Kinetics and Mechanisms of the Vanadium(IV)-Catalyzed Oxidation of Iodide Ion in the Presence of Molecular Oxygen in an Acid Solution

Masaru Kimura,* Tomoko Hara, and Keiichi Tsukahara*

Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

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The kinetics of the oxidation of iodide ion to iodine by molecular oxygen catalyzed by VO^{2+} ions were studied in sulfuric acid solutions in the dark. After an induction period during which time the $I_2^{-\bullet}$ radical anion forms, the rate of formation of iodine increased due to catalysis by VO^{2+} ions. The rate of reaction depended on the concentrations of VO^{2+}, H^+, and I^-, and was independent of the ionic strength. The reaction was inhibited by either radical scavengers or the complex-forming substances of ethylenediaminetetraacetic acid and chloride ions. A chain mechanism containing $I_2^{-\bullet}/I_2$, VO^{2+}/V^{3+}, and $O_2/HO_2^{\bullet}$ redox cycles is presented.

The disturbing effect of molecular oxygen in iodometry is most familiar. In acid solutions the dissolved oxygen oxidizes the iodide ion in accordance with the following overall equation:

$$4I^- + 4H^+ + O_2 \longrightarrow 2I_2 + 2H_2O. \qquad (1)$$

Although the reaction is slow, its rate increases in proportion to an increase in the concentration of H^+ as well as O_2. The oxidation of I^- by O_2 is accelerated by either the irradiation of light or by some catalytic substances in solution.[1] The mechanisms of catalyzed reactions in the presence of oxygen have not been well investigated. Previously, we investigated the kinetics of reaction 1 catalyzed by nitrous acid[2] and copper(II) sulfate.[3]

Historically, one of the best-studied catalysts for reaction 1 is vanadium(V) ions.[4—7] Several possibilities in the reaction mechanism have been considered for the explaining the V(V)–I^- reaction with oxygen. Ditz and Bardach[4] first observed that two equiv (sometimes even more) of I_2 is liberated in the reduction of V(V) by I^-. Therefore, it was initially thought that the V(III) ion is formed as a product (or an intermediate species). However, Edgar[5] assumed that it is possible to account for the experimental results that V(III) is rapidly oxidized to V(IV) by the V(V) ion. Next, Bray and Ramsey[6] observed that the induction factor (F_i(=equiv O_2 reduced/equiv V(V) reduced)) initially increased with increasing acidity of the solution; however, from a concentration of about 2.5 M (1 M=1 mol dm^{-3}) H_2SO_4 there was no further change. It was also found that F_i is no longer affected by adding the product of vanadium(IV) ion (VO^{2+}). It is of interest that at lower acid concentrations the values of F_i increase with increasing the I^- concentration, although above 3 M acid the iodide ion no longer influences the induced reaction. The possibility of V(III) ion formation has been excluded, since the V(III)–O_2 reaction is fairly slow, and also because V(III) can not be detected in the reaction mixture.[1] Accordingly, up to now one of the most well-known mechanism is as follows, where the conditions are 1—3 M $HClO_4$ or H_2SO_4:[7]

$$VO_2^+ + I^- + 2H^+ \longrightarrow VO^{2+} + I^{\bullet} + H_2O \qquad (2)$$

$$I^- + I^{\bullet} \longrightarrow I_2^{-\bullet} \qquad (3)$$

$$2I_2^{-\bullet} \longrightarrow I_3^- + I^- \qquad (4)$$

$$I_2^{-\bullet} + O_2 + H^+ \longrightarrow I_2 + HO_2^{\bullet} \qquad (5)$$

$$I^- + HO_2^{\bullet} + H^+ \longrightarrow I^{\bullet} + H_2O_2 \qquad (6)$$

$$2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O \qquad (7)$$

Reaction 5 is regarded as being the rate-determining step, and reaction 2 is assumed to be rapid and to induce all other reactions (3—7). Thus, the same induced reaction is expected for other oxidizing substances, such as Ir(IV) or Ce(IV).

In the present work we found that although a simple oxidizing substance, such as Ir(IV), could not accelerate reaction 1, VO^{2+} could catalytically accelerate the reaction. The kinetic study of the catalyzed reaction using VO^{2+} mentioned in the present paper is the first one, as far as we know.

Experimental

Materials. All of the chemicals were of guaranteed grade from Wako Pure Chemical Industries, Ltd. Doubly distilled water from alkaline permanganate solutions was used for all of the solutions.

