Chain Decomposition of Bis(oxalato)peroxotitanate(IV) Complex Initiated by Ti(III), Cr(II), and V(II)

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(Received November 16, 1993)

The chain decomposition of the bis(oxalato)peroxotitanate(IV) complex $[Ti(O_2)(ox)_2]^{2-}$ ($ox=C_2O_4^{2-}$) is initiated by the addition of a very small amount of reducing agent, such as Ti(III), Cr(II) or V(II). The chain length increases with increasing the concentrations of added $[TiO(ox)_2]^{2-}$ and oxalate ion; the maximum chain length was 600 under the experimental conditions. The decomposition reaction gave 2 mol of CO_2 per 1 mol of decomposed $[Ti(O_2)(ox)_2]^{2-}$. Ti(III), Cr(II), and V(II) reductions of $[Ti(O_2)(ox)_2]^{2-}$ produced ·OH, identified by the spin-trapping technique using a 5,5-dimethyl-1-pyrroline-*N*-oxide radical trap. Oxygen is an inhibitor of the chain reaction in this system. The chain-decomposition mechanism is discussed.

The redox of H_2O_2 and peroxo complexes is an important chemical problem because of intrinsic interest and biological significance.[1] It is well known that the reduction of H_2O_2 by transition-metal reductants, such as Fe(II), Ti(III), Cr(II), and Ru(II), proceeds predominantly by a one-electron path with the formation of a hydroxyl radical (·OH) as the intermediate.[2—8] The reaction of H_2O_2 with Ti(III) as well as Fe(II) has been widely used as a device for the generation of organic-free radicals in an aqueous media.[9—12] Recently, the reduction of the peroxochromium(IV) complex, $[Cr^{IV}(O_2)_2(dien)]$, with V(IV), $[Fe(CN)_6]^{4-}$, Ti(III), and hydroxylamine has also been studied.[13,14] It was found that both the Cr(IV) and peroxo functions are rapidly reduced by $[Fe(CN)_6]^{4-}$ and by Ti(III), whereas VO^{2+} reduces only the Cr(IV) center.[13] In addition, although the peroxo chromium complex reacts very slowly with hydroxoylamine, the reaction is markedly catalized by Fe(II) or Fe(III).[14]

We have found that the decomposition of $[Ti(O_2)(ox)_2]^{2-}$ is initiated by transition-metal reductants, such as Ti(III), Cr(II), and V(II), and proceeds by a chain reaction. This report deals with the chain decomposition mechanism of $[Ti(O_2)(C_2O_4)_2]^{2-}$ initiated by the reductants.

Experimental

Materials. $K_2[Ti(O_2)(ox)_2]$[15] and $K_2[TiO(ox)_2]$[16] were prepared by methods described in the literature, and recrystallized. Sodium oxalate was recrystallized before use; all other chemicals used were of reagent grade. The spectrum of $[Ti(O_2)(ox)_2]^{2-}$ was invariant in the pH 2.2 to 3.5 region in the presence of oxalate ion of the 10-fold concentration of $[Ti(O_2)(ox)_2]^{2-}$. Most of our experiments were carried out in the presence of $[TiO(ox)_2]^{2-}$ and excess oxalate ion at pH≈3, where the peroxo titanium(IV) complex exists in the form of $[Ti(O_2)(ox)_2]^{2-}$. The predominant species of the oxalate ion in this pH region are $C_2O_4^{2-}$ and $C_2O_4H^-$ ($C_2O_4H_2\rightleftarrows C_2O_4H^-+H^+$ $pK_1=1.37$, $C_2O_4H^-\rightleftarrows C_2O_4^{2-}+H^+ pK_2=3.81$).[17] Oxotitanium(IV) and titanium (III) exist in the form of $[TiO(ox)_2]^{2-}$ [18,19] and $[Ti(ox)_2]^-$ [20,21] under our experimental conditions. A titanium(III) chloride solution was used, and an analysis for Ti^{3+} was made at 502 nm ($\varepsilon=3.97$ mol^{-1} dm^3 cm^{-1}).[22] A solution of chromium(II) was prepared by reducing chromate with zinc amalgam[23a] or electrolytically.[23b] The chromate concentration was determined spectrophotometrically ($\varepsilon_{372}=4830$ mol^{-1} dm^3 cm^{-1}).[24] A solution of V(II) was produced by reducing a VO^{2+} solution with zinc amalgam[25] or electrolytically.[23b] A stock solution of VO^{2+} was prepared from vanadium(IV) oxide sulfate trihydrate and barium perchlorate.[26] The concentration of the vanadium ion was determined spectrophotometrically ($\varepsilon_{760}=17.5$ mol^{-1} dm^3 cm^{-1} for VO^{2+} [25] and $\varepsilon_{560}=4.37$ mol^{-1} dm^3 cm^{-1} for V^{2+} [27]).

