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The Radiolysis of Crystalline Oxalato Metal Complexes. The Effects of Coordinating Metal Ions on the Radiolysis of Oxalate

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Coordinated oxalates in metal complexes are more reactive under γ-irradiation than are ionic oxalates. This suggests that the covalency between the metal ion and the ligand in oxalato metal complexes promotes the reactivity of the ligand. The reaction of the ligand is also affected by the central metal ions. In $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ and $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, the coupled reduction of central metal ions with the oxidative decomposition of the ligand to carbon dioxide occurs at relatively high G values. In $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$, the redox reaction of the central metal ion is small and the ligand decomposes into carbon dioxide and carbon monoxide. In $K_3[Al(C_2O_4)_3]\cdot 3H_2O$, the formation of glyoxal and formic acid instead of carbon monoxide is significant.

It is well-known that the reactions of the ligand molecule in coordination compounds are affected by the central metal ions. As for the photochemistry of metal complexes, the photochemical reactions of oxalato metal complexes have been studied extensively.[1,2] It has been concluded that the photo-induced electron transfer from the ligand to such central metal ions as iron(III), cobalt(III) and manganese(III) results in the high quantum yield of the decomposition of the ligand molecule.

Our study aims at the elucidation of the effects of central metal ions on the radiolytic decomposition of the ligand molecule (in this case, oxalate) by comparing the results of radiolysis with those of photolysis.

Several papers have dealt with the radiation-induced reactions of metal complexes in aqueous solutions.[3-6] The radiation-induced reaction of an aqueous system is, however, not suitable for comparison with the photo-induced reaction, because the radiation-induced reaction is initiated by the reactive intermediates produced by the radiolysis of water, while the photochemical reaction is initiated by the direct excitation of the solute. On the other hand, the direct excitation of the complexes by an ionizing radiation can be expected in the radiolysis of crystalline complexes. Therefore, the radiolysis of crystalline oxalato metal complexes was studied in order to elucidate the effects of metal ions in the excitation of the complexes by ionizing radiations. A preliminary report has already been published.[7] Moreover, recently, a study of the radiolysis of several oxalatocobalt(III)-complex salts was reported by Sano, Matsubara and Saito.[8]

Results and Discussion

The Reactivities of Ionic Oxalate in Salts and Coordinated Oxalate in Metal Complexes.—The radiation-chemical reactivities of ionic

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1) C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc.*, **A235**, 518 (1956); *J. Phys. Chem.*, **63**, 22 (1959).

2) G. B. Porter, J. G. W. Doering and S. Karanka, *J. Am. Chem. Soc.*, **84**, 4028 (1962).

3) E. A. Hausman and T. W. Davis, ibid., **76**, 5341 (1954).

4) J. W. Swinnerton, *Dissertation Abstr.*, **20**, 527 (1959).

5) A. Sugimori and G. Tsuchihashi, This Bulletin, **34**, 713 (1960).

6) N. Matsuura, N. Shinohara and M. Takizawa, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **86**, 590 (1965).

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

8) H. Sano, N. Matsubara and N. Saito, ibid., **38**, 333 (1965).

oxalate and of coordinated oxalate were compared. In order to avoid the additional effects caused by the reduction or oxidation reactions of central metal ions in metal complexes, the radiolysis of potassium trioxalatoaluminate(III), the central ion of which is resistant to reduction and oxidation, was compared with that of oxalate salts.

Table I lists the *G* values for the decomposition (the number of molecules decomposed per 100 eV. of the absorbed energy of radiation) of ionic and coordinated oxalates, values which were determined by titration with potassium permanganate.

Table I. The decrease in the reducing power of the oxalate salts and the oxalato metal complex by γ-irradiation

Compound	Dose rate eV./g.hr.	Dose eV./g.	G(−Reducing power)
$H_2C_2O_4 \cdot 2H_2O$			10.1*
$H_2C_2O_4$	2.6×10^{19}	8.2×10^{21}	8.0
$K_3[Al(C_2O_4)_3] \cdot 3H_2O$			9.9*
$Na_2C_2O_4 \cdot H_2O$	1.4×10^{19}	2.8×10^{21}	0.4
	2.5×10^{19}	7.9×10^{21}	0.03
$K_2C_2O_4 \cdot H_2O$	4.5×10^{19}	9.6×10^{21}	0.8
	4.5×10^{19}	1.2×10^{22}	0.8
$NaHC_2O_4 \cdot H_2O$	2.4×10^{19}	8.5×10^{21}	1.5
$FeC_2O_4 \cdot 2H_2O$	8.8×10^{19}	8.1×10^{21}	0.1

* Is obtained from the yield-dose curve.