Kinetic Measurements. The procedure for the kinetic measurements was the same as that in a previously reported method.[3)] All of the reactions were carried out in the dark under the following experimental conditions: $[I^-]=0.02$—0.2 M, $[VO^{2+}]=(0.2$—$2.0)\times10^{-5}$ M, $[O_2]=2.3\times10^{-4}$ M (air-sat.) and 1.16×10^{-3} M (O_2-sat.), and $[H_2SO_4]=5\times10^{-3}$—0.1 M. The formation of I_3^- was monitored at 350 nm ($\varepsilon_{350}=2.50\times10^4$ $M^{-1}\,cm^{-1}$)[8)] during the reaction, because the following equilibrium is attained:

$$I_2+I^- \rightleftarrows I_3^-, \qquad (8)$$

where $k_8=5.6\times10^9$ $M^{-1}\,s^{-1}$ and k_8/k_{-8} (or K_8) $=710$ M^{-1}.[9,10)]

Results and Discussion

Figure 1 shows the formation of iodine in the oxidation of I^- by molecular oxygen in the presence of Ir(IV), V(IV), or V(V). In the case of Ir(IV), the Ir(IV) ion reacts quantitatively with I^- to produce I_2 in accordance with reaction 9, and there is no further formation of iodine (see the inset in Fig. 1),

$$2I^- + 2[IrCl_6]^{2-} \longrightarrow I_2 + 2[IrCl_6]^{3-}. \qquad (9)$$

On the other hand, in the case of V(V) or V(IV), the formed iodine gradually increased along with the reaction time and exceeded the equivalent concentrations of added VO_2^+ or VO^{2+}. It is of interest that the formation rate for I_2 in the presence of VO^{2+} is very slow during the first periods, but then becomes as fast as the rate in the VO_2^+ reaction. Therefore, the VO^{2+} ion seems to be essentially the same as the VO_2^+ ion regarding its catalytic behavior for reaction 1. The slow induction step during the first period of the VO^{2+} reaction was dependent on the concentrations of acid and oxygen, and almost disappeared in 0.1 M sulfuric acid in an oxygen-saturated solution. The steady-states' cycle due to reactions 17 and 18 (vide infra) would be satisfied after such an induction period. Plots of $[I_2]_{\rm formed}$ vs. t were linear after the induction period and, thus, the rate of the formation of I_2 for the catalytic reaction ($V={\rm d}[I_2]/{\rm d}t$ or ${\rm d}[I_3^-]/{\rm d}t$) could be obtained with relatively good accuracy. For example, the coefficient of variation for 10 runs was 4%: $V=(4.35\pm0.17)\times10^{-9}$ $M\,s^{-1}$ at 5×10^{-6} M VO^{2+} in O_2-saturated solutions (Fig. 2).

