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Radiolysis of Co^{III}-EDTA in Aqueous Solution; the Yields of Hydrogen and Hydrogen Peroxide in 0.8 N Sulfuric Acid

Niro Matsuura, Nobuyoshi Shinohara and Masaru Nishikawa

Department of Pure and Applied Sciences, College of General Education, The University of Tokyo
Komaba, Meguro-ku, Tokyo

and Masao Takizawa

Radiation Chemistry Laboratory, Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo

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The hydrogen and hydrogen peroxide produced in the radiolysis of Co^{III}-EDTA ($Co^{III}Y^-$) in 0.8 N sulfuric acid have been measured. The yields of hydrogen and hydrogen peroxide were found to be $G_\infty(H_2)=0.4$ and $G_\infty(H_2O_2)=2.5$ for the aerated system, $G_\infty(H_2)=3.2$ and $G_\infty(H_2O_2)=0$ for the deaerated system where G_∞ denotes the yield at the infinite solute concentration. The decomposition mechanism proposed previously was discussed in detail on the basis of the observed $G_\infty(H_2)$ and $G_\infty(H_2O_2)$ and of the effect of chloride ion on the decomposition yield $G_\infty(-Co^{III}Y^-)$. A similar experiment was carried out for EDTA alone and the decomposition mechanism was discussed.

In the previous paper[1,2] $G_\infty(-Co^{III}Y^-)$[*1] for the radiolysis of Co^{III}-EDTA was reported to be 2.5 in the aerated solution and 5.0 in the deaerated solution. Two components of the complex Co^{III}-EDTA, *i. e.*, Co^{3+} aquo-ion[3] and ligand EDTA[1,2] were separately investigated as for their degradation under the equivalent condition. $G(Co^{2+})$ for the radiolysis of Co^{3+} aquo-ion were found to be 2.3 both in the aerated and deaerated medium and $G_\infty(-\mathrm{EDTA})$ for the radiolysis of EDTA was found to be 3.6 in the aerated solution and 4.0 in the deaerated solution. Extention of the work was attempted in which G values of hydrogen formation from irradiated dilute Co^{III}-EDTA solution were measured in order to obtain informations on the reaction mechanism for the decomposition of Co^{III}-EDTA. One of the reaction paths conceivable is the attack of the complex by atomic H either in accordance with reaction (1) or (2);

$$Co^{III}Y^- + H = Co^{II}Y^{2-} + H^+ \qquad (1)$$

$$Co^{III}Y^- + H = Co^{III}Y\cdot^- + H_2 \qquad (2)$$

The latter appeared to be more appropriate for explaining observed G values for Co^{III}-EDTA degradation and measurements of H_2 yield were needed in order to confirm the assumption. The hydrogen peroxide yield was also expected to provide equally important informations in determining the reactivity of radical HO_2 for which following two reaction paths are conceivable, since the number of moles of H_2O_2 production per HO_2 is different in reactions (3) and (4).

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (3)$$

$$Co^{III}Y^- + HO_2 = Co^{III}Y\cdot^- + H_2O_2 \qquad (4)$$

From observed G values of H_2 and H_2O_2 formation the radiolysis of Co^{III}-EDTA will be described in further detail.

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1) N. Matsuura, N. Shinohara and M. Takizawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 897 (1963).

2) N. Matsuura, N. Shinohara and M. Takizawa, *Scientific Papers of the College General Education of University of Tokyo*, **13**, 179 (1963).

[*1] G_∞ denotes the yield at the infinite solute concentration.

3) N. Matsuura, N. Shinohara and M. Takizawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 259 (1965).

Experimental

Materials. Triplly distilled water was used throughout the work, distilled water being redistilled over acid potassium permanganate and dilute alkaline solution. The ethylenediaminetetraacetatocobaltate(III) salt (K Co^{III}-EDTA·$2H_2O$) was prepared by the method of Dwyer *et al.*[4] and then twice recrystallized. The other materials used were reagent grade.

