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Radiolysis of Co^{III}-EDTA in Aqueous Solution; The Effect of pH

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The hydrogen and hydrogen peroxide produced in the radiolysis of Co^{III}-EDTA ($Co^{III}Y^-$) in various pH's have been measured. $G_\infty(H_2)$ in the deaerated system sharply dropped from the value of 3.2 at $pH<1$ to the value of 0.8 at $pH>4$ where G_∞ denotes a limiting value which is reached with increasing solute concentration. $G_\infty(H_2O_2)$ in the aerated system was found to be 2.5—2.0. $G_\infty(-Co^{III}Y^-)$ ($=4.4$) was not affected by the addition of N_2O. $G_\infty(N_2)$ and $G_\infty(H_2)$ were found to be 2.6 and 0.8 respectively. From the results, it is concluded that H atoms and OH radicals reduce Co(III) to Co(II) through the dehydrogenation from the ligand, while e_{aq}^- reduce the complex without any degradation of the ligand.

In the previous papers of the series of study on the radiolysis of Co^{III}-EDTA, we reported that OH radicals and H atoms abstract hydrogen from α-carbon position of EDTA molecule of the complex and that the free radical $Co^{III}Y\cdot^-$ formed by hydrogen abstraction is reduced to $Co^{II}Y'$ by intramolecular electron transfer from ligand to central cobalt(III) ion where Y′ denotes a degraded EDTA.[1-4]

In this paper the study of radiolysis of Co^{III}-EDTA in dilute solution was extended to higher pH region where hydrated electrons are the predominant reducing species.[5,6] We are particularly interested to see whether hydrated electrons react with Co^{III}-EDTA in a similar way as H atoms do in the acidic medium. Following reactions (1) and (2) are conceivable for e_{aq}^- and Co^{III}-EDTA.

$$Co^{III}Y^- + e_{aq}^- \xrightarrow{H_2O} Co^{III}Y\cdot^- + H_2 + OH^- \tag{1}$$

$$Co^{III}Y^- + e_{aq}^- \longrightarrow Co^{II}Y^{2-} \tag{2}$$

By the determination of the hydrogen yields, one can select one of the alternatives as the plausible reaction for e_{aq}^-. Some of the experiment was carried out in the presence of N_2O as the electron scavenger.[7]

Experimental

Material. Triply distilled water was used throughout the study. Ethylenediaminetetraacetatocobaltate(III) salt (KCo^{III}-EDTA·$2H_2O$) was prepared by the method, described previously[1] and then twice recrystallized. The other material used were of reagent grade.

Preparation of Samples and Their Irradiation. Sample solutions were prepared by dissolving the complex salt in 0.4 M sulfate solutions whose pH has been adjusted by adding the required amounts of sulfuric acid and potassium sulfate. The experiment was carried out in the range of pH 0.4—5.0. The irradiation vessel used was the same as that reported previously.[1] Deaerated solutions were prepared by bubbling nitrogen washed with alkaline pyrogarol solution or by thoroughly degassing by repeated freezing-pumping-thawing. The irradiation vessel for solution containing N_2O was cylindrical one of the capacity of 45 m*l*. The vessel containing 15 m*l* of the solution was thoroughly degassed and N_2O was introduced to various pressure. After being sealed off, the vessel was shaken and then irradiated with ^{60}Co γ-rays at the dose rate of 7.2×10^{18}—8.1×10^{18} eV·ml^{-1}hr^{-1} determined by the Fricke dosimeter, taking $G(Fe^{3+})=15.5$.

Analysis of Products. Hydrogen peroxide was determined polarographically.[4] The gases produced by irradiation were pumped from the solution by the freeze-thaw technique, passed thorugh traps at −196°C in order to condense N_2O, and collected in a gas burette. The amount of hydrogen was determined either by passing the gases over heated cupric oxide, or by the gas chromatographic method described previously[4]; these results agreed within experimental error.

Results

Hydrogen Peroxide. Hydrogen peroxide from irradiated solution of Co^{III}-EDTA in the presence of oxygen were determined at various values of pH. The yields of hydrogen peroxide were found to depend on the dose absorbed but little on the solute concentration and initial pH of the solution. The good straight lines were obtained between the yield and the dose absorbed up to 4×10^{18} eV·ml^{-1}. Figure 1 shows the hydrogen peroxide yields as the function of solute concentration at a given pH, which shows that the yield is virtually constant except in the lower concentration region. The curve in Fig. 1 approaches to a limiting G value $G_\infty(H_2O_2)$ with increasing solute concentration. By the inverse plot method described in previous paper[1,3] the limiting G value can be calculated and plotted as function of pH in Fig. 2.