Technique. Deaeration of the solutions was carried out by bubbling with pure nitrogen, which was passed over heated copper. The purified nitrogen gas was also used to provide an inert-atmosphere blanketing gas over air-sensitive solutions. A vessel equipped with an injector was used as the reaction vessel. This vessel was 10 ml in volume; after deaeration of a $[Ti(O_2)(ox)_2]^{2-}$ solution in the vessel, a very small amount of a transition-metal reductant (Ti(III), Cr(II), or V(II)) as a chain-reaction initiator was injected into the vessel as uniformly as possible using a gas-tight micro syringe. The solution in the cell was stirred at constant speed with a magnetic stirrer; the same results were obtained within 3% experimental error. A very small volume of the reductant solution was used at higher concentrations (10^{-3}—10^{-2} mol dm^{-3}) in order to avoid any oxidation of the reductants by oxygen coming in from outside.

Analysis. The amount of decomposed $[Ti(O_2)(ox)_2]^{2-}$ was determined spectrophotometrically ($\varepsilon_{383}=1130$ mol^{-1} dm^3 cm^{-1}).[28] Carbon dioxide was determined gaschromatographically. Oxygen was determined by using an oxygen monitor with a Clark-type electrode (Yellow Spring Instrument YSI 5300) at 25 °C. Kinetic data for the reactions between $[Ti(O_2)(ox)_2]^{2-}$ and the reductants were obtained on a stopped-flow spectrophotometer at 25 °C. The reaction of the peroxo titanium(IV) complex with the reductant was carried out while avoiding a chain reaction in the presence of a large excess of the reductant. The decrease of $[Ti(O_2)(ox)_2]^{2-}$ obeyed pseudo-first-order kinetics.

The ESR spin-trapping technique with spin-trapping agents has proven to be useful as a diagnostic tool in the detection of intermediates that are produced in an H_2O_2 reduction.[29—33] 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was employed as a radical-trapping agent by following a method similar to those previously reported.[33]

The rates of ·OH formation in Fenton-like reactions are relatively slow (being 10^2—10^4 $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$) compared to the reaction of its decay. Therefore, the rate constants for the reactions of ·OH with an ·OH scavenger cannot be directly measured in these Fenton-like reactions. However, from competitive kinetics of the reactions of DMPO and of scavengers for ·OH, it is possible to measure the relative rate constant using a method reported by Finkelstein et al.[34] and Yamazaki et al.[35] We measured the ratio of the rate constants for the reaction of ·OH with ·OH scavengers (k) to those for the reaction of ·OH with DMPO (k_{DMPO}) in a $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$/Ti(III) system. The electron spin resonance was recorded on a conventional X-band spectrometer (JEOL JES-RE2X ESR spectrometer).

Results and Discussion

Ti(III) as an Initiator. Ti(III) was used as a reductant which was reactive toward $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$. The chain decomposition of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ was initiated by the addition of a very small amount of Ti(III), which caused a fading of the yellow color of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$. The rate constant of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ with Ti(III) was 2.2×10^4 $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$ in oxalate buffer (pH 3.2) and the rate constant was independent of the concentration of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ and Ti(III). Typical data of the chain decomposition are presented in Table 1. The chain length was independent of the concentration of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ and almost independent of the concentration of Ti(III). On the other hand, the chain length increased with increasing the concentration of $[\text{TiO(ox)}_2]^{2-}$.

Most of our experiments were carried out in the presence of $[\text{TiO(ox)}_2]^{2-}$, where free H_2O_2 does not exist. However, a small amount of H_2O_2 existed in the solution due to the dissociation of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ ($\log K=5.5$) in some of the experiments carried out. Therefore, the effect of free H_2O_2 on the chain length was examined, and some decrease of the chain length was observed upon the addition of a small amount of H_2O_2 (Table 1). A large portion of Ti(III) will react with $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$, judging from the reaction rate constants of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ with Ti(III) (2.2×10^4 $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$) and of H_2O_2 with Ti(III) (1.0×10^4 $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$) as well as the concentrations of free H_2O_2 and $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ in the solution. Even if a small amount of Ti(III) reacts with free H_2O_2, the OH radical is formed as a reaction product,[33] which enters into the chain-reaction process. Thus, the decrease is attributed to the decrease of $[\text{TiO(ox)}_2]^{2-}$ due to the reaction of free H_2O_2 with $[\text{TiO(ox)}_2]^{2-}$ to give $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$. If H_2O_2 is not added to the solution, free H_2O_2 does not essentially affect the chain decomposition. The chain length increased with an increase in the concentration of not only $[\text{TiO(ox)}_2]^{2-}$, but also the oxalate ion (Tables 1 and 2). The maximum chain length was 600 under the present experimental conditions, and the chain decomposition gave 2 mol of CO_2 per 1 mol of the decomposed $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ (Table 3).