Preparation of Samples and Their Irradiation. Sample solutions of Co^{III}-EDTA or EDTA were prepared by dissolving it in 0.8 N sulfuric acid. Deaerated solutions were obtained by bubbling nitrogen washed with alkaline pyrogarol solution. Aerated and deaerated sample solutions were irradiated with γ-rays from ^{60}Co source of 1500 curie, at the dose rate of 7.7×10^{18}—8.1×10^{18} eV$ml^{-1}hr^{-1}$ (determined by the Fricke dosimeter, taking $G(Fe^{3+})=15.5$).

Analysis of Products. After irradiation, the analysis of hydrogen produced was performed as described below. Hydrogen was determined by a gas chromatographic method developed in this laboratory[5] using a GC-1B type Shimadzu gas chromatograph equipped with a liquid-separating apparatus and a precolumn of Molecular Sieve. A similar method has been reported for the determination of minute amounts of dissolved gases in aqueous solutions by Swinnerton *et al.*[6-8]

Hydrogen peroxide in the irradiated EDTA solutions was determined colorimetrically by the titanium method. In the case of the irradiated Co^{III}-EDTA solutions, however, hydrogen peroxide was determined polarographically in pH 4.0 buffer solution of acetic acid and sodium acetate, because of the interference of the reddish color of Co^{III}-EDTA.

Results

Hydrogen Yields from Co^{III}-EDTA System. Hydrogen yields were determined from irradiated solution of different concentration of Co^{III}-EDTA in 0.8 N sulfuric acid. The amount of hydrogen evolved for a given dose of gamma irradiation showed a fine linear relationship for the dose up to the value 4.0×10^{18} eV ml^{-1} $G(H_2)$ are plotted against the Co^{III}-EDTA concentration in Fig. 1. In the case of aerated solution $G(H_2)$ was found to be equal to that of primary molecular yield from water, $G_{H_2}=0.45$*[2] and is independent of the complex concentration in the range studied.

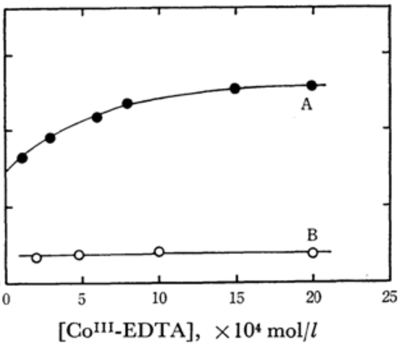

Fig. 1. Relation between $G(H_2)$ and Co^{III}-EDTA concentration.

A: deaerated B: aerated

On the other hand $G(H_2)$ in the deaerated system shows the tendency to increase with the concentration of Co^{III}-EDTA and reaches the maximum G value of 3.2. The $G(H_2)$ at the infinite concentration in deaerated solution can be determined by the inverse plot method[1,10] taking the $1/(G(H_2)-G_0(H_2))$ values against the reciprocal of the complex concentration where $G_0(H_2)$ denotes the intercept of Fig. 1.

Hydrogen Yields from EDTA System. Hydrogen yields were measured also for the solution of EDTA in 0.8 N sulfuric acid. The hydrogen yields were found to obey a rigorous proportionality to the gamma doses in the region studied. The plots of $G(H_2)$ against EDTA concentrations are shown in Fig. 2, where the results for the aerated and deaerated solutions are seen to lie on separate curves. It is perhaps to be noted that the curve A in Fig. 2 are essentially the same type as the curve A shown in Fig. 1. However the $G_\infty(H_2)$ is 4.4 which is slightly higher than that found in the complex system.

