The Radiolysis of Crystalline Oxalatocobalt(III) Complex Salts

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Many attempts have already been made to investigate the hot-atom effect in neutron-irradiated metal complex salts.[1-3] The study of radiation effect is quite important in hot-atom chemistry. However, little attention has so far been paid to the radiolysis of these complex salts. Sugimori and Tsuchihashi have studied the radiolysis in trioxalato complex salts of trivalent metals, such as cobalt, chromium, iron, aluminum.[4] The present authors have recently reported that ninety per cent

TABLE I. $G(Co^{2+})$ VALUES ESTIMATED

Compound	$G(Co^{2+})$ value[a]
$[Co(en)_3](NO_3)_3$	0.4 ± 0.1
$[Co(NH_3)_6](NO_3)\cdot H_2O$	1.1 ± 0.2
$[Co(NH_3)_6](C_2O_4)_3\cdot 4H_2O$	2.9 ± 0.2
$[Co(C_2O_4)(NH_3)_4]NO_3\cdot H_2O$	3.1 ± 0.2
$[Co(C_2O_4)(NH_3)_4]Cl$	4.3 ± 0.2
$NH_4[Co(C_2O_4)_2(NH_3)_2]\cdot 2H_2O$	8.9 ± 0.05
$K_3[Co(C_2O_4)_3]\cdot 3H_2O$	$11._6\pm0.2$

a) From least squares analysis of plot of log (retention of complex) vs. dose.

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2) "Proceedings of International Symposium on Chemical Effects of Nuclear Transformation," IAEA, Vienna (1962).

3) N. Saito, T. Tominaga and H. Sano, *J. Inorg. and Nucl. Chem.*, 24, 1539 (1962); *Nature*, 194, 466 (1962); This Bulletin, 36, 230, 232 (1963).

4) A. Sugimori and G. Tsuchihashi, This Bulletin, 34, 449 (1961).

or more of radiocobalt atoms are found as cationic divalent species after the dissolution of the neutron-irradiated oxalatocobalt(III) complex salts.[5] In this paper, the radiolysis of the oxalatocobalt(III) complex salts will be reported.

The seven kinds of crystalline complex salts listed in Table I were irradiated with Co-60 gamma rays at room temperature, at a dose rate of $2.2-3.0\times10^5$ r./hr. in the presence of air. The irradiated salts were dissolved in water or dilute hydrochloric acid. The amount of cationic cobalt(II) species was determined by the β-nitroso-α-naphthol method[6] or the nitroso-R salt method,[7] after the separation of cobalt(II) species from parent cobalt(III) complex ions by procedures includiding anion exchange or solvent extraction. The results were practically the same irrespective of the analytical method employed.

It was found that the amount of cobalt(II) species produced increases with an increase in the gamma-ray dose. Table I shows the estimated $G(Co^{2+})$ values. It should be mentioned that the G value depends on the content of oxalate ions in the nearest coordination sphere, and that the G value of hexamminecobalt(III) oxalate is definitely greater than that of hexamminecobalt(III) nitrate. The results may be explained by assuming the electron transfer process from oxalate to cobalt ions during the radiation-induced decomposition of complex salts.

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6) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, Inc., N. Y. (1959), p. 420.
7) Ibid., p. 415.