A possible mechanism for the chain reaction is as follows:

$$[\text{Ti(O}_2\text{)(ox)}_2]^{2-} + [\text{Ti(ox)}_2]^{-} + \text{H}_2\text{O} \longrightarrow 2[\text{TiO(ox)}_2]^{2-} + \cdot\text{OH} + \text{H}^+ \quad (1)$$

$$[\text{TiO(ox)}_2]^{2-} + \cdot\text{OH} + \text{H}^+ \longrightarrow [\text{TiO(ox)}] + \text{CO}_2 + \cdot\text{CO}_2{}^- + \text{H}_2\text{O} \quad (2)$$

$$[\text{TiO(ox)}] + \text{C}_2\text{O}_4{}^{2-} \longrightarrow [\text{TiO(ox)}_2]^{2-} \quad (3)$$

$$\cdot\text{CO}_2{}^- + [\text{TiO(ox)}_2]^{2-} + 2\text{H}^+ \longrightarrow \text{CO}_2 + [\text{Ti(ox)}_2]^{-} + \text{H}_2\text{O} \quad (4)$$

The overall reaction is

$$[\text{Ti(O}_2\text{)(ox)}_2]^{2-} + \text{C}_2\text{O}_4{}^{2-} + 2\text{H}^+ \longrightarrow [\text{TiO(ox)}_2]^{2-} + 2\text{CO}_2 + \text{H}_2\text{O}. \quad (5)$$

The peroxotitanium(IV) complex probably reacts with Ti(III) to give the ·OH radical according to Eq. 1.[36] Kristine et al.[37] also inferred the elimination of the ·OH radical from $[\text{Ti(O}_2\text{)(edta)}]^{2-}$ in the reduction of the peroxo complex by $[\text{Ti(edta)(H}_2\text{O)}]^{-}$.

Although the chain length was small in the absence of added oxalate ion, it increased with increasing the concentration of added oxalate ion (Tables 1 and 2). This fact can probably be attributable to the relative slowness of the regeneration of $[\text{TiO(ox)}_2]^{2-}$ (Eq. 3), which is necessary to continue the chain reaction, compared to reactions (2) and (4). Radical reactions (2) and (4) take place very rapidly; therefore, $[\text{TiO(ox)}_2]^{2-}$ must be regenerated very rapidly to continue the chain reaction. In fact, no chain reaction was observed in the solution containing equimolar quantities of $\text{Ti(O}_2\text{)}^{2+}$ and oxalate ion, where $[\text{Ti(O}_2\text{)(ox)}]$ was predominant. The chain length was dependent of the concentration of $[\text{TiO(ox)}_2]^{2-}$, but independent of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ (Table 1). This fact also suggests that the reaction of $\cdot\text{CO}_2^-$ with $[\text{TiO(ox)}_2]^{2-}$ (Eq. 4) is more likely than with $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$. The termination reaction is probably:

$$\cdot\text{CO}_2{}^- + \cdot\text{CO}_2{}^- \longrightarrow \text{C}_2\text{O}_4{}^{2-} \quad (k = 6.5\times10^8\ \text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}).^{38)} \quad (6)$$

The strong dependence of the chain length on the concentration of $[\text{TiO(ox)}_2]^{2-}$ is explained by a competitive reaction between Eqs. 4 and 6. The chain length was independent of the concentration of $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ (Table 1) under the experimental conditions that $[\text{Ti(O}_2\text{)(ox)}_2]^{2-}$ was in excess at the beginning of each experiment, so as to complete the chain reaction. This fact can be accounted for by assuming the above-mentioned chain reaction mechanism in which the peroxo complex decomposes only by reaction (1) and subsequent reactions ((2)—(4) and (6)) are not concerned

Table 1. Typical Data of Chain Decomposition of $[Ti(O_2)(ox)_2]^{2-}$ Initiated by Ti(III) at pH=3.2[a]

$[Ti(III)]$	$[TiO(ox)_2]^{2-}$	$-[Ti(O_2)(ox)_2]^{2-}$ [b]	n[c]
$10^5/mol\,dm^{-3}$	$10^3/mol\,dm^{-3}$	$10^5/mol\,dm^{-3}$	
1.50	0	14.5	10
1.50	0	15.0	10[d]
1.50	0	16.5	11[e]
1.50	0	5.4	3.6[f]
2.70	0	29.5	11
2.70	0	18.9	7.0[g]
2.50	0	25.0	10
1.00	0.50	32.0	32
0.60	1.00	21.0	35
0.90	1.00	33.3	37
1.20	1.00	45.6	38
1.60	1.00	62.4	39
1.00	3.00	54.0	54
0.50	5.00	29.5	59
1.00	5.00	64.0	64
0.65	10.0	42.9	66
1.00	10.0	75.0	75
0.50	30.0	43.6	87
0.50	50.0	47.3	95

a) A desired amount of Ti(III) was added to the 1.0×10^{-3} mol dm^{-3} $[Ti(O_2)(ox)_2]^{2-}$ aqueous solutions containing 1.0×10^{-2} mol dm^{-3} oxalate ion. b) Decomposed $[Ti(O_2)(ox)_2]^{2-}$. c) Chain length n; $(-[Ti(O_2)(ox)_2^{2-}])/[Ti(III)]$. d) $[Ti(O_2)(ox)_2^{2-}]=5.0\times10^{-4}$ mol dm^{-3}. e) $[Ti(O_2)(ox)_2^{2-}]=2.0\times10^{-3}$ mol dm^{-3}. f) No oxalate ion was added. g) H_2O_2 was added: $[H_2O_2]=5.0\times10^{-5}$ mol dm^{-3}. Calculated from the consumed CO_2 by using Eq. 4.