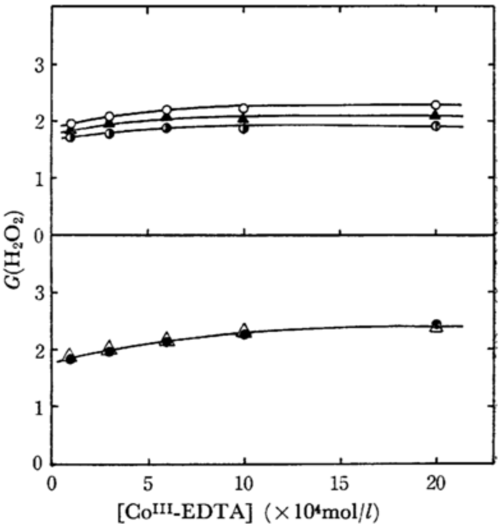

Fig. 1. Hydrogen peroxide yields in aerated Co^{III}-EDTA solution at various pH's.
Initial pH: ● 1.0, △ 2.0, ○ 3.0, ▲ 4.0, ◑ 5.0

Hydrogen peroxide could not be detected from the irradiated Co^{III}-EDTA solution, if oxygen is removed.

Hydrogen Yields. Hydrogen formed in the irradiated solution of Co^{III}-EDTA in the presence and absence of oxygen was measured. The amount depends both on the dose absorbed and initial pH of the irradiated solution. Straight lines were obtained between the yield and the dose absorbed

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[1] N. Matsuura, N. Shinohara and M. Takizawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 897 (1964).

[2] N. Matsuura, N. Shinohara and M. Takizawa, Scientific Papers of the College General Education of University of Tokyo, **13**, 179 (1964).

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

[4] N. Matsuura, N. Shinohara and M. Takizawa, This Bulletin, **40**, 2042 (1967).

[5] G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, **66**, 471 (1962).

[6] E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

[7] F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, **A267**, 443 (1962).

(below 4×10^{18} eV·ml^{-1}). Figure 3 shows $G(H_2)$ in the deaerated system as function of solute concentration of various pH's. Each curve in Fig. 3 approaches to a limiting G value with increasing solute concentration. By the inverse plot method each limiting G value in deaerated solution was calculated and plotted as function of pH in Fig. 4 (black circle). $G(H_2)$ in aerated solution was 0.4 independent of the solute concentration and the initial pH; the results were shown as open circle in Fig. 4.

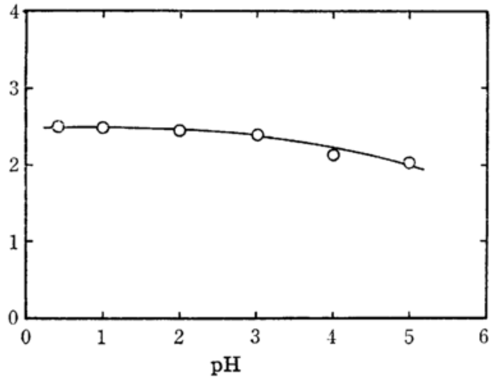

Fig. 2. Hydrogen peroxide yields in aerated Co^{III}-EDTA solution as a function of pH.

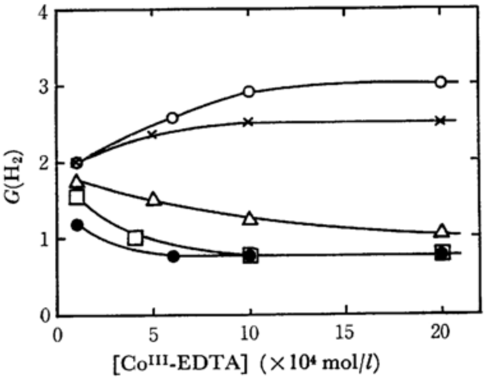

Fig. 3. Hydrogen yields in deaerated Co^{III}-EDTA solution at various pH's.
Initial pH: ○ 1.0, × 2.0, △ 3.0, □ 4.0, ● 5.0