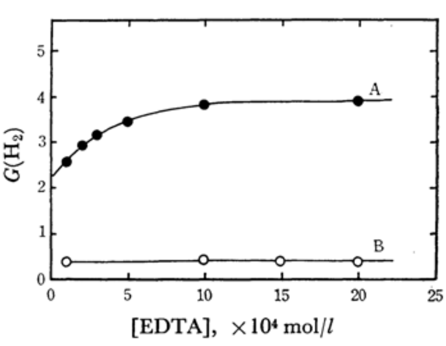

Fig. 2. Hydrogen yield at various EDTA concentration.

A: deaerated B: aerated

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[4] F. P. Dwyer, E. C. Garfas and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1956).

[5] M. Takizawa, S. Ishikawa, K. Koda and H. Aoki, The 13th Annual Meeting of the Japan Society for Analytical Chemistry, Sendai, Japan, September, 1964.

[6] J. W. Swinnerton, V. J. Linnenbom and C. H. Cheek, *Anal. Chem.*, **34**, 483 (1962).

[7] J. W. Swinnerton, V. J. Linnenbom and C. H. Cheek, *ibid.*, **34**, 1509 (1962).

[8] C. H. Cheek, V. J. Linnenbom and J. W. Swinnerton, *Radiation Res.*, **19**, 636 (1963).

*[2] G_p denotes the primary radical and molecular yields from water radiolysis. We accept $G_H=3.65$, $G_{OH}=2.95$, $G_{H_2O_2}=0.8$ and $G_{H_2}=0.45$.[9]

[9] A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostland, Princeton, New Jersey (1961).

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

Hydrogen Peroxide Yields from Co^{III}-EDTA System. Hydrogen peroxide yields were determined from irradiated solution of different concentration of Co^{III}-EDTA. The relation between $G(H_2O_2)$ and solute concentration for the aerated Co^{III}-EDTA system is shown in Fig. 3.

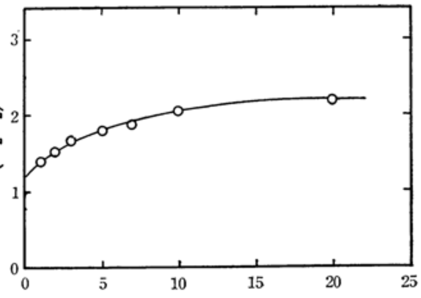


Fig. 3. Hydrogen peroxide yield in the aerated solution at various Co^{III}-EDTA concentration.

The inverse plot method was also applied to this case in order to find hydrogen peroxide yield at infinite solute concentration and $G_\infty(H_2O_2)$ thus obtained is 2.5. In the case of deaerated Co^{III}-EDTA system, on the other hand, hydrogen peroxide could not be detected.

Hydrogen Peroxide Yields from EDTA System. Hydrogen peroxide was produced in the radiolysis of both aerated and deaerated EDTA solution, which is different from Co^{III}-EDTA system. As shown in Fig. 4, $G(H_2O_2)$ is independent of solute concentration in the deaerated system, while it shows some dependency in the aerated system and the $G_\infty(H_2O_2)$ are 4.0 for aerated and 0.7 for deaerated system.

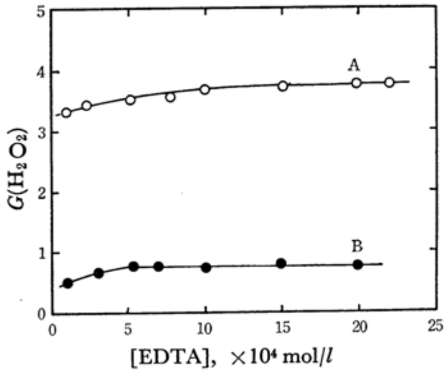


Fig. 4. Hydrogen peroxide yield at various EDTA concentration.