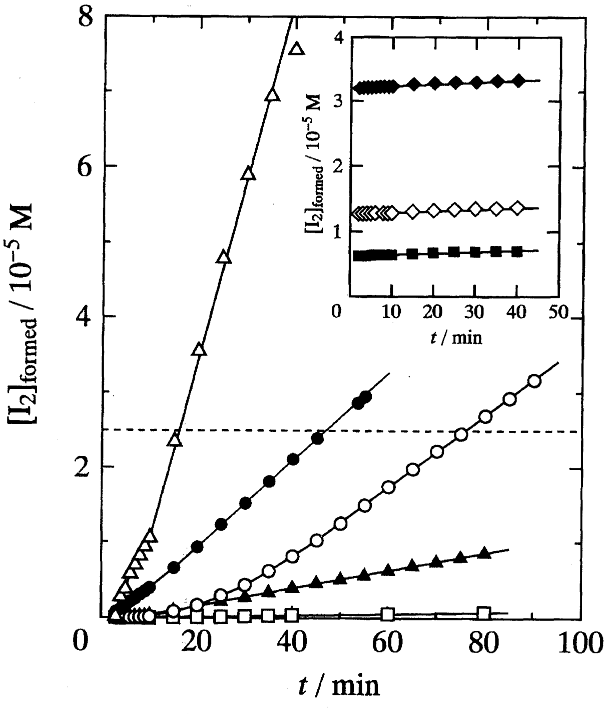

Fig. 1. Plots of $[I_2]_{\rm formed}$ vs. t for the reaction between I^- and VO_2^+ (2.5×10^{-5} M) or VO^{2+} (5×10^{-5} M) in O_2-saturated solutions in the dark at 0.1 M KI, 0.01 M H_2SO_4, and 25 °C. ○: VO^{2+}, ●: VO_2^+, △: VO^{2+} in 0.1 M H_2SO_4, ▲: VO^{2+} in 0.1 M H_2SO_4 at air-sat., and □: in the absence of metal ions. Inset shows those for the reaction between I^- and $[IrCl_6]^{2-}$ at $[Ir(IV)]=1.3\times10^{-5}$ M (■), 2.6×10^{-5} M (◇), and 6.4×10^{-5} M (◆).

Dependence of Concentrations of VO^{2+} and O_2. The formation rate of I_2 increased proportionally to the concentrations of VO^{2+} (Fig. 2). The dependence of the dissolved oxygen is of interest. No formation of I_2 was observed in the absence of O_2, and the ratios of the rate saturated with oxygen against that saturated with air increased with increasing $[VO^{2+}]_{\rm added}$; the rate ratios were always larger than 5 ($=[O_2]$ (at O_2-sat.)/$[O_2]$ (at air-sat.)). This fact indicates that the following reaction can be excluded for the catalytic reaction by VO^{2+}:

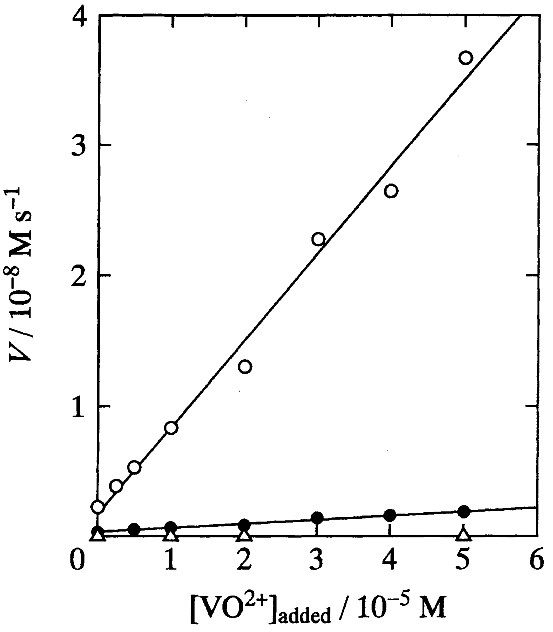

Fig. 2. Plots of the reaction rate V vs. $[VO^{2+}]_{\rm added}$. Conditions are the same as in Table 1 except for 0.1 M H_2SO_4 and N_2-sat. (△), air-sat. (●), and O_2-sat. (○).

$$2I^- + 2VO^{2+} + 4H^+ \longrightarrow I_2 + 2V^{3+} + 2H_2O. \qquad (10)$$

The redox potentials[11] for the $I_2/2I^-$ and VO^{2+}/V^{3+} couples are 0.54 and 0.36 V, respectively; that is, the equilibrium constant of Eq. 10 is $10^{-9.9}$ at $[H^+]$=0.1 M, suggesting that reaction 10 is extremely hard to occur.

Effect of Acidity. The formation rate of I_2 (or I_3^-) is affected by the acid concentration. The rate of the VO^{2+}-catalyzed reaction (V) and that of the noncatalyzed reaction (V_0) are listed in Table 1. Both rates increased with increasing the concentrations of acid, and the acidity dependence was much larger for V than that for V_0.

Effect of Concentration of I^-. The values of V_0 and ($V-V_0$) were plotted against the concentration of I^- added (Fig. 3). The rate of the catalyzed reaction ($V-V_0$) increased abruptly at a certain concentration of I^-, then gradually increased with increasing $[I^-]$ at almost the same increasing step in the rate.

Temperature Dependence. The effect of temperature on rates V and V_0 was examined under the conditions that [KI]=0.1 M and $[H_2SO_4]$=0.1 M in O_2-saturated solutions without or with $VOSO_4$ (1×10^{-5} M). The values of $V_0/10^{-9}$ M s^{-1} and $V/10^{-9}$ M s^{-1} are 1.33 and 3.47, 1.89 and 5.35, 3.02 and 9.70, and 4.70 and 13.0 at 6.0, 15.0, 25.0, and 35.0 °C, respectively. Plots of both log V_0 vs. T^{-1} and log V vs. T^{-1} are well rectilinear (Fig. 4) with 31 kJ mol^{-1} as the activation energy, indicating that only the frequency factor of the V(IV)-catalyzed reaction is larger than that of the noncatalyzed reaction. This suggests that only the turnover of the system with the VO^{2+}/V^{3+} couple is different from that of the one without a couple, and that the rate-determining step is the same in both cases.

Ionic Strength Dependence. The formation rate of I_2 was independent of the ionic strength within experimental error (see Table 2). This indicates that the rate-determining reaction is composed of the neutral species such as O_2.

Effect of Radical Scavengers and Complex-Forming Substances. As can be seen in Table 2, both acrylamide and acrylonitrile greatly retarded the formation rate of iodine; also, the rate decreased remarkably upon adding ethylenediaminetetraacetic acid (EDTA), which is capable of complex-forming with VO^{2+}. The chloride ion also retarded the formation rate of I_2. The chloride ion retardation may be due to the formation of a chloro complex with VO^{2+} and/or V^{3+}; the equilibrium reactions of iodo complexes of V(IV) and V(III) with chloride ions may exist and the iodo complexes may be a more active species for the catalytic reaction.

Table 1. Effect of Acidity on the I_2 Formation Rate[a)]

$[H_2SO_4]$/M	$V_0/10^{-9}$ M s^{-1}	$V/10^{-9}$ M s^{-1}
0.005	0	6.51
0.01	0.167	7.78
0.02	0.444	15.6
0.05	1.21 1.13	26.2 29.8
0.10	2.22	38.1

a) Conditions: 0.1 M KI, 5×10^{-5} M $VOSO_4$, O_2-sat., dark, and 25 °C, where no $VOSO_4$ was added for the V_0 experiments.

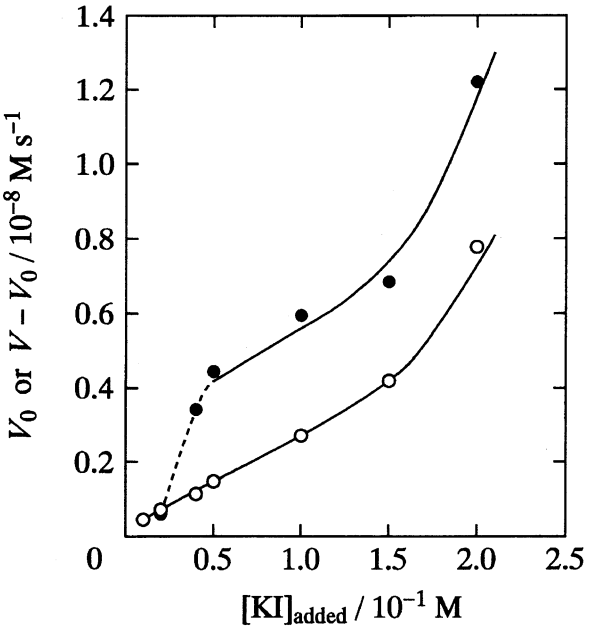

Fig. 3. Plots of the reaction rate V_0 or $V-V_0$ vs. $[I^-]_{\text{added}}$. Conditions are the same as in Table 1 except for 0.1 M H_2SO_4 and 1×10^{-5} M $VOSO_4$. ○: for V_0 and ●: for $V-V_0$.

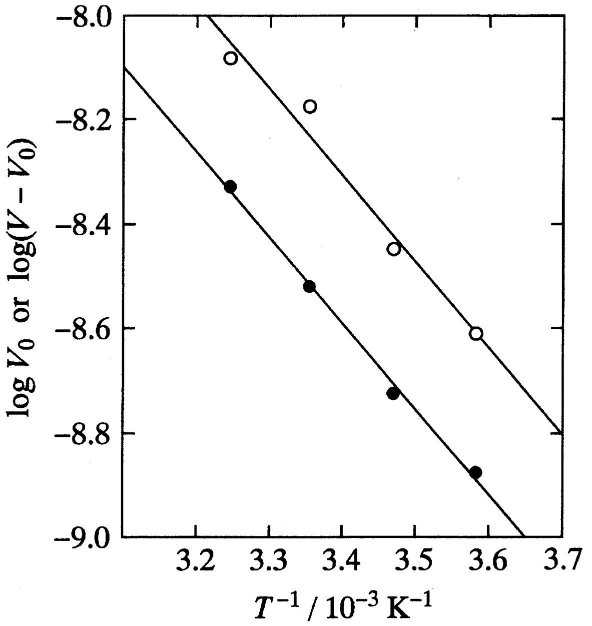

Fig. 4. Temperature dependence of the reaction rate for the VO^{2+}-catalyzed reaction (○) and the noncatalyzed reaction (●). Conditions are the same as in Table 1 except for 0.1 M H_2SO_4 and 1×10^{-5} M $VOSO_4$.

Table 2. Effect of Ionic Strength, Radical Scavengers, and Complex-Forming Substances

Additives	Reaction rate $(d[I_2]/dt)/10^{-9}$ M s^{-1}		
	V	V_0	$V-V_0$
None[a)]	10.4	2.58	7.82
0.05 M $NaClO_4$[a)]	12.1	2.58	9.52
0.10 M $NaClO_4$[a)]	10.8	2.58	8.22
0.15 M $NaClO_4$[a)]	12.0	2.58	9.42
0.20 M $NaClO_4$[a)]	10.7	2.58	8.12
0.50 M $NaClO_4$[a)]	9.84	2.58	7.26
None[b)]	11.6	2.38	9.22
0.5 (w/v)% acrylamide [b)]	9.42		
2.0 (w/v)% acrylamide [b)]	7.62		
0.5 (v/v)% acrylonitrile[b)]	4.53		
2.0 (v/v)% acrylonitrile[b)]	3.29		
None[c)]	7.78	0.167	7.61
1×10^{-3} M EDTA[c)]	0.933	0.183	0.750
None[d)]	29.8 11.6[b)]	1.13 2.38[b)]	28.5 9.22[b)]
0.05 M NaCl[d)]	26.5	1.13	25.4
0.10 M NaCl[d)]	24.6 8.67[b)]	1.13 2.38[b)]	23.5 6.29[b)]
0.15 M NaCl[d)]	24.2	1.13	23.1
0.20 M NaCl[d)]	13.2	1.13	12.1
0.25 M NaCl[d)]	4.58	2.38	2.20
0.50 M NaCl[d)]	10.7 3.56[b)]	1.13 2.38[b)]	9.57 1.18[b)]

a) At 0.1 M NaI, 0.1 M H_2SO_4, 1×10^{-5} M $VOSO_4$, O_2-sat., and 25 °C. b) At 0.1 M KI, 0.1 M H_2SO_4, 1×10^{-5} M $VOSO_4$, O_2-sat., and 25 °C. c) At 0.01 M H_2SO_4, 0.09 M NaCl, 5×10^{-5} M $VOSO_4$, and the others as in b). d) At 0.05 M H_2SO_4, 5×10^{-5} M $VOSO_4$, and the others as in b), where no $VOSO_4$ was added for the V_0 experiments.

Mechanism of Reaction. On the basis of the redox potentials,[11,12)]

$$O_2 + H^+ + e^- \rightleftarrows HO_2^{\bullet} \qquad E^0 = -0.13\ \mathrm{V} \quad (11)$$

$$VO^{2+} + 2H^+ + e^- \rightleftarrows V^{3+} + H_2O \qquad E^0 = 0.36\ \mathrm{V} \quad (12)$$

$$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O \qquad E^0 = 1.00\ \mathrm{V} \quad (13)$$

$$I_2 + e^- \rightleftarrows I_2^{-\bullet} \qquad E^0 = 0.11\ \mathrm{V} \quad (14)$$

$$I_2^{-\bullet} + e^- \rightleftarrows 2I^- \qquad E^0 = 1.04\ \mathrm{V}, \quad (15)$$

the reduction of VO^{2+} by $I_2^{-\bullet}$ to V^{3+} can occur more easily than the oxidation of VO^{2+} by $I_2^{-\bullet}$ to VO_2^+, although we could not detect the V^{3+} ion under the present experimental conditions. Moreover, the formation of the V(V) species with the oxidation of VO^{2+} by $I_2^{-\bullet}$ indicates the retardation of I_2 formation, being contrary to the observed results. Therefore, the following mechanism can be represented, where only the forward reaction sign is written for brevity:

$$I^- + O_2 + H^+ \longrightarrow I^{\bullet} + HO_2^{\bullet} \quad [\text{slow}] \qquad (16)$$