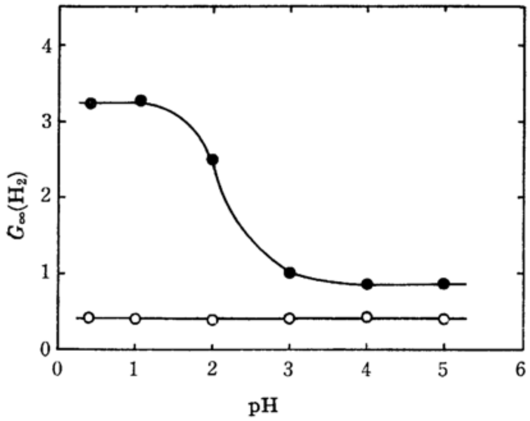

Fig. 4. Hydrogen yields in deaerated Co^{III}-EDTA solution as a function of pH.
● deaeraed, ○ aerated

Effect of N_2O. Figure 5 illustrates the effect of N_2O on $G(H_2)$ together with $G(N_2)$ at the fixed concentration of Co^{III}-EDTA 10^{-3} mol/l (pH=4.0) in the absence of oxygen. $G(H_2)$ decreases and $G(N_2)$ increases with N_2O concentration until they reach constant values of 2.6 and 0.8 at the concentration of $\sim10^{-2}$ mol/l, indicating the complete scavenging of e_{aq}^-. Effect of variation of Co^{III}-EDTA concentration upon $G(H_2)$ and $G(N_2)$ in deaerated Co^{III}-EDTA solution containing N_2O in sufficiently high concentration to scavenge e_{aq}^- (2.5×10^{-2} mol/l) is shown in Fig. 6. It is readily seen that both $G(N_2)$ and $G(H_2)$ depend on Co^{III}-EDTA concentration up to $\sim10^{-3}$ mol/l, beyond which $G(N_2)$ and $G(H_2)$ were 2.6 and 0.8, respectively.

$G(-Co^{III}Y^-)$ in the presence of 2.5×10^{-2} mol/l of N_2O increases with Co^{III}-EDTA concentration,

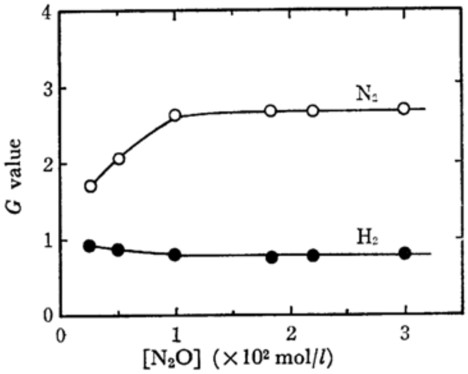

Fig. 5. Yields of nitrogen and hydrogen in the solution of N_2O and 1.0×10^{-3} mol/l Co^{III}-EDTA.

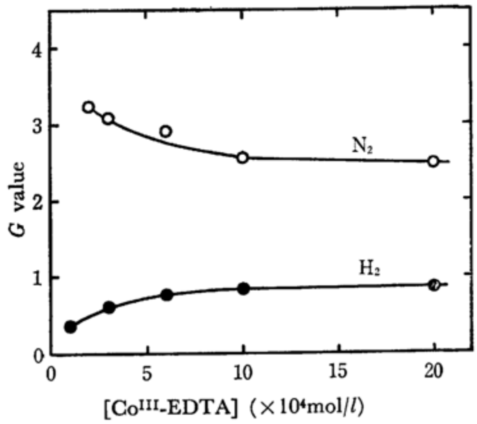

Fig. 6. Yields of nitrogen and hydrogen in the solution of 2.4×10^{-2} mol/l N_2O and Co^{III}-EDTA.

TABLE 1. OBSERVED MAXIMUM *G* VALUES

	pH	Co^{III}-EDTA + O_2	pH	Co^{III}-EDTA	pH	Co^{III}-EDTA+N_2O
$G(-Co^{III}Y^-)$*	0.4—2	2.5—2.8	0.4—5	5.0—4.5	4	4.4
	2—3	decrease				
	3—5	1.8				
$G(H_2)$	0.4—5	0.4	0.4—2	3.2	4	0.8
			2—3	decrease		
			3—5	0.8		
$G(H_2O_2)$	0.4—5	2.5—2.0	0.4—5	0		
$G(N_2)$					4	2.6

* These *G* values have been reported in the previous paper.[3]