with the peroxo complex. Therefore, the chain length was independent of the concentration of the peroxo complex. The chain length was almost independent of the concentration of Ti(III) (Table 1). This fact is probably attributable to the finding that regardless of the amount of added Ti(III), reaction (4) occurs predominantly under our experimental conditions, compared to reaction (6); it is reasonable to assume that reaction (4) occurs predominantly, judging from the observed large chain length. Under these conditions the chain length is only slightly affected by the concentration of Ti(III).

Oxygen is an inhibitor of the chain reaction (Table 3). The reaction-rate constant of Ti(III) with $[Ti(O_2)(ox)_2]^{2-}$ ($k=2.2\times10^4$ mol^{-1} dm^3 s^{-1}) is about ten-times larger than that with O_2 ($k=2.0\times10^3$ mol^{-1} dm^3 s^{-1}). Therefore, Ti(III) reacts with $[Ti(O_2)(ox)_2]^{2-}$ in an oxygenated solution. The yields for decomposed $[Ti(O_2)(ox)_2]^{2-}$, consumed O_2, and produced CO_2 are given in Table 3. This observation in the O_2-saturated solution (Table 1) appears to be consistent with the sequence in Eqs. 7, 8, 9, 10, and 11, where Eq. 7 was obtained from Eqs. 1 and 2:

$$[Ti(O_2)(ox)_2]^{2-} + [Ti(ox)_2]^- + C_2O_4{}^{2-} \longrightarrow 2[TiO(ox)_2]^{2-} + CO_2 + \cdot CO_2{}^- \tag{7}$$

$$\cdot CO_2{}^- + O_2 \longrightarrow CO_2 + O_2{}^- \quad (k = 2.0\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}})^{39)} \tag{8}$$

$$O_2{}^- + H^+ \rightleftarrows HO_2 \quad (pK_a = 4.8)^{40)} \tag{9}$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad (k = 8.3\times10^5\ \mathrm{mol^{-1}\,dm^3\,s^{-1}})^{41)} \tag{10}$$

$$[TiO(ox)_2]^{2-} + H_2O_2 \longrightarrow [Ti(O_2)(ox)_2]^{2-} + H_2O \tag{11}$$

The overall reaction is as in

$$[Ti(O_2)(ox)_2]^{2-} + 2[Ti(ox)_2]^- + 2C_2O_4{}^{2-} + O_2 + 2H^+ \longrightarrow 3[TiO(ox)_2]^{2-} + 4CO_2 - 1pt + H_2O. \tag{12}$$

Kimura et al.[42—44] reported on a mechanism for the formation of hydrogen peroxide in a Mn(II)/oxalate/O_2 system initiated by oxidants (Mn(VII), Ce(IV), Cr(VI), Co(III) etc.) and by irradiation of $[Ru(bpy)_3]^{2+}$ with light. The formation mechanism of hydrogen peroxide, which was accounted for by a chain reaction, was studied in detail. In this system HO_2 formed by reactions (8) and (9) reacts with Mn(II) to give Mn(III), which is essential to carry forward the chain reaction. In our system, HO_2 probably forms $[Ti(O_2)(ox)_2]^{2-}$ by Eqs. 10 and 11. Therefore, Ti(III), which is essential to continue the chain reaction, will not regenerate. The identified products and their yields for decomposition in $[Ti(O_2)(ox)_2]^{2-}$/Ti(III)/O_2 systems are given in Table 3, which are in good agreement with the values calculated from Eq. 12. On the other hand, although the observed values for the consumed O_2 are in good agreement with the expected value in an aerated system, those for de-

Table 2. Effect of Added Oxalate Ion on Chain Decomposition at pH=3.2[a)]