A: aerated B: deaerated

Effects of Chloride Ion on Decomposition Yield of Co^{III}-EDTA. The addition of chloride ion reduces $G(-Co^{III}Y^-)$ as shown in Fig. 5. In the aerated solution of 10^{-3} mol/l Co^{III}-EDTA, $G(-Co^{III}Y^-)$ decreases with chloride ion concentration and reaches zero at 10^{-2} mol/l chloride ion. In the deaerated solution of 10^{-3} mol/l Co^{III}-EDTA $G(-Co^{III}Y^-)$ also decreases with chloride ion concentration but reaches 2.2 at 10^{-2} mol/l chloride ion, which remains constant at least up to 5×10^{-2} mol/l. $G(-Co^{III}Y^-)$ from deaerated Co^{III}-EDTA solution containing 5×10^{-2} mol/l chloride ion, which is sufficient to scavenge all the OH radicals, are plotted as the function of Co^{III}-EDTA concentration in Fig. 6. $G(-Co^{III}Y^-)$ increases with Co^{III}-EDTA concentration and approaches a limiting value of 2.8, while in the aerated solution containing 5×10^{-2} mol/l chloride ion, Co^{III}-EDTA do not decompose irrespective of Co^{III}-EDTA concentration. The G values obtained in the radiolysis of Co^{III}-EDTA and EDTA are summarized in Table 1.

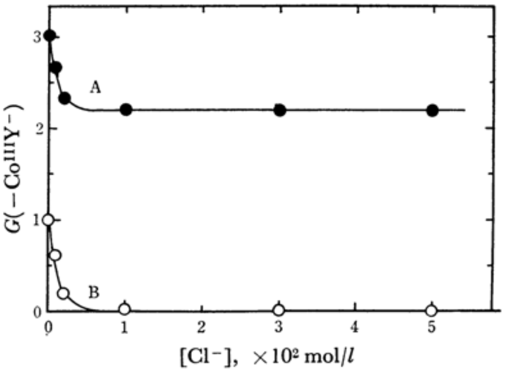


Fig. 5. Variation of $G(-Co^{III}Y^-)$ with Cl$^-$ concentration for aqueous solution containing 1.00 ×10^{-3} mol/l Co^{III}-EDTA.

A: deaerated B: aerated

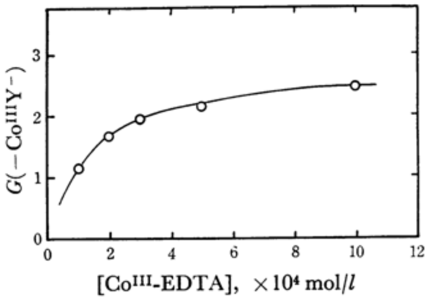


Fig. 6. Variation of $G(-Co^{III}Y^-)$ for deaerated solution containing 5.0×10^{-2} mol/l Cl$^-$.

TABLE 1. OBSERVED G VALUES

	$G_\infty(-S)$	$G_\infty(H_2O_2)$	$G_\infty(H_2)$
Co^{III}-EDTA-O_2	2.5	2.5	0.4
Co^{III}-EDTA	5.0	0	3.2
Co^{III}-EDTA-Cl$^-$-O_2	0	—	—
Co^{III}-EDTA-Cl$^-$	2.8	—	—
EDTA-O_2	3.6	4.0	0.4
EDTA	4.0	0.7	4.4

Discussion

Decomposition of Co^{III}-EDTA. Co^{III}-EDTA is reduced to Co(II) state in aqueous medium under the effect of gamma irradiation. On the basis of polarographic behavior of irradiated Co^{III}-EDTA solution and also from the fact that the original complex can be recovered from the irradiated solution by reoxidation with H_2O_2 (this reaction occurs only at elevated temperature) only in the presence of EDTA, the decomposition products of Co^{III}-EDTA is neither Co^{2+} simple aquo-ion nor Co^{II}-EDTA, but Co(II) complex chelated with a degraded EDTA[1,2] which will be described as $Co^{II}Y'$ (Y' denotes a degraded EDTA) henceforth whose structure has not been determined as yet.