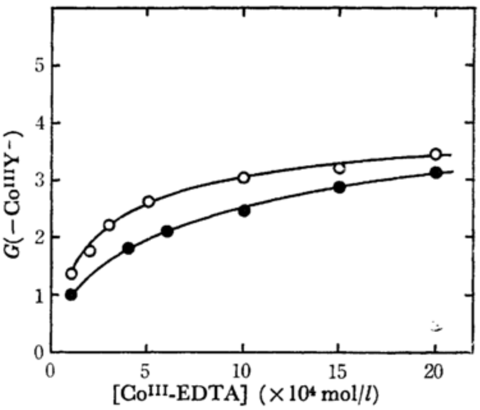

Fig. 7. $G(-Co^{III}Y^-)$ as a function of Co^{III}-EDTA concentration.
○ Co^{III}-EDTA
● Co^{III}-EDTA+2.4×10^{-2}mol/l N_2O

as shown in Fig. 7 together with the result of the system in the absence of N_2O. Each curve in Fig. 7 approaches to a limiting *G* value with increasing Co^{III}-EDTA concentration. By the inverse plot method, $G_\infty(-Co^{III}Y^-)$ was determined to be 4.5 for Co^{III}-EDTA system and 4.4 for Co^{III}-EDTA-N_2O system. The various limiting *G* values obtained were summarized in Table 1.

Discussion

Decomposition Mechanism in Deaerated System. Co^{III}-EDTA is reduced to Co(II) state in aqueous medium under the effect of irradiation and the decomposition mechanism of Co^{III}-EDTA in the 0.8 N sulfuric acid solution was explained in terms of a series of the processes of (3), (4), (5), (6), (7) and (8) as described in the previous papers,[1,2,4] where Y and Y′ denoted EDTA and a degraded form of EDTA, respectively.*[1]

$$Co^{III}Y^- + H \longrightarrow Co^{III}Y\cdot^- + H_2 \quad (3)$$

$$Co^{III}Y\cdot^- \longrightarrow Co^{II}Y' + H^+ \quad (4)$$

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

$$H + O_2 \longrightarrow HO_2 \quad (6)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad (7)$$

$$H + H_2O_2 \longrightarrow OH + H_2O \quad (8)$$

In the present discussion we attempt to explain stoichiometrically the *G* values observed in higher pH solution. It seems reasonable to assume that oxidizing radicals OH, whose $pK_a=11.2$,[8] react as such with Co^{III}-EDTA by reaction (5) also at $pH\simeq5$ as in 0.8 N sulfuric acid, while it is expected that reactions of the reducing radicals in higher pH range are different. In the radiolysis of deaerated Co^{III}-EDTA solution, $G_\infty(H_2)$ sharply dropped from the value of 3.2 in the acidic medium to the value of 0.8 at pH=4 as shown in Fig. 4. $G(H_2)=0.8$ in the deaerated system is larger than the primary hydrogen yield $G_{H_2}=0.4$ from water. This suggests that H atoms ($G_H=0.55$)[9] are produced in higher pH region besides hydrated electrons, and it is only H atom that abstracts hydrogen from ligand EDTA of the complex by reaction (3) as in 0.8 N sulfuric acid medium. The facts that $G(H_2)\fallingdotseq G_H+G_{H_2}$ appears to indicate the absence of the reaction (1).

We found that the reduction yield of the complex was almost independent of pH as shown in Table 1. This may be interpreted as the result of the direct attack of e_{aq}^- to the central cobalt(III) ion of the complex *via* reaction (2).

$$Co^{III}Y^- + e_{aq}^- \longrightarrow Co^{II}Y^{2-} \quad (2)$$

The evidence for the participation of the hydrated electrons in the reduction of the complex is provided by $G_\infty(N_2)$ and $G_\infty(-Co^{III}Y^-)$ from the irradiated Co^{III}-EDTA in deaerated solution at pH=4 in the presence of N_2O which is believed to convert the hydrated electron to radical OH by reaction (9).

$$N_2O + e_{aq}^- \xrightarrow{H_2O} N_2 + OH + OH^- \quad (9)$$

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*[1] Concievable forms of the species of Y· and Y′ were shown in Ref. 4.

8) J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.*, **86**, 3175 (1964).

9) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *ibid.*, **85**, 1375 (1963).

TABLE 2. COMPARISON BETWEEN THE OBSERVED G VALUES AND THE CALCULATED G VALUES FROM POSTULATED MECHANISM AT $\mathrm{pH}=4.0$

System	$G(-\mathrm{Co^{III}Y^-})$	$G(\mathrm{H_2})$
$\mathrm{Co^{III}}$-EDTA	$G_{e_{aq}^-} + G_H + G_{OH} = 5.10$ (4.5)	$G_H + G_{H_2} = 1.00$ (0.8)
$\mathrm{Co^{III}}$-EDTA + O_2	$G_{OH} = 2.25$ (1.8)	$G_{H_2} = 0.45$ (0.4)
$\mathrm{Co^{III}}$-EDTA + N_2O	$G_{e_{aq}^-} + G_H + G_{OH} = 5.10$ (4.4)	$G_H + G_{H_2} = 1.00$ (0.8)

System	$G(\mathrm{H_2O_2})$	$G(\mathrm{N_2})$
$\mathrm{Co^{III}}$-DTA	(0)	—
$\mathrm{Co^{III}}$-EDTA + O_2	$G_{OH} + (G_{e_{aq}^-} + G_H)/2 = 2.14$ (2.1)	—
$\mathrm{Co^{III}}$-EDTA + N_2O	—	$G_{e_{aq}^-} = 2.3$ (2.6)

( ) denotes the observed G values.

As shown in Table 1 $G_\infty(\mathrm{N_2})$ and $G_\infty(-\mathrm{Co^{III}Y^-})$ were 2.6 and 4.4, respectively and $G(-\mathrm{Co^{III}Y^-})$ was almost the same value regardless of the presence or absence of N_2O. This observation may be explained by the reduction of $\mathrm{Co^{III}Y^-}$ to $\mathrm{Co^{II}Y'}$ *via* reactions (5) and (4) by OH radicals from reaction (9), which supplements the decreases of the reaction (2).

In the radiolysis of $\mathrm{Co^{III}}$-EDTA in deaerated 0.8 N sulfuric acid solution, hydrogen peroxide was not detected, probably because it is destroyed by H atoms through reaction (8).[4] The fact that hydrogen peroxide can neither be detected in higher pH region may be explained by invoking a similar reaction of hydrated electron with hydrogen peroxide (reaction (10)).[9,10]

$$\mathrm{H_2O_2} + e_{aq}^- \longrightarrow \mathrm{OH} + \mathrm{OH^-} \qquad (10)$$

If H atoms react quantitatively with hydrogen peroxide (reaction (8)) $G(\mathrm{H_2})$ observed should be equal to the primary hydrogen yield ($G_{H_2}=0.45$) from water.

From the above consideration, it may be concluded that all the reacting species (H, e_{aq}^- and OH) from water radiolysis contribute to the reduction of the complex. H atoms and OH radicals reduce the complex through the hydrogen abstraction from the ligand, while e_{aq}^- reduced the complex by direct attack of the central cobalt(III) ion.

Decomposition Mechanism in Aerated System. As seen in the radiolysis in the 0.8 N sulfuric acid medium not only H atoms but also hydrated electrons are scavenged by oxygen to form anion O_2^- by the reaction (11).

$$e_{aq}^- + \mathrm{H^+} + \mathrm{O_2} \longrightarrow \mathrm{HO_2} \rightleftarrows \mathrm{H^+} + \mathrm{O_2^-} \qquad (11)$$

The anion O_2^- does not usually participate in the reduction of complex, because the radiolysis of the aerated solution gives much smaller $G_\infty(-\mathrm{Co^{III}Y^-})$ than in the deaerated one as shown in Table 1. The $G_\infty(\mathrm{H_2O_2})$ in the aerated solution is 2.1 as shown in Fig. 2, which may be explained if we assume one equivalent of O_2^- is consumed for producing half equivalent of hydrogen peroxide by reaction (12) without any reaction with $\mathrm{Co^{III}}$-EDTA.[1]

$$\mathrm{O_2^-} + \mathrm{O_2^-} \longrightarrow \mathrm{H_2O_2} + 2\mathrm{OH^-} \qquad (12)$$

It implies that in the aerated system only OH radicals decompose the complex by reactions (5) and (4) as in 0.8 N sulfuric acid.

The decomposition mechanism of $\mathrm{Co^{III}}$-EDTA invoking the reactions described above are consistent with the obtained results in that it satisfies the stoichiometric relationship between observed G values and the primary radical and molecular yields (taking $G_H=0.55$, $G_{e_{aq}^-}=2.30$, $G_{OH}=2.25$, $G_{H_2O_2}=0.71$, $G_{H_2}=0.45$).[11] As shown in Table 2, our observed G value can be explained quantitatively using the primary radical and molecular yields from water, except $G(-\mathrm{Co^{III}Y^-})$ where small discrepancy between calculated G values from the mechanism and observed G values exists. Nevertheless the discrepancy would not affect greatly the essential part of the decomposition mechanism.

The authors express thanks to Professor Y. Yoshino and his co-workers for many useful discussions.

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10) J. P. Keene, *Rad. Res.*, **22**, 1 (1964).
11) E. Hayon, *Trans. Faraday Soc.*, **61**, 723 (1965).