Reductant[b)]	Oxalate ion 10^2/mol dm^{-3}	$[TiO(ox)_2]^{2-}$ 10^3/mol dm^{-3}	$-[Ti(O_2)(ox)_2]^{2-}$ 10^5/mol dm^{-3}	n
Ti(III)	3.0	0	5.1	17
	9.0	0	21.3	71
	15.0	0	25.8	86
	3.0	10.0	24.1	172
	6.0	10.0	51.8	370
	9.0	10.0	57.4	410
	15.0	10.0	84.0	600
Cr(II)	3.0	0	0.9	3
	9.0	0	3.6	12
	15.0	0	5.1	17
	3.0	10.0	23.0	164
	6.0	10.0	36.4	260
	9.0	10.0	48.2	344
	15.0	10.0	68.6	490
V(II)	3.0	0	2.7	9
	9.0	0	13.8	46
	15.0	0	19.5	65
	3.0	10.0	11.5	82
	6.0	10.0	35.0	250
	9.0	10.0	38.0	271
	15.0	10.0	61.6	440

a) $[Ti(O_2)(ox)_2^{2-}]=1.0\times10^{-3}$ mol dm^{-3}. b) [reductant]$=3.0\times10^{-5}$ mol dm^{-3} in the absence of $[TiO(ox)_2]^{2-}$ and [reductant]$=1.4\times10^{-5}$ mol dm^{-3} in the presence of 1.0×10^{-2} mol dm^{-3} $[TiO(ox)_2]^{2-}$.

Table 3. Yields of Decomposed $[Ti(O_2)(ox)_2]^{2-}$, Consumed O_2, and Prodused CO_2 in the $[Ti(O_2)(ox)_2]^{2-}$/Ti(III) Systems in the Presence and Absence of O_2 [a)]

Medium	[Ti(III)] 10^4/mol dm^{-3}	$-[Ti(O_2)(ox)_2{}^{2-}]$ 10^4/mol dm^{-3}	$-[O_2]$ 10^4/mol dm^{-3}	$[CO_2]$ 10^4/mol dm^{-3}
Deoxygenated	0.27	2.95	—	5.73 (5.90)
	0.46	7.43	—	13.3 (14.8)
Aerated	0.93	1.77 (0.47) (1.30)[b)]	0.48 (0.47)	4.40 (1.85) (2.55)[b)]
	1.85	3.81 (0.93) (2.88)[b)]	0.96 (0.93)	8.93 (3.70) (5.23)[b)]
O_2 saturated	1.85	1.00 (0.93)	1.17 (0.93)	3.53 (3.70)
	4.63	2.97 (2.32)	2.90 (2.32)	8.50 (9.26)

a) $[Ti(O_2)(ox)_2^{2-}]=1.0\times10^{-3}$ mol dm^{-3}, [oxalate]$=1.0\times10^{-2}$ mol dm^{-3}, values in parentheses were calculated from the reaction mechanisms in text (Eq. 4) or/and (Eq. 11). b) Observed value minus calculated value.

composed $[Ti(O_2)(ox)_2]^{2-}$ and for the produced CO_2 are much larger than the calculated values. The values of the observed value minus the calculated value for CO_2 are two-times larger than those for $[Ti(O_2)(ox)_2]^{2-}$. This fact indicates that the chain reaction partially occurs in an aerated system (Eq. 5).

Cr(II) as an Initiator. Cr(II) acts as an initiator on the chain decomposition of $[Ti(O_2)(ox)_2]^{2-}$ as well as Ti(III),

$$[Ti(O_2)(ox)_2]^{2-} + Cr(II)\ (or\ V(II)) + H^+ \longrightarrow [TiO(ox)_2]^{2-} + \cdot OH + Cr(III)\ (or\ V(III)). \quad (13)$$

The reaction rate constant of $[Ti(O_2)(ox)_2]^{2-}$ with Cr(II) was 2.5×10^4 mol^{-1}dm^3 s^{-1}, which was similar to that with Ti(III). The typical data of the chain decomposition of $[Ti(O_2)(ox)_2]^{2-}$ are listed in Table 4. The chain length was small compared to that in the $[Ti(O_2)(ox)_2]^{2-}$/Ti(III) system in the absence of $[TiO(ox)_2]^{2-}$ added initially. This fact is probably attributed to the smaller amount of $[TiO(ox)_2]^{2-}$ initially produced. $[TiO(ox)_2]^{2-}$ is initially produced from Ti(III) in the Ti(III) system (Eq. 1), but not produced in the Cr(II) system (Eq. 13). The chain length depended only slightly on the concentration of Cr(II), and increased

Table 4. Typical Data of Chain Decomposition of $[Ti(O_2)(ox)_2]^{2-}$ Initiated by Cr(II) at pH=3.2[a)]

[Cr(II)] 10^5/mol dm^{-3}	$[TiO(ox)_2]^{2-}$ 10^3/mol dm^{-3}	$-[Ti(O_2)(ox)_2]^{2-}$ 10^5/mol dm^{-3}	n
1.60	0	1.76	1.7
2.80	0	5.04	1.8
1.60	0.1	4.32	2.7
0.70	2.0	13.3	19
1.41	2.0	29.5	21
2.10	2.0	46.2	22
0.90	5.0	26.2	29
0.42	10.0	15.4	37
0.90	10.0	35.6	40
1.30	10.0	51.6	40
0.90	20.0	49.5	55
0.55	50.0	44.0	80
0.90	50.0	80.1	89

a) $[Ti(O_2)(ox)_2^{2-}]=1.0\times10^{-3}$ mol dm^{-3}, [oxalate]$=1.0\times10^{-2}$ mol dm^{-3}.

with increasing the concentration of $[TiO(ox)_2]^{2-}$ and oxalate ion (Tables 3 and 4). The maximum value of the chain length was 490 under our experimental conditions. The pattern for the dependence of the chain length on the concentration of $[TiO(ox)_2]^{2-}$ or oxalate ion is similar to that in the Ti(III) system.

