SHORT COMMUNICATIONS

Radiolysis of Crystalline Oxalato Complexes

By Akira SUGIMORI and Gen-ichi TSUCHIHASHI

(Received December 2, 1960)

The effects of metal ions on the radiolysis of organic compounds have mainly been studied in aqueous solutions[1]. The present authors previously studied the radiation chemistry of aqueous metal salicylate complexes, and found that chelated Fe^{3+} and Cu^{2+} effectively increase the decarboxylation of salicylic acid[2]. The study on the radiolysis of crystalline metal complexes was also considered to be very helpful for the elucidation of the mechanism of the reaction affected by metal ions. In this paper, the radiolysis of various crystalline metal oxalato complexes is repoted.

Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$), anhydrous oxalic acid ($H_2C_2O_4$), ferrous oxalate ($Fe(C_2O_4) \cdot 2H_2O$), sodium oxalate ($Na_2C_2O_4$), potassium trisoxalatoaluminate ($K_3Al(C_2O_4)_3 \cdot 3H_2O$), potassium trisoxalatochromate ($K_3Cr(C_2O_4)_3 \cdot 3H_2O$), potassium trisoxalatocobaltate ($K_3Co \cdot (C_2O_4)_3 \cdot 3H_2O$) and potassium trisoxalatoferrate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) were irradiated with Co-60 gamma rays at room temperature, mainly

---

[1] J. H. Baxendale and D. Smithies, *J. Chem. Phys.*, **23**, 604 (1955); *J. Chem. Soc.*, **1959**, 779.

[2] A. Sugimori and G. Tsuchihashi, This Bulletin, **33**, 713 (1960).

TABLE I. THE ANALYSIS OF THE GASEOUS PRODUCTS

Compound	Dose rate r./hr.	Dose, r.	G(gas)	CO/CO_2
$H_2C_2O_4 \cdot 2H_2O$	4.4×10^5	1.45×10^8	1.1	0.0
$Na_2C_2O_4$	4.4×10^5	1.45×10^8	0.03	0.1
$K_3Al(C_2O_4)_3 \cdot 3H_2O$	4.4×10^5	1.31×10^8	2.0	0.1
$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	4.4×10^5	1.45×10^8	1.5	0.6
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	4.4×10^5	1.45×10^8	7.5	0.0
$K_3Co(C_2O_4)_3 \cdot 3H_2O$	4.4×10^5	1.45×10^8	9.8	0.0

TABLE II. THE DECOMPOSITION OF THE COMPLEXES

Compound	Condition	Dose rate r./hr.	Dose, r.	G(-complex)
$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	vacuum	4.4×10^5	1.45×10^8	0.7
	air	4.6×10^5	1.46×10^8	0.7
$K_3Co(C_2O_4)_3 \cdot 3H_2O$	vacuum	4.4×10^5	1.31×10^8	8.9
	air	4.6×10^8	1.46×10^8	9.1

TABLE III. THE DECOMPOSITION OF $C_2O_4^{2-}$

Compound	Condition	Dose rate r./hr.	Dose, r.	$G(-C_2O_4^{2-})$
$H_2C_2O_4 \cdot 2H_2O$	vacuum	4.6×10^5	1.46×10^8	2.3
	air	2.6×10^5	5.15×10^7	5.1
$H_2C_2O_4$	vacuum	4.6×10^5	1.46×10^8	3.6
	air	4.6×10^5	1.46×10^8	4.3
$Na_2C_2O_4$	vacuum	4.6×10^5	1.46×10^8	<0.03
	air	2.6×10^5	5.15×10^7	<0.3
$K_3Al(C_2O_4)_3 \cdot 3H_2O$	vacuum	4.4×10^5	1.31×10^8	4.6
	air	4.4×10^5	1.46×10^8	5.5
$Fe(C_2O_4) \cdot 2H_2O$	vacuum	1.6×10^5	1.46×10^8	0.1

at a does rate of 4.4×10^5 r./hr. and at a total dose of 1.5×10^8 r. both in the presence and in the absence of air.

After the quantity of evolved gas was measured, the gas was analyzed mass-spectrometrically. The quantity of decomposed complex was measured by visible light absorption spectrometry of aqueous solutions of irradiated complexes. The quantity of decomposed oxalate was measured by titrating the solutions of irradiated samples with acid permanganate solution. G(gas) (the number of the molecules of evolved gas), the ratio of CO to CO_2 in the evovled gas, $G(-\text{complex})$ (the number of the decomposed molecules of the complex) and $G(-C_2O_4^{2-})$ are shown in Tables I, II and III. From the experimental results, the followings are concluded.

(1) Oxalate ions such as in sodium oxalate and ferrous oxalate are very stable to gamma ray irradiation, compared with those in metal oxalato complexes. The fairly large reactivity of oxalic acid and potassium trisoxalatoaluminate toward gamma irradiation might be attributed to the covalent character of oxalate-M (M=metal ion or hydrogen) bond. Oxalate ions with larger covalent character decompose more easily by gamma irradiation.

(2) The much larger G values of Fe^{3+} and Co^{3+} complex than those of Al^{3+} complex can not be explained only by the covalent character of oxalato-metal bond. They seem to be related with the reduction of metal ions. On gamma irradiation of Fe^{3+} and Co^{3+} complex, the reduction of the metal ions also occurs, and ferrous and cobaltous oxalate precipitates when the irradiated complexes are dissolved in water. Therefore, the electron transfer from oxalate to metal ions might increase the radiation-induced decomposition of oxalate.

(3) Chromium is stable in the state Cr^{3+} and Cr(VI) whereas very unstable in the state Cr^{2+}; therefore on gamma irradiation of $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ the electron transfer from oxalato to metal ion might be difficult and this might cause the lower G values of Cr^{3+} complex than those of Fe^{3+} and Co^{3+} complex. But on the reaction of Cr^{3+} complex, the oxidation of Cr^{3+} to Cr(VI) might occur, and a fairly large amount of CO is formed in place of CO_2 which is the main product in the gamma irradiation of oxalic acid and the oxalate complexes other than those with Cr^{3+}.

Details of this study will be published later.

Radiation Applications Division
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken