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Kinetics and Mechanism of the Copper(II)-Catalyzed Oxidation of the Iodide Ion to Iodine by the Vanadium(V) Ion in an Aqueous Solution

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(Received April 27, 1998)

The vanadium(V) ion, which is described as V^V herein, could hardly oxidize the iodide ion to iodine at pH $\geqq 2.8$; however, the oxidation reaction occurred catalytically upon adding traces of copper(II) ion. When a copper(II) solution of 10^{-8}—10^{-5} M (M = mol dm^{-3}) was mixed with an iodide solution, after a rapid formation of iodine, the iodine concentration remained constant. After such iodine formation had occurred, if a V^V solution was added into the reacting mixture, the iodine began to form again in accordance with a rate law of $2(d[I_2]/dt) = -d[V^V]/dt = k[CuI][V^V]$, in which [CuI] is a steady-states' concentration in a chain cycle CuI^+/CuI. The reaction rate was independent of the time to add the V^V ion, and the formation of iodine I_2 (or triiodide ion I_3^-) stopped at the time when all of the V^V was consumed, indicating the stoichiometry to be $2I^- + 2V^V \rightarrow I_2 + 2V^{IV}$. The initial rate ($V_i$) after V^V addition was proportional to the concentrations of not only the added V^V over the range 10^{-6}—10^{-5} M, but also the added copper(II) ion. Although a self-inhibiting effect did not appear over the pH range 2.8—3.6, it occurred at pH > 3.6. It was found that such a retarding effect was caused by the vanadium(IV) ion (denoted as V^{IV} herein), which was the reduced product of V^V; the V^{IV} inhibiting effect was extremely dependent on the pH in the reacting solution. The mechanisms for the retardation reaction as well as iodine formation are discussed in terms of accounting for the obtained results.

Previously,[1] we studied the kinetics of the vanadium(IV)-catalyzed oxidation of the iodide ion to iodine in the presence of molecular oxygen (O_2) under relatively high acidic conditions of pH $\leqq 2.0$ in 0.005—0.10 M sulfuric acid; the catalysis was not due to the redox cycle of V^V/V^{IV}, but arose from making the redox cycle of V^{IV}/V^{III} with $O_2/HO_2^{\bullet}$. Recently,[2] we found that trace amounts of the chromate(VI) ion could greatly accelerate the oxidation reaction of the iodide ion to iodine by the reaction between I^- and Cu^{2+}, which is described by an overall reaction of $4I^- + 2Cu^{2+} \rightarrow I_2 + 2CuI$, comprising a chain cycle of CuI^+/CuI (or Cu^{II}/Cu^{I}). Such studies[1,2] indicate that an analogous reaction is capable of being made by adding traces of the vanadium(V) ion or the vanadium(IV) ion at a suitable pH. Actually, the vanadium(V) ion could act similarly as the chromium(VI) ion at a suitable pH. On the contrary, the vanadium(IV) ion acted as a specific retarder or reducer against iodine formation; such an inhibiting effect of V^{IV} was extremely dependent on the acidity of the reaction solution, and appeared under the conditions pH > 3.6. The results in the present study showed that such a retardation effect by V^{IV} could have arisen due to the occurrence of reaction (B) with (A). However, reaction (C) had been deduced in our previous study.[1]

$$CuI^+ + 2I^- \rightleftharpoons CuI + I_2^{-\bullet} \qquad (A)$$

$$V^{IV} + I_2^{-\bullet} \longrightarrow V^V + 2I^- \qquad [pH > 3.6] \qquad (B)$$

$$V^{IV} + I_2^{-\bullet} \longrightarrow V^{III} + I_2 \qquad [pH \leqq 2.0] \qquad (C)^{1)}$$

It is interesting to mutually compare these two reactions, (B) and (C), which are not yet well known. The evidence concerning the reversible reaction (A) involving radical species, $I_2^{-\bullet}$, is novel and interesting. It would also be interesting to compare the obtained rate constant k_7 (vide infra) for the oxidation of CuI by V^V with that by Cr^{VI}.[1] Considering the constants of $[HVO_3][H^+]/[VO_2^+] = 10^{-3.70}$ M and $[VO_3^-][H^+]/[HVO_3] = 10^{-3.80}$ M at 25 °C,[3] the vanadium(V) ion existed as a mixture containing VO_2^+, HVO_3, and VO_3^- under conditions of 2.8—4.5 in the present study. For the sake of brevity, we used V^V and V^{IV} for the vanadium(V) and (IV) ions, respectively.

Experimental

Chemicals. Potassium iodide (KI), copper(II) sulfate ($CuSO_4 \cdot 5H_2O$), ammonium vanadate (NH_4VO_3), vanadium(IV)-oxide sulfate ($VOSO_4 \cdot 3.5H_2O$), and the other chemicals were guaranteed grade of Wako Pure Chemical Industries, Ltd.