From the facts that in the radiolysis of deaerated Co^{III}-EDTA solution $G_\infty(-Co^{III}Y^-)$ is 5.0 which is higher than the G value of primary atomic hydrogen 3.65 in 0.8 N sulfuric acid and that Co^{III}-EDTA is reduced to Co(II) even when H atom from water is scavenged by oxygen, we have suggested that not only H atom but also OH radical[*3] will take part in the reduction of Co^{III}-EDTA.[1,2]

The observation that $G(H_2)$ in deaerated system is larger than the primary hydrogen yield of the radiolysis of water can be accounted for by a process such as reaction (2). Since, if H atom attacks the central metal of Co^{III}-EDTA as in reaction (1) which is the case for the radiolysis of Co^{3+} aquo-ion,[3,11] $G(H_2)$ must not be greater than the molecular yield from water 0.45.

On the other hand, the following results suggest the presence of a reaction of OH radical with Co^{III}-EDTA such as reaction (5); (i) $G_\infty(-Co^{III}Y^-)=5.0$ is larger than H atom yield from water, (ii) Co^{III}-EDTA is reduced to Co(II) state with $G_\infty(-Co^{III}Y^-)=2.5$ only in the case that H atom is scavenged by dissolved oxygen and (iii) chloride ion inhibits the complex decomposition as described later.

$$Co^{III}Y^- + OH = Co^{III}Y\cdot^- + H_2O \qquad (5)$$

Rabani and Stein[12] postulated a mechanism of OH radical reducing the complex in the radiolysis of Fe^{III}-cytochrome C to a similar compound of Fe(II). The similar type of mechanism may account for our observation, however, the intermolecular electron transfer in their mechanism from the complex radical designated by $Fe^{III}RH\cdot$ to the starting complex of Fe^{III}-cytochrome C ($Fe^{III}RH_2$) by reaction (6) does not agree with our observation.

$$Fe^{III}RH\cdot + Fe^{III}RH_2 = Fe^{III}R + Fe^{II}RH_2 + H^+ \qquad (6)$$

Experimental results that in the radiolysis of Co^{III}-EDTA the complex are reduced to Co(II) state and at the same time its ligand EDTA was decomposed provides the evidence of intramolecular electron transfer inside the radical $Co^{III}Y\cdot^-$ produced by reaction (2) or (5) resulting in a stable $Co^{II}Y'$ species by reaction (7).

$$Co^{III}Y\cdot^- = Co^{II}Y' + H^+ \qquad (7)$$

As stated above, it seems clear that the reduction of the complex is due to its reaction with both H atom and OH radical. This is shown most clearly by the partial inhibition of the complex decomposition by the addition of chloride ion which are known to interfere only the reaction of OH radicals.[9,13] In the deaerated solution with added chloride ion, there occurs a considerable reduction of $G_\infty(-Co^{III}Y^-)$ from 5.0 to 2.8 as shown in Table 1. The decrease in $G_\infty(-Co^{III}Y^-)$ in the presence of chloride ion are, to the first approximation, equal to the primary yield of OH radical 2.95 in 0.8 N sulfuric acid medium, indicating that all the OH radicals are converted into less reactive Cl atoms for Co^{III}-EDTA by reaction (8).

$$Cl^- + OH = Cl + OH^- \qquad (8)$$

$G_\infty(-Co^{III}Y^-)=2.8$ obtained in the presence of chloride ion may be assigned to the reaction with H atoms. Observed $G_\infty(H_2)$ and $G_\infty(H_2O_2)$ are consistent with this interpretation, since the results that the observed $G_\infty(H_2)=3.2$ is lower by 0.9 than $G_H+G_{H_2}=4.1$ from water and that H_2O_2· ($G_{H_2O_2}=0.8$) could not be detected can be reasonably explained by invoking a reaction of H atom with H_2O_2 (reaction (9)) which does not react with Co^{III}-EDTA.