V(II) as an Initiator. It was found that V(II) also acts as an initiator on the chain decomposition of $[Ti(O_2)(ox)_2]^{2-}$ (Eq. 13). The reaction rate constant of $[Ti(O_2)(ox)_2]^{2-}$ with V(II) was 6.9×10^2 mol^{-1} dm^3 s^{-1}, which was smaller by about 2 orders than those with Ti(III) and Cr(II). The typical data of the decomposition are given in Table 5. The chain length in the V(II) system was small, similar to that for the Cr(II) system in the absence of $[TiO(ox)_2]^{2-}$ added initially. The chain length increased with increasing the concentration of $[TiO(ox)_2]^{2-}$ and oxalate ion at the fixed concentration of V(II) (Tables 2 and 5), and the maximum chain length obtained under our experimental conditions was 440. Although the chain length in the V(II) system was similar to that in the Cr(II) system at lower concentrations of the reductant, it decreased with increasing the concentration of V(II). This behavior is different from those obtained in the Ti(III) and Cr(II) systems. The ESR spectrum obtained after completion of the reaction in the V(II) system gave an eight-line spectrum, as shown in Fig. 1. This spectrum was identical to that given by various vanadium(IV) complexes.[45)] The decrease in the chain length can be attributed to the reaction.

$$\cdot CO_2^- + V(IV) \longrightarrow CO_2 + V(III). \qquad (14)$$

The resulting V(III) is probably oxidized by an oxidant, such as ·OH. When a small amount of V(IV) was added initially, the chain length decreased (Table 4). This fact shows that reaction (14) occurs more predominantly than does reaction (4) with increasing the concentration of V(IV). Fe(II) did not act as an initiator of the chain reaction in our system.

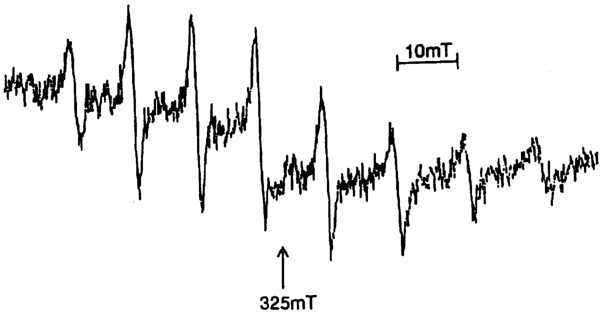


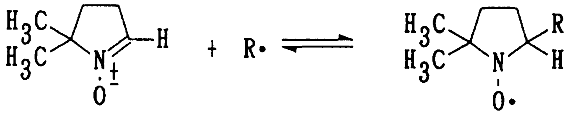
Fig. 1. ESR spectrum obtained after completion of the chain reaction in the $[Ti(O_2)(ox)_2]^{2-}$/V(II) couple. Microwave power, 10 mW; field modulation width, 0.63 mT; scan time, 4 min; measured at room temperature; $[Ti(O_2)(ox)_2^{2-}]=1.0\times10^{-3}$ mol dm^{-3}; $[TiO(ox)_2^{2-}]=1.0\times10^{-2}$ mol dm^{-3}; [ox]$=1.0\times10^{-2}$ mol dm^{-3}; [V(II)]$=3.7\times10^{-4}$ mol dm^{-3}; RG(reciever gain)=1600.

Spin-Trapping Studies. The spin-trapping procedure was used to characterize the products of metal ion/peroxide redox reactions.[46,47)] The reduction of H_2O_2 by labile Fe^{2+}, Cr^{2+} or Ti^{3+} proceeds predominantly by a one-electron path with the formation of the hydroxyl radical (·OH) as the initial product.[3—7)] The reaction of H_2O_2 with $Ti(H_2O)_6^{3+}$ was studied by the spin-trapping technique using DMPO traps;[31—33)] it was found that the Ti^{3+} reduction of H_2O_2 produces the ·OH radical. Further, the radical is intercepted by chemical mediator R (e.g. CH_3OH) to provide a more long-lived secondary carbon-centered radical, R· (·CH_2OH), which is trapped by DMPO. The trapping reaction for DMPO is shown for all radicals, ·R, according to

Table 5. Typical Data of Chain Decomposition of $[Ti(O_2)(ox)_2]^{2-}$ Initiated by V(II) at pH=3.2[a]

