Recoil Reactions in Irradiated Tris-(nitrosonaphtholato)- and Tris-(dimethylglyoximato)-cobalt(III) Complexes

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Hot-atom chemistry of radiocobalt has been studied by several authors on the irradiated octahedral cobalt(III) complexes of the formula, CoA_3, containing organic bidentate ligands, A (A=glycinate, acetylacetonate, oxinate, etc.)[1-4]. With a view to clarifying the relationship between distribution of induced ^{60}Co activity in various chemical forms and any chemical or physical property of the ligand, the present authors have selected, in addition to those mentioned above, three complex compounds of the similar type, tris-(α-nitroso-β-naphtholato)-,

TABLE I. PERCENTAGE OF ^{60}Co ACTIVITY SEPARABLE AS Co(II)

Target	Time of irradiation hr.	Time of storage*	^{60}Co activity separable as Co(II) %	Method of separation**
Tris-(α-nitroso-β-naphtholato)-cobalt(III)	1	1 day	39.1	a
		5 days	21.0	a
		2 months	17.2	a
	5	2 days	27.4	a
		5 days	27.0	a
		2 months	14.3	a
Tris-(β-nitroso-α-naphtholato)-cobalt(III)	1	1 day	28.9	a
		5 days	16.0	a
		2 months	10.9	a
	5	1 day	17.4	a
		5 days	16.9	a
		2 months	9.1	a
Tris-(dimethyl-glyoximato)-cobalt(III)	1	1 day	82.2	a
		4 days	77.4	a
		4 days	74.6	b
		2 months	75.4	a
	5	5 days	83.9	a
		5 days	83.3	b
		5 days	73.7	c
		5 days	85.0	d
		2 months	57.6	a
		2 months	57.1	b
		2 months	42.6	c
		2 months	57.6	d

* Storage at room temperature

** a: solvent extraction, b: precipitation, c: ion exchange, d: paper electrophoresis

1) A. Zuber, USAEC Document NYO-6142 BNL.
2) A. Nath, J. Shankar and S. B. Srivastava, Proc. 2nd Intern. Conf., Peaceful Uses of Atomic Energy, Geneva, **20**, 58 (1958).
3) A. Nath, J. Shankar et al., Papers presented at the IAEA Symposium on the Chemical Effects of Nuclear Transformations, Prague, 1960.
4) L. L. Williams, N. Sutin and J. M. Miller, *J. Inorg. Nuclear Chem.*, **19**, 175 (1961).

tris-(β-nitroso-α-naphtholato)- and tris-(dimethylglyoximato)-cobalt(III) complexes, and investigated the recoil reactions of radiocobalt in such compounds.

These crystalline complex compounds 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. All bombardments were made in the presence of air.

After the bombardments tris-(nitrosonaphtholato)-cobalt(III) complexes were dissolved in chloroform, and shaken four times with (1 : 1) nitric acid. The ^{60}Co activity as cobalt(II) was extracted into aqueous phase with enrichment factors more than 150, while ^{60}Co as complexes remained in organic phase.

The irradiated tris-(dimethylglyoximato)-cobalt(III) complex was dissolved in water and ^{60}Co-labeled species were separated by means of procedures involving paper electrophoresis (in acetate buffer or in 1% sodium chloride solution), solvent extraction (cobalt(II) extracted into benzene as β-nitroso-α-naphtholato-complex), precipitation, or ion exchange. By the solvent extraction method, ^{60}Co was extracted into benzene with enrichment factors more than 100. For the dimethylglyoximato-complex, the ^{60}Co activity separable as cobalt(II) was considerably decreased unless the irradiated complex was dissolved in water containing cobalt(II) carrier beforehand. Since no isotopic exchange was observed in practice between ^{60}Co(II) and tris-(dimethylglyoximato)-cobalt(III) complex within 6 hr. (at 24.5°C), the decrease might be mainly attributed to consumption of ^{60}Co(II) (in micro quantities) due to probable comlpex formation with free dimethylglyoximate ions present in the solution. Therefore adequate amounts of cobalt(II) carrier was added beforehand to minimize the loss of activity.

The percentages of ^{60}Co activity separable as cobalt(II) for samples irradiated and stored for varied times were summarized in Table I.

As seen in Table I, nitrosonaphtholato-cobalt(III) complexes showed considerably low percentages for cobalt(II) fraction. Since it was reported that more than 70% of the induced ^{60}Co activity could be separated as cobalt(II) from most of the CoA_3 type complexes freshly irradiated*, such a low extractability seemed to be rather unusual.

It is worthy of mentioning that α-nitroso-β-naphtholato-complex represented higher extractability of radiocobalt as cobalt(II) than β-nitroso-α-naphtholato-complex. This fact might possibly be related to some differences in configuration of their ligands or chemical properties of these complexes.

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* Based on the values reported in the papers cited above (1—4) as well as those for tris-(dimethylglyoximato)-cobalt(III) reported in the present paper. Though the irradiation condition employed by different authors were not identical the integrated neutron flux and gamma flux in the present experiment were estimated rather lower than those employed by other authors. Most irradiations by the other authors were also made at pile temperature.