$$H_2O_2 + H = OH + HO_2 \qquad (9)$$

In the aerated system all the H atoms would be scavenged by oxygen to yield H_2O_2 by the fast reactions (10) and (3), and $G(H_2)$ is not expected to exceed 0.45 in agreement with the observation.

$$H + O_2 = HO_2 \qquad (10)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (3)$$

Therefore, in the aerated solution only OH radical will decompose the complex by reactions (5) and (7), which is supported by the fact that in the presence of chloride ion and oxygen, Co^{III}-EDTA was not decomposed as shown in Table 1. Comparison of observed G's with those expected from the stoichiometric considerations are summarized in Table 2.

[*3] In the radiolysis of Co^{3+} aquo-ion OH radical is believed to oxidize Co^{2+} formed back to Co^{3+}.[3,11]

11) M. Lefort, *J. Chim. Phys.*, **54**, 782 (1957).

12) J. Rabani and G. Stein, *Radiation Res.*, **17**, 327 (1962).

13) T. Rigg, G. Scholes and J. Weiss, *J. Chem. Soc.*, **1952**, 3034.

TABLE 2. COMPARISON OF OBSERVED *G* VALUES WITH THOSE ESTIMATED FROM STOICHIOMETRY

	O_2 Present		O_2 Absent	
Reaction	$H+O_2=HO_2$ $HO_2+HO_2=H_2O_2+O_2$ $Co^{III}Y^-+OH=Co^{II}Y'+H_2O+H^+$		$Co^{III}Y^-+H=Co^{II}Y'+H_2+H^+$ $Co^{III}Y^-+OH=Co^{II}Y'+H_2O+H^+$ $H_2O_2+H=OH+H_2O$	
Yield	$G_\infty(-Co^{III}Y^-)=G_H=2.95$	(2.5)	$G_\infty(-Co^{III}Y^-)=G_H+G_{OH}=6.60$	(5.0)
	$G_\infty{}^{Cl^-}(-Co^{III}Y^-)=0$	(0)	$G_\infty{}^{Cl^-}(-Co^{III}Y^-)=G_H-G_{H_2O_2}=2.85$	(2.8)
	$G_\infty(H_2O_2)=G_H/2+G_{H_2O_2}=2.63$	(2.5)	$G_\infty(H_2O_2)=0$	
	$G_\infty(H_2)=G_{H_2}=0.45$	(0.4)	$G_\infty(H_2)=G_H+G_{H_2}-G_{H_2O_2}=3.30$	(3.2)

( ) shows the observed *G* value.

TABLE 3. COMPARISON OF OBSERVED *G* VALUES WITH THOSE ESTIMATED FROM STOICHIOMETRY

	O_2 Present		O_2 Absent	
Reaction	$H+O_2=HO_2$ $HO_2+HO_2=H_2O_2+O_2$ $Y+OH=Y\cdot+H_2O$ $Y\cdot+O_2=Y'+HO_2$		$Y+H=Y\cdot+H_2$ $Y+OH=Y\cdot+H_2O$ $2Y\cdot=Y+Y'$	
Yield	$G_\infty(-Y)=G_{OH}=2.95$	(3.6)	$G_\infty(-Y)=(G_H+G_{OH})/2=3.30$	(4.0)
	$G_\infty(H_2O_2)=(G_H+G_{OH})/2+G_{H_2O_2}=4.10$	(4.0)	$G_\infty(H_2O_2)=G_{H_2O_2}=0.8$	(0.7)
	$G_\infty(H_2)=G_{H_2}=0.45$	(0.4)	$G_\infty(H_2)=G_H+G_{H_2}=4.10$	(4.4)

( ) shows the observed *G* value.