[V(II)] 10^5/mol dm^{-3}	$[TiO(ox)_2]^{2-}$ 10^3/mol dm^{-3}	$-[Ti(O_2)(ox)_2]^{2-}$ 10^5/mol dm^{-3}	n
0.90	0	2.5	2.8
2.00	0	5.6	2.8
0.40	1.0	45.2	11
2.60	1.0	28.6	11
0.90	5.0	20.9	23
0.40	10.0	13.1	33
0.60	10.0	21.3	36
0.90	10.0	27.0	30
0.90	10.0	18.9	21[b]
0.90	10.0	9.0	10[c]
0.90	10.0	27.0	30
2.00	10.0	45.0	23
0.55	30.0	35.5	65
0.90	30.0	50.8	56
0.30	50.0	24.8	83
0.60	50.0	45.8	76
0.75	50.0	52.6	70
0.90	50.0	60.6	67

a) $[Ti(O_2)(ox)_2^{2-}]=1.0\times10^{-3}$ mol dm^{-3}, [oxalate]$=1.0\times10^{-2}$ mol dm^{-3}. b) V(IV) was added: $[V(IV)]=5.0\times10^{-6}$ mol dm^{-3}. c) V(IV) was added: $[V(IV)]=5.0\times10^{-5}$ mol dm^{-3}.



(15)

It would be interesting to obtain information regarding whether the same radical species is produced in the $[Ti(O_2)(ox)_2]^{2-}$/Ti(III) couple as the H_2O_2/Ti(III) couple. We applied the spin-trapping method to the $[Ti(O_2)(ox)_2]^{2-}$/Ti(III) couple; the obtained ESR spectrum was the same as that obtained in the H_2O_2/Ti(III) couple (Fig. 2). The spectrum obtained in H_2O_2/Ti(III) couple was also in good agreement with that reported by Shepherd et al.[33] A similar result was obtained in the Cr(II) and V(II) systems. The ESR spectrum obtained in the $[Ti(O_2)(ox)_2]^{2-}$/Ti(III) couple containing CH_3OH was the same as that obtained in the H_2O_2/Ti(III)/CH_3OH couple (Fig. 2). This fact indicates that the carbon-centered radical $\cdot CH_2OH$ is also formed in the $[Ti(O_2)(ox)_2]^{2-}$/Ti(III) couple,

$$CH_3OH + \cdot OH \longrightarrow \cdot CH_2OH_2 + H_2O$$

$$k = 9.7\times10^8\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}.^{48)} \qquad (16)$$

The spin Hamiltonian parameters for the isotropic coupling constants of a_N and a_H for the radical-DMPO adducts are given in Table 6. These obtained coupling constants were the same as those generated via H_2O_2 with Ti(III). All of these constants are in good agreement with the literature values obtained for the H_2O_2/Ti(III)/CH_3OH couple.[33]

Table 6. Spin Hamiltonian Parameters (mT) for Radicals Prodused by $[Ti(O_2)(ox)_2]^{2-}$/Reductants[a]

Reductant	Substrate	DMPO	
		a_N	a_H
Ti(III)	H_2O	1.49	1.49
	CH_3OH	1.57	2.25
Cr(II)[b]	H_2O	1.49	1.48
	CH_3OH	1.57	2.24
V(II)	H_2O	1.49	1.49
	CH_3OH	1.59	2.26

a) $[Ti(O_2)(ox)_2^{2-}]=3\times10^{-3}$ mol dm^{-3}, [reductant]$=3\times10^{-4}$ mol dm^{-3}, $[CH_3OH]=1$ mol dm^{-3}, [DMPO]$=9\times10^{-3}$ mol dm^{-3}. b) [DMPO]$=5.0\times10^{-2}$ mol dm^{-3}.

Gould et al.[14] have suggested that a homolytic reduction by Ti(III) of an O–O bond in a peroxo-Cr(III) intermediate, formed during the reduction of peroxo-Cr(IV) complex with Ti(III), yields a Cr(III)–O· fragment. In the $[Cr(O_2)_2(dien)]$/Ti(III) system, no ESR spectrum was detected using a spin-trapping method. This fact supports the idea that Cr(III)–O· is rapidly converted via an internal electron transfer and protonation to a Cr^{IV}–OH complex without the formation of free ·OH, as proposed by Gould et al.