Ionic oxalates in sodium oxalate, potassium oxalate, and iron(II) oxalate showed lower *G* values for decomposition than the coordinated oxalate in potassium trioxalatoaluminate(III). The *G* value of the aluminum complex was similar to that of oxalic acid (hydrous and anhydrous). Sodium hydrogen oxalate showed an intermediate *G* value. These results suggest that the covalency between oxygen and metal/or hydrogen is important for the reactivity of oxalates against ionizing radiation.

Crystal water has a slight effect on the radiolysis of oxalate. Hydrated oxalic acid and hydrated iron(II) oxalate have reactivities similar to those of anhydrous oxalic acid and anhydrous sodium oxalate respectively.

The Radiolysis of Trioxalato Metal Complexes.—*General Features.*—In addition to the effect of the covalency described above, the oxidation and reduction of the central metal ions affect the reaction mechanism of the ligand. Before discussing this problem, however, the general features of the radiolysis of trioxalato metal complexes should be described. Gamma-irradiation brings about the decomposition of the ligand and a change in the oxidation state of metal ions, and gives gaseous, liquid and solid products. Among the reaction products, gaseous products show an interesting feature. Gamma-irradiation gave two kinds of gaseous products: the gas evolved by irradiation, and the gas evolved by dissolving the irradiated complex in water. In some cases, the content of the gas evolved from the γ-ray irradiated complex was different from that of the gas evolved by dissolving the irradiated complex in water. The most remarkable example is the case of potassium trioxalatochromate(III). When it was irradiated at a total dose of 2.3×10^{22} eV./g., it gave a gaseous product at a *G* value of 1.8; this product consisted of 58% carbon dioxide, 37% carbon monoxide, and 5% hydrogen. The *G* value of the gas evolved by treating the irradiated complex with water was 0.5; this gas consisted solely of carbon dioxide. This fact suggests that the gas evolved by dissolving the irradiated complex is not the gas occluded in the irradiated complex crystals. The existence of a precursor for carbon dioxide may be expected. An infrared spectroscopic study of irradiated potassium trioxalatochromate(III) suggested that carbon dioxide was trapped in the form of hydrogen carbonate ions.[9]

The quantities of the evolved gas and the decomposed oxalato metal complexes are plotted against the absorbed radiation dose in Figs. 1, 2 and 3.

As is shown in the figures, the quantities of the evolved gas and the decomposed complexes are proportional to the absorbed dose.

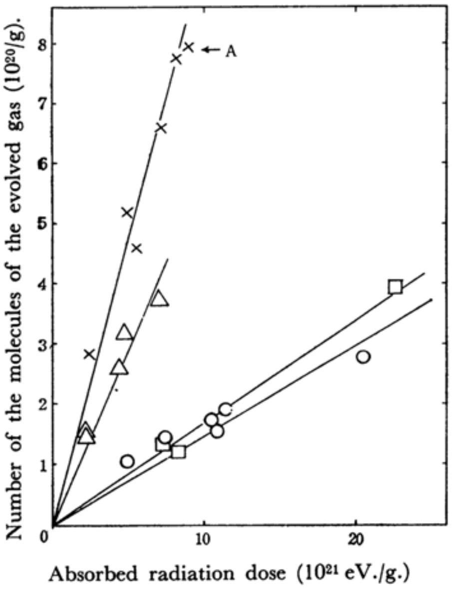

Fig. 1. Relations between the number of the molecules of the evolved gas and the absorbed radiation dose.

—○— $K_3[Al(C_2O_4)_3] \cdot 3H_2O$
—□— $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$
—△— $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$
—×— $K_3[Co(C_2O_4)_3] \cdot 3H_2O$
A Irradiated at −50°C

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[9] A. Sugimori, To be published.

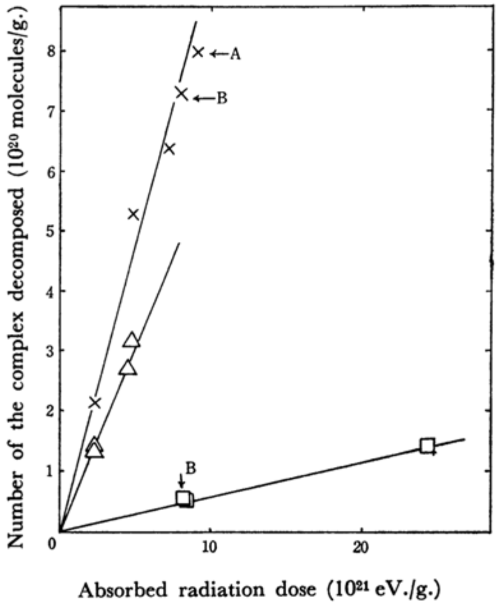


Fig. 2. Relations between the number of the complex decomposed and the absorbed radiation dose.
—□— $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$
—△— $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$
—×— $K_3[Co(C_2O_4)_3]\cdot 3H_2O$
A　Irradiated at −50°C
B　Irradiated in the air

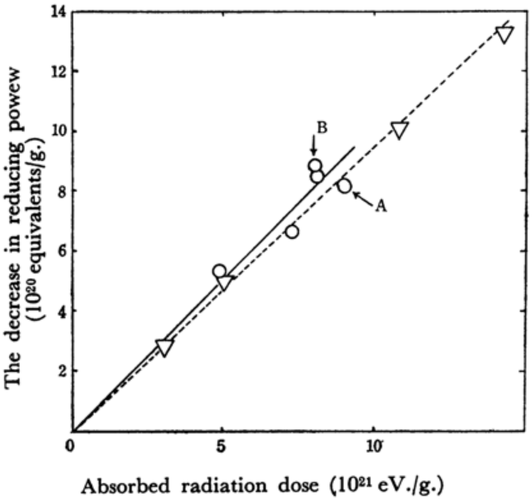


Fig. 3. Relations between the decrease in reducing power and the absorbed radiation dose.
—○— $K_3[Al(C_2O_4)_3]\cdot 3H_2O$
—▽— $H_2C_2O_4\cdot 2H_2O$
A　Irradiated at −50°C
B　Irradiated in the air

The existence of air and the change in the irradiation temperature from room temperature to −50°C slightly affect the decomposition of the complex (Figs. 1, 2 and 3).

Effects of Central Metal Ions on the Decomposition of the Ligand.—The decomposition of the ligand depends on the nature of the central metal ions.

i) $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and $K_3[Co(C_2O_4)_3]\cdot 3H_2O$.

The results of the radiolysis of potassium trioxalatoferrate(III) and potassium trioxalatocobaltate(III) are summarized in Table II.

TABLE II. THE RADIOLYSIS OF POTASSIUM TRIOXALATOFERRATE(III) AND POTASSIUM TRIOXALATOCOBALTATE(III)

$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$

	Dose (eV./g.)	*G* value	Composition of the gas (%)
Evolved gas		6.8*	
	7.1×10^{21}	6.3	H_2 0 CO 0 CO_2 100
The gas evolved by dissolving the irradiated complex	7.1×10^{21}	1.5	H_2 0 CO 0 CO_2 100
Fe(II)		7.2*	
The decrease of the complex		6.1*	

$K_3[Co(C_2O_4)_3]\cdot 3H_2O$

	Dose (eV./g.)	*G* value	Composition of the gas (%)
Evolved gas		11.1*	
	5.4×10^{21}	8.6	H_2 0 CO 0 CO_2 100
The gas evolved by dissolving the irradiated complex	5.4×10^{21}	1.3	H_2 0 CO 0 CO_2 100
The decrease of the complex		10.3*	

* Is obtained from the yield-dose curve.

The features of the radiolysis of these complexes are:

1) The *G* values of the gaseous products and the decomposed complexes were greater than those of the other complexes.

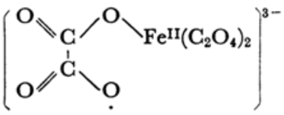
2) The gaseous product consisted entirely of carbon dioxide.

3) In the case of potassium trioxalatoferrate(III), iron(II) was produced at a *G* value similar to those of the total gaseous product and the decomposed complex.

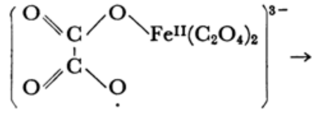
The radiation-induced reaction of potassium trioxalatoferrate(III) is very simple. The main reaction of the ligand is the decomposition to carbon dioxide; side reactions to give carbon monoxide and hydrogen are negligible. The coupled reduction of the central metal ion with the oxidative decomposition of coordinated oxalate takes place solely. This reaction is the same as that of the photolysis of the complex. Excited states which are the same as that in photolysis may be produced selectively and effectively by γ-irradiation. The reaction mechanism proposed for the photolysis[1] may be applied to the radiation-induced reaction:

$$[Fe^{III}(C_2O_4)_3]^{3-} \xrightarrow{\gamma\text{-rays}} [Fe^{III}(C_2O_4)_3]^{3-*} \quad (1)$$
(excited state)

$[Fe^{III}(C_2O_4)_3]^{3-*} \rightarrow$



(2)



$$C_2O_4^{\cdot -} + [Fe^{II}(C_2O_4)_2]^{2-} \quad (3)$$

$$C_2O^{-}{}_4^{\cdot} + [Fe^{III}(C_2O_4)_3]^{3-} \rightarrow$$
$$2CO_2 + [Fe^{II}(C_2O_4)_3]^{4-} \quad (4)$$

Similar reactions would take place in the radiolysis of potassium trioxalatocobaltate(III). In this case, the structure of the cobalt(II) complex has been studied by the infrared spectroscopic method.[9] The cobalt(II) produced by γ-irradiation preferentially forms four coordinate dioxalato complexes. This means that the reduction of the central metal ion is followed by the elimination of one oxalate ion and a reorganization in the coordination sphere.

ii) $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$.

1) The formation of carbon monoxide and hydrogen was remarkable.

2) The *G* value for the decomposition of the complex was small.

3) The content of the evolved gas was different from that of the gas obtained by dissolving the irradiated complex in water.

The radiolysis of potassium trioxalatochromate(III) is very different from those of potassium trioxalatoferrate(III) and potassium trioxalatocobaltate(III). The reduction of chromium(III) to chromium(II) was not observed. On the other hand, the oxidation of the central metal ion was observed, although the yield was very small. The *G* value of chromium(VI) was found to be 0.003—0.004. The lack of a conjugation of reactions between the ligand and the central metal ion in potassium trioxalatochromate(III) would result in a lower reactivity toward γ-irradiation.

TABLE III. THE RADIOLYSIS OF POTASSIUM TRIOXALATOCHROMATE(III)

	Dose (eV./g.)	*G* value	Composition of the gas (%)	
Evolved gas		1.8*		
	2.3×10^{22}	1.8	H_2	5
			CO	37
			CO_2	58
	8.0×10^{21}	—	H_2	2
			CO	36
			CO_2	62
The gas evolved by dissolving the irradiated complex	2.3×10^{22}	0.5	H_2	0
			CO	0
			CO_2	100
The decrease of the complex		0.6*		

* Is obtained from the yield-dose curve.

The lower reactivity of the complex has also been observed in the photolysis of the complex.[2] Trioxalatocobaltate(III) and trioxalatoferrate(III) are easily decomposed by ultraviolet irradiation, but trioxalatochromate(III) is very resistant to ultraviolet light. This fact also suggests that, in the radiation-induced reaction, the same excited molecules as in the photochemical reaction are preferentially produced.

iii) $K_3[Al(C_2O_4)_3]\cdot 3H_2O$

TABLE IV. THE RADIOLYSIS OF POTASSIUM TRIOXALATOALUMINATE(III)

	Dose (eV./g.)	*G* value	Composition of the gas (%)	
Evolved gas		1.5*		
	1.0×10^{22}	1.7	H_2	2
			CO	5
			CO_2	93
The gas evolved by dissolving the irradiated complex	1.0×10^{22}	2.9	H_2	0
			CO	0
			CO_2	100
Decrease in the reducing power		9.9*		

* Is obtained from the yield-dose curve.

The reaction of the complex is similar to that of potassium trioxalatochromate(III). However, some quantitative differences were observed:

1) The carbon dioxide content in the evolved gas was larger than that of the chromium complex.

2) The contribution of the gas obtained by dissolving the irradiated complex to the total gaseous product is larger than that in the case of the chromium complex.

In this case, the yield of carbon dioxide, the oxidized product, was much superior to the yield of carbon monoxide, the reduced product, if the large contribution of the gas evolved by dissolving the irradiated complex in water was taken into account. Since the oxidation and the reduction of aluminum(III) are difficult, the reduction products of oxalate ions may be expected. The formation of aldehyde and formic acid was observed. The infrared spectra of the aldehyde 2,4-dinitrophenylhydrazone suggest that the aldehyde consists mainly of glyoxal: $G=0.2$ was given for the aldehydic product. A volatile acidic substance, presumably formic acid, and with a *G* value of 0.4, was formed.

A similar reaction occurs in the radiolysis of oxalic acid. The formation of glyoxal and formic acid was also observed.

Since the decomposition of oxalate occurred in a small yield in the case of ionic oxalate, it is evident that the coordination bond between aluminum(III) and oxalate plays an important role in the radiation-induced reaction of the coordinated oxalate ion.

Experimental

Materials.—Commercially-available oxalic acid, sodium oxalate, potassium oxalate (guaranteed-grade reagent of the Kanto chemical Co.) and iron(II) oxalate (extra pure-grade reagent of the Kanto Chemical Co.) were used without any further purification. Sodium hydrogen oxalate was prepared by mixing the solutions of oxalic acid and sodium oxalate in an equal molar ratio. Potassium trioxalatoaluminate(III), potassium trioxalatochromate(III), potassium trioxalatoferrate(III) and potassium trioxalatocobaltate(III) were prepared according to the method described in "Inorganic Synthesis."[10]

Gamma-Ray Irradiation.—The irradiation cell was a cylindrical tube with a break-off seal. About one gram of the crystalline oxalato metal complexes or oxalate salts was put in the cell, and the cell was sealed off in a vacuum. The cell was covered with black paper to protect the contents from the light when the sample was sensitive to light.

Cobalt-60 γ-ray sources of 10000 and 16000 curies were used. The dose rate was measured by Fricke dosimetry, which was modified for the measurements of larger doses by using acidic solutions of ferrous sulfate saturated with nitrogen gas. The dose was calculated assuming that $G(\mathrm{Fe}^{3+})=8.2$.

The correction of the absorbed radiation energy arising from the difference in the electron densities of the dosimeter and samples was also applied.

Irradiation at low temperatures was carried out by using a thermostat placed in the irradiation facility.

Analysis of the Products.—*i) Gaseous products.*—The vessel containing the irradiated complex was connected to the vacuum system, the volume of which had been measured. Then the break-off seal was cut off. The total volume of the gaseous products was calculated from the pressure increase in the vacuum system. The composition of the gas was determined by means of mass spectrometric analysis.

ii) The Gas Evolved by Dissolving the γ-Ray Irradiated Complex.—The vessels containing the irradiated complex and water were arranged in a vacuum line, as is shown in Fig. 4. The water in B was degassed by boiling the contents several times in a vacuum. Then the whole system except for B was evacuated thoroughly. After evacuation, the vacuum system was isolated from the pump. Then the water in B was introduced into A, and the irradiated complex in A was dissolved. After the whole sample had been dissolved in water, the vessel, A, was cooled with dry ice. Then the volume and the composition of the gas were determined in the same way as in *i*).