Decomposition of EDTA. According to the mechanism in the previous section, both H atom and OH radical from irradiated water are supposed to decompose one molecule of Co^{III}-EDTA. Results in the case of EDTA alone suggest the decomposition mechanism is different from the case of Co^{III}-EDTA. In the radiolysis of aerated EDTA solution, $G\,(H_2)$ is equal to the primary hydrogen yield from water, while $G_\infty(H_2O_2)$ of 4.0 is larger than the primary hydrogen peroxide yield from water, as shown in Table 1. These *G* values may be explained in terms of reactions (3), (10), (11) and (12).

$$H + O_2 = HO_2 \qquad (10)$$

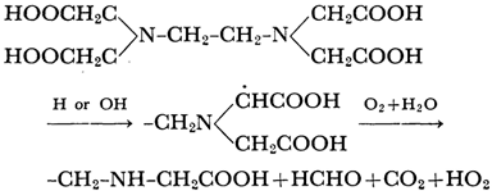
$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (3)$$

$$Y + OH = Y\cdot + H_2O \qquad (11)$$

$$Y\cdot + O_2 = Y' + HO_2 \qquad (12)$$

Similar reactions are proposed for the radiolysis of amino acid,⁽¹⁴⁾ where the decomposition is assumed to be initiated by the dehydrogenation by H atom and OH radical from α-carbon position of amino acid. Also in EDTA system the initial attack on α-carbon of EDTA by H atom and OH radical is quite conceivable which Joussot-Dubien *et al.*⁽¹⁵⁾ suggested for the photolysis of EDTA.

In the aerated system H atom reacts with oxygen to produce H_2O_2 by reactions (10) and (3), therefore only OH radical is expected to decompose EDTA by reactions (11) and (12). Y′ in reaction (12) represents a precursor which ultimately leads to the formation of the final products HCHO and CO_2. Although quantitative determination of these products has not been completed yet, reaction such as (13) is conceivable for the production of HCHO and CO_2.



$$\begin{matrix}HOOCH_2C \\ HOOCH_2C\end{matrix}\Big\rangle N\text{-}CH_2\text{-}CH_2\text{-}N\Big\langle\begin{matrix}CH_2COOH \\ CH_2COOH\end{matrix} \xrightarrow{\text{H or OH}} \text{-}CH_2N\Big\langle\begin{matrix}\dot{C}HCOOH \\ CH_2COOH\end{matrix} \xrightarrow{O_2+H_2O}$$

$$\text{-}CH_2\text{-}NH\text{-}CH_2COOH+HCHO+CO_2+HO_2 \qquad (13)$$

In the deaerated system H atom and OH radical will attack α-carbon position of EDTA as in the radiolysis of amino acid by reactions (11) and (14).

$$Y + H = Y\cdot + H_2 \qquad (14)$$

Large $G_\infty(H_2)$ shown in Table 1 suggests the occurrence of reaction such as (14). Hydrogen peroxide is formed with $G_\infty(H_2O_2)=0.7$, which is markedly different from the case of Co^{III}-EDTA system, suggesting that hydrogen peroxide from water does not react with any other radicals or solute. One of the possibilities for the fate of Y·, radical produced by reactions (11) and (14) is the disappearance by disproportionation as shown by reaction (15), although other possibilities are not excluded.

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14) W. M. Garrison, *Radiation Res. Suppl.* **4**, 158 (1964).

15) J. Jonssot-Dubien and J. Faure, *J. Chim. Phys.*, **60**, 1214 (1963).

$$Y\cdot + Y\cdot = Y' + Y \qquad (15)$$

Under the above assumption the quantitative interpretation of the *G* values observed are tabulated in Table 3. As is clearly seen in Tables 2 and 3 our observed *G* values for H_2 and H_2O_2 can be explained quantitatively using the primary radical and molecular yields from pure water. Although the deviations of observed $G_\infty(-\mathrm{Co^{III}Y^-})$ and $G_\infty(-\mathrm{Y})$ from those calculated cannot be overlooked, the essential part of the mechanism would not be affected greatly.