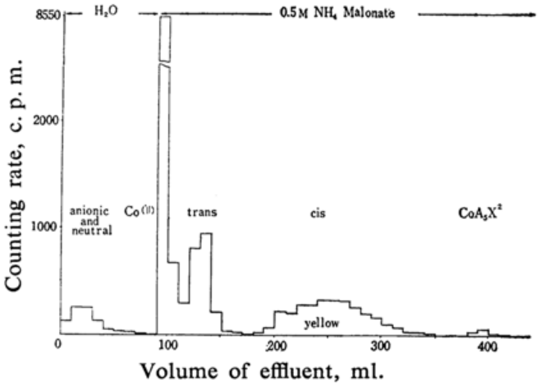

Fig. 1. Elution of ^{60}Co in the 1 hr.-irradiated cis salt.

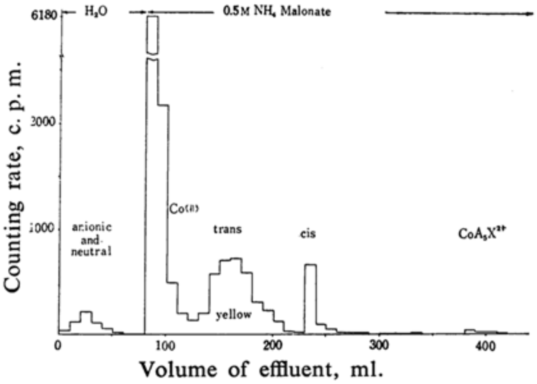

Fig. 2. Elution of ^{60}Co in the 1 hr.-irradiated trans salt.

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[9] E. L. King and R. R. Walters, ibid., **74**, 1674 (1952).

* From the experiments employing the technique of paper electrophoresis it was found that the species had no charge.

[10] M. Maki, *Japan Analyst* (*Bunseki Kagaku*), **4**, 217 (1955).

[11] E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers, Inc., New York (1959), p. 415.

TABLE I. PERCENTAGE DISTRIBUTION OF ^{60}Co AFTER DISSOLUTION OF IRRADIATED CIS SALT

Irrad. time hr.	Storage time	Percentage distribution of ^{60}Co							Procedure of separation
		Anionic	Neutral	Co(II)	Trans	Cis (retn.)	CoA_5X^{2+}	Resin	
1	0~5 min.	1.2	5.2	58.4	11.9	20.5	1.0	1.7	Ion exchange malonate
1	2 months	4.5		56.4	4.5	29.1	3.9	1.6	Ion exchange malonate
5	2 weeks	1.1	3.2	42.8	4.0	46.5	1.4	0.0	Ion exchange NaCl; Pptn.
5	5 months	0.3	5.6	39.9	4.1	43.5	6.6	0.0	Ion exchange malonate
5	5 months	6.2		41.1	4.9	45.7	2.1	0.0	Ion exchange malonate
5	12 months	0.0	7.3	42.7	50.0		—	—	Electrophoresis
Enrichment factor		40		340	81	0.46	26	—	

TABLE II. PERCENTAGE DISTRIBUTION OF ^{60}Co AFTER DISSOLUTION OF IRRADIATED TRANS SALT

Irrad. time hr.	Storage time	Percentage distribution of ^{60}Co							Procedure of separation
		Anionic	Neutral	Co(II)	Trans (retn.)	Cis	CoA_5X^{2+}	Resin	
1	0~5 min.	5.0		63.0	23.3	6.7	0.9	1.1	Ion exchange malonate
1	2 months	4.6		48.7	43.2	1.4	1.3	0.8	Ion exchange malonate
5	2 weeks	0.4	3.1	46.1	45.4	4.6	0.4	0.0	Ion exchange NaCl; Pptn.
5	2 weeks	0.0	4.6	39.1	49.8	2.5	4.0	0.0	Ion exchange malonate
5	5 months	4.6		35.3	57.1	1.3	1.6	0.1	Ion exchange malonate
5	2 days	0.0	3.3	42.9	44.7	9.1	0.0	—	Electrophoresis
5	5 days	0.0	4.7	43.4	45.4	6.5	0.0	—	Electrophoresis
5	6 months	0.0	5.8	41.6	45.8	5.8	0.0	—	Electrophoresis
Enrichment factor		10		380	0.51	23	13	—	

the other isomeric form for either cis or trans targets. Cis isomer was found with an enrichment factor of 23 in the irradiated trans salt, while trans isomer with an enrichment factor of 80 was found in the irradiated cis salt. These results are also shown in Tables I and II.

Discussion

The distribution of ^{60}Co in *cis*-$[Co(NH_3)_4 \cdot (NO_2)_2]NO_3$ irradiated for one hour is 20.5 per cent in the cis form and 11.9 per cent in the trans form. On storage at room temperature (15~25°C), the retention in the cis form reaches a value of 29.1 per cent, while the distribution of ^{60}Co in the trans form decreases to 4.5 per cent. The distribution of ^{60}Co in *trans*-$[Co(NH_3)_4(NO_2)_2]NO_3 \cdot H_2O$ irradiated for one hour is 23.3 per cent in the trans form and 6.7 per cent in the cis form. On storage at room temperature, the retention in the trans form increases to 43.2 per cent, while the distribution of activity in the cis form decreases to 1.4 per cent. The ratio of isomer formation to retention as parent species is 1/2 to 1/3 in terms of the radioactivity without storage, whereas the ratio decreases to 1/7 to 1/30 after two months storage. It seems important to determine the ratio of isomer formation to retention in a condition where the irradiation is conducted for an extremely short time at solid carbon dioxide temperature, because one-hour irradiation at reactor temperature, as conducted in our experiment, would produce additional annealing, both thermal and radiation.

These facts may indicate that one should prefer a model such as the hot-zone mode[14] to a billiard-ball mode[15], to account for the mechanism of the recoil processes.

It is also worth mentioning that geometric isomerization during recoil processes occurs more remarkably in cis salts than in trans salts. Although it is too difficult for us at the present stage to give a clear explanation of this, it may be supposed that the cis species yielded in the irradiated trans salts are not so stable to additional annealing processes as the trans species yielded in the irradiated cis salts*.

Summary

The Szilard-Chalmers reaction of cobalt in *cis*- and *trans*-dinitrotetrammine cobalt(III) nitrate have been investigated. After a given isomer was irradiated, ^{60}Co was found in an appreciable amount in the other isomeric form. The distribution of ^{60}Co in *cis*-$[Co(NH_3)_4 \cdot (NO_2)_2]NO_3$ irradiated for one hour is 20.5 per cent in the cis form and 11.9 per cent in the trans form. The distribution in *trans*-$[Co(NH_3)_4(NO_2)_2]NO_3 \cdot H_2O$ is 23.3 per cent in the trans form and 6.7 per cent in the cis form. This observation is consistent with a hot-zone model, where one would except that the original configuration would not be essentially preserved.

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[*] It has been well-known that radiolysis occurs more easily in cis-isomers than in trans-isomers. For example, Dimotakis and Maddock have reported that *trans*-$[Co(en)_2 \cdot Cl_2]NO_3$ and *trans*-$[Co(en)_2Br_2]NO_3$ show a greater stability to radiolysis than do the corresponding cis salts. (International Symposium on Chemical Effects of Nuclear Transformation, Prague, 1960. CENT/18).