As mentioned previously, it is impossible to directly measure the rate constants for the reactions of ·OH formed in the Fenton-like reaction, because the ·OH formation is slow when compared to its decay. By the ESR spin-trapping technique, only the k/k_{DMPO} ratio can be measured. See Table 7, where the k/k_{DMPO} ratios, calculated from the rate constants for free ·OH

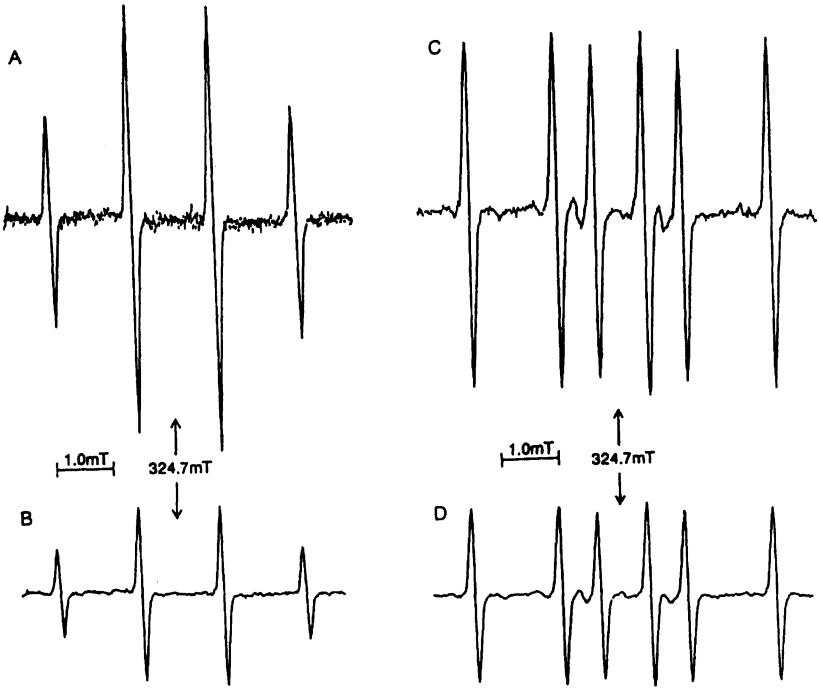


Fig. 2. ESR spectra of DMPO radical adducts generated by the $[Ti(O_2)(ox)_2]^{2-}/Ti(III)$ couple and $H_2O_2/Ti(III)$ couple. Microwave power, 10 mW; field modulation width, 0.05 mT; scan time, 4 min; measured at room temperature; $[Ti(III)]=3.0\times10^{-4}$ mol dm^{-3}; (A) $[Ti(O_2)(ox)_2^{2-}]=3.0\times10^{-3}$ mol dm^{-3}, H_2O alone, RG=250; (B) $[H_2O_2]=1.0\times10^{-1}$ mol dm^{-3}, H_2O alone, RG=500; (C) $[Ti(O_2)(ox)_2^{2-}]=3.0\times10^{-3}$ mol dm^{-3}, $[CH_3OH]=1.0$ mol dm^{-3}, RG=250; (D) $[H_2O_2]=3.0\times10^{-1}$ mol dm^{-3}, $[CH_3OH]=1.0$ mol dm^{-3}, RG=500.

Table 7. k/k_{DMPO} for ·OH Radical Formed in $[Ti(O_2)(ox)_2]^{2-}/Ti(III)$ System and Pulse Radiolysis

	k/k_{DMPO}		
	MeOH	*t*-BuOH	Mannitol
Pulse radiolysis	0.23[a)]	0.14[a)]	0.40[a)]
MeOH	0.29		
t-Butanol		0.10	
Mannitol			0.48

a) These ratios were calculated from the rate constants (10^9 mol^{-1} dm^3 s^{-1}) for free ·OH, being 0.97 for CH_3OH,[48] 0.60 for *t*-butanol,[52] 1.7 for mannitol,[53] and 4.3 for DMPO.[54]

produced by pulse-radiolysis, are given. The values are very sensitive to the type of radical trapped.[49—52] If the ratio is the same as that measured in the pulse radiolysis system within the experimental error, the ·OH is very likely to be free. Thus, the ·OH formed in the reduction of $[Ti(O_2)(ox)_2]^{2-}$ by Ti(III) is probably free due to the fact that the ratio k/k_{DMPO} obtained in our system was the same as those obtained in pulse radiolysis (Table 7).

In conclusion, Ti(III), Cr(II), and V(II) initiate the chain decomposition of $[Ti(O_2)(ox)_2]^{2-}$; the chain length increased with increasing the amount of added $[TiO(ox)_2]^{2-}$ and added oxalate ion. The maximum value of the chain length obtained under our experimental conditions was 600, and the reaction products were CO_2 and $[TiO(ox)_2]^{2-}$. Fe(II) did not act as an initiator of the chain reaction in this system. Oxygen is an inhibitor of the chain reaction. The results obtained by the spin-trapping method with DMPO suggest the formation of ·OH. The resultant radical adducts RDMPO· obtained in the $[Ti(O_2)(ox)_2]^{2-}$/reductant systems have been characterized by ESR spectroscopy in good agreement with the literature values obtained in the $H_2O_2/Ti(III)$ system.

We are grateful to Dr. K. Shinozaki for valuable discussions and to Professor J. Noro for measuring of the electron spin resonance spectra.

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