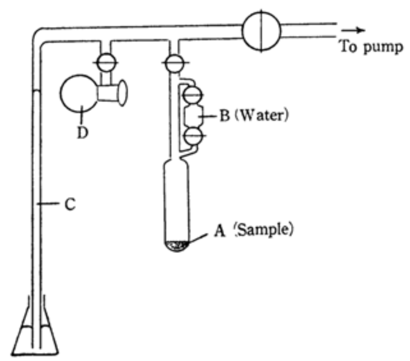


Fig. 4. Vacuum system for the analysis of the gas evolved by dissolving the irradiated complex in water.
A Irradiated sample, B Water,
C Mercury manometer, D Gas sampler for mass spectrometric analysis.

iii) Reducing Power.—After irradiation, the whole contents of the irradiation vessel were transfered into a measuring flask and dissolved in water. The solution was then titrated with potassium permanganate in acidic media. The comparison of the reducing power before and after γ-irradiation gave the decomposition of oxalate ions. This analysis was, however, applied only to oxalic acid, oxalte salts and potassium trioxalatoaluminate(III).

iv) Carbonyl Compound.—The determination of the carbonyl compounds produced in the irradiated oxalic acid and potassium trioxalatoaluminate(III) was

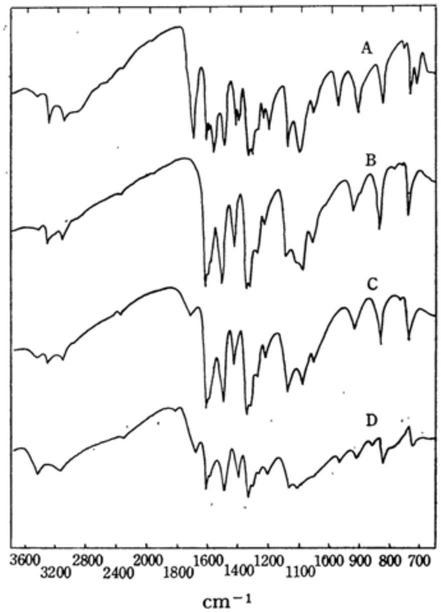


Fig. 5. Infrared spectra of the 2,4-dinitrophenylhydrazones of glyoxylic acid (A), glyoxal (B), and radiolytically-produced aldehydes from $H_2C_2O_4\cdot 2H_2O$ (C) and $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ (D).

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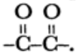
[10] J. C. Bailar, Jr., and E. M. Jones, "Inorganic Synthesis," Vol. 1, Mcgraw-Hill, New York (1939), p. 35.

carried out by precipitating them with 2, 4-dinitrophenylhydrazine. The melting point of the 2, 4-dinitrophenylhydrazone was 280°C in the radiolytic product of oxalic acid, and 240°C in the radiolytic product of potassium trioxalatoaluminate(III). Since the melting point of glyoxal 2, 4-dinitrophenylhydrazone is 328°C, the carbonyl compound obtained in radiolysis is not considered to be pure glyoxal. However, the 2, 4-dinitrophenylhydrazone was turned purple by the action of alkali, which is specific for bis-2, 4-dinitrophenylhydrazone of  $-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-$. The infrared spectra of the 2, 4-dinitrophenylhydrazone of the radiolytically-produced aldehyde, together with those of glyoxal and glyoxylic acid, are shown in Fig. 5. Since the infrared spectra of the 2, 4-dinitrophenylhydazone of the radiolytically-produced aldehyde, especially in oxalic acid, were very similar to those of glyoxal, the main component of the radiolytically produced aldehyde may be assumed to be glyoxal. However, a small peak at $\sim$1700 cm^{-1} which can not be explained by glyoxal is to be ascribed to an impurity, presumably glyoxylic acid.

v) Volatile Acidic Substance.—The solution of the γ-ray irradiated sample was acidified with sulfuric acid. The solution was steam-distilled, and the distillate was titrated with a sodium hydroxide solution.

vi) Iron(II).—Iron(II), which was produced in the radiolysis of potassium trioxalatoferrate(III), was determined to be a bipyridyl complex.

vii) Residual Metal Complex.—The irradiated oxalato metal complex was dissolved in water, and the residual oxalato metal complex was determined by the spectrophotometric method. For the determination of potassium trioxalatochromate(III), the absorption bands at 420 and 570 mμ were used. For potassium trioxalatocobaltate(III), the bands at 420 and 605 mμ were used. For the determination of potassium trioxalatoferrate(III), the shoulder at 263 mμ was used.

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