$$I^- + HO_2^{\bullet} + H^+ \longrightarrow I^{\bullet} + H_2O_2 \qquad (6)$$

$$2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O \qquad (7)$$

$$I^{\bullet} + I^- \longrightarrow I_2^{-\bullet} \qquad (3)$$

$$2I_2^{-\bullet} \longrightarrow I_2 + 2I^- \qquad (4)$$

$$I_2^{-\bullet} + O_2 + H^+ \longrightarrow I_2 + HO_2^{\bullet} \quad [\text{slow}] \qquad (5)$$

$$I_2^{-\bullet} + VO^{2+} + 2H^+ \longrightarrow I_2 + V^{3+} + H_2O \qquad (17)$$

$$V^{3+} + O_2 + H_2O \longrightarrow VO^{2+} + HO_2^{\bullet} + H^+. \qquad (18)$$

The overall reaction 1 is described by these reactions, i.e., (1)=(16)+2(6)+2(7)+3(3)+(4)+(5) in the absence of VO^{2+}, and (1)=(16)+3(6)+3(7)+4(3)+2(5) with (5)=(17)+(18) in the presence of VO^{2+}. This relationship indicates that both cases are described by a set comprising the same elementary reactions, and that reactions 17 and 18 accelerate reactions 6, 7, and 3 related to reaction 5. The dependence of the rate on the concentrations of VO^{2+} and O_2 in Fig. 2 indicates the significant contribution of reactions 17 and 18. That is, the higher is the concentration of VO^{2+}, the greater is the contribution of $[O_2]$ with reaction 18. The temperature dependence of the activation energy for both cases was the same, and the ionic strength dependence was not observed (see Fig. 4 and Table 2). Therefore, the rate-determining step is thought to be reaction 16 in both cases.

The hydrogen ion dependence of the rate of the catalyzed reaction was much larger than that of the noncatalyzed reaction (Table 1), indicating that reaction 17 acts as a significant reaction to govern the overall reaction. The dependence of V_0 and $(V-V_0)$ on $[I^-]$ may also indicate that the elementary reactions in both cases are essentially the same. The catalyzed reaction seems to disappear at lower concentrations of I^- after an abrupt decrease in the rate (see Fig. 3). This suggests that reactions 6, 7, and 3 are important to make the $I_2^{-\bullet}$ radical cation compete with reaction 4 (or $2I^\bullet \rightarrow I_2$; it will be neglected at the high concentrations of I^- and is not written in our mechanism), in order to make the chain reaction. The hydrogen ion dependence shown in Table 1 also indicates the importance of Eqs. 6, 7, and 17 in the VO^{2+}-catalyzed reaction.

As stated in our introduction section, the vanadium(III) ion, as a product in the vanadium(V)–iodide–oxygen reaction, has been excluded for long time, and the mechanism of the reaction has been believed to be reactions 2—7, in which reaction 5 is assumed to be the rate-determining step. Our proposed mechanism for the V(IV)–iodide–oxygen also induces reactions 3—7. Upon increasing $[H^+]$, the noncatalyzed reaction inducing reaction 5 becomes faster, and when the rate of reaction 5 exceeds that of reaction 17, the vanadium(IV) ion should be no longer the catalyst. Such conditions may be the same as that used in the earlier researchers' studies,[6,7] which were carried out in 1—3 M $HClO_4$ or H_2SO_4.

We now comment that the mechanisms of Eqs. 2 3, 4, 5, 6, and 7 may always be satisfied by not only the VO_2^+ ion, but also by any other oxidants at extremely high $[H^+]$. However, the noncatalyzed reaction must be as fast as the catalyzed one. When more than 1 M acid is used, trace impurities of the active metal ions in the acid, for example, copper and iron ions, are extraordinarily sensitive to accelerate reaction 1. Therefore, it can be thought that even inevitably low level impurities can seriously disturb the noncatalyzed reaction 1, and that it is extremely hard to give noncatalyzed reaction 1 as well as reaction 16 as absolute evidence. In the presence of a strong complex-forming chelate reagent, EDTA, it seems that only the catalyzed-reaction parts after some induction periods are retarded (Table 2). This fact may support the evidence of reactions 1 and 16, because EDTA can make a chelated complex with some impurities, such ions of Cu^{2+}, Fe^{2+}, and Fe^{3+} to retard the induced reactions which might be assumed in most acid media.

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