Procedure. The reaction was started by mixing an iodide solution into a copper(II) solution without or with V^V and/or V^{IV}; in some runs the V^V and/or V^{IV} solution was added at some times after having mixed an iodide solution with the copper(II) solution. The reaction rate was obtained by measuring the absorbance of the formed I_3^- with a Shimadzu UV-150-02 spectrophotometer. The temperature of the reaction solutions was controlled to (25.0±0.1) °C. The dissolved oxygen was removed by bubbling N_2-gas through the reaction solution; after starting the reaction, N_2-gas was continuously supplied to the surface of the solution during the reaction. Aliquot solutions were taken out at appropriate time intervals in order to measure the concentration of the formed iodine (I_2). The iodine was rapidly converted to the triiodide ion (I_3^-) in the presence of the iodide ion:

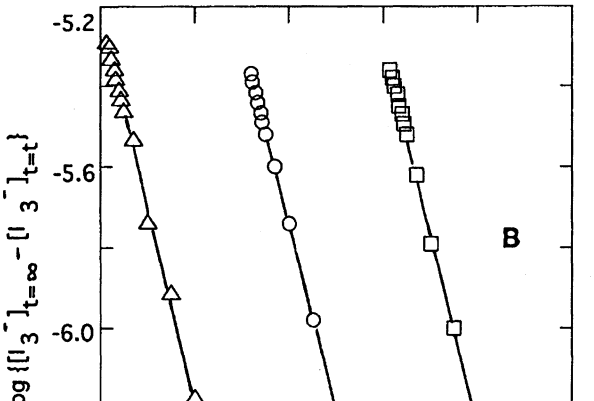

Fig. 1. Evidence of the copper(II)-catalyzed reaction.
A: Plots of ● indicate results in the solution containing 4.4×10^{-6} M $CuSO_4$, 0.10 M KI, 0.05 M CH_3COOH–0.005 M CH_3COONa (pH 3.60) in the N_2-saturated at 25 °C. Plots △, ○, and □ indicate the cases 1.0×10^{-5} M in NH_4VO_3 was added into the reacting solution in the plots ● at $t = 0$, 30, and 60 min, respectively.
B: Plots of $\log\{[I_3^-]_{t=\infty}-[I_3^-]_{t=t}\}$ vs. t for each plots △, ○, and □ in A.

$$I_2+I^- \rightleftarrows I_3^-, \tag{1}$$

where $k_1 = 5.6\times10^9$ M^{-1} s^{-1} and k_1/k_{-1} (or K_1) = 710 M^{-1}.[4,5] The I_3^- ion has large absorption coefficients of 3.82×10^4 and 2.50×10^4 M^{-1} cm^{-1} at 288 and 350 nm, respectively. The concentrations of I_3^- were actually equivalent to those of I_2, containing I^- in large excess. Thus, the absorbance of I_3^- could be used as a monitor for kinetic measurements.[6] All of the kinetic runs were carried out under conditions that the iodide ion was in at least 10^4-fold excess over the I_2 formed by the reaction.

Results

Under any conditions of the pH range in the present study, preliminary experiments showed that V^V did not directly oxidize I^-, and that V^{IV} did not directly reduce I_2 and/or I_3^-.

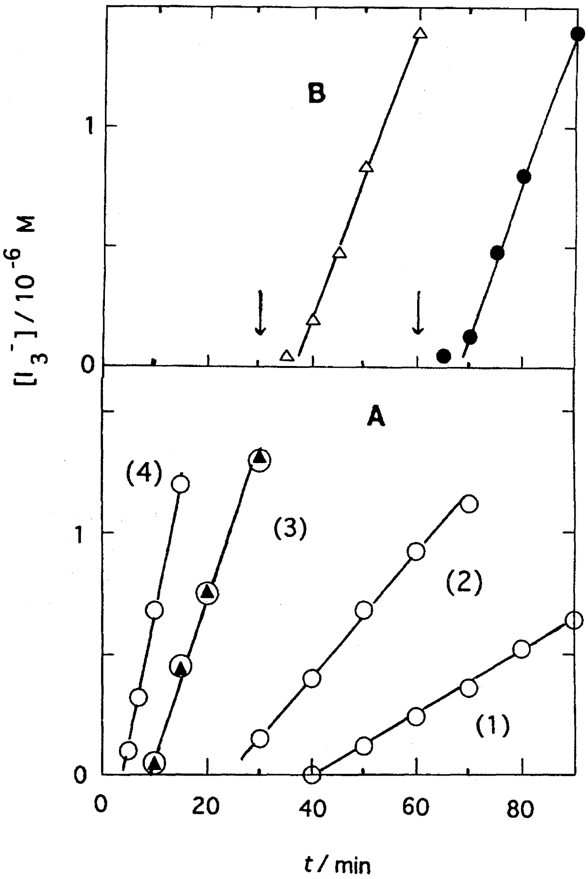

Fig. 2. Induction period in the low concentrations of copper(II).
A: 1.0×10^{-5} M V^V was added at $t = 0$ with varied concentrations of copper(II): i.e., $[Cu^{2+}]_{added} = 5.0\times10^{-8}$, 1.0×10^{-7}, 2.5×10^{-7}, and 5.0×10^{-7} M for plots (1), (2), (3), and (4), respectively. The plots ▲ in the line (3) indicate the results in 10 (v/v)% EtOH. The other conditions are the same as in Fig. 1.
B: 1.0×10^{-5} M V^V was added at $t = 30$ and 60 min for the plots △ and ●, respectively. The other conditions are the same as those of the plots ▲ in A.

Evidence of Induced Catalysis. Figure 1A shows plots of the concentrations of I_3^- formed against the reaction times for a solution at pH 3.60. We can recognize from Fig. 1 that traces of the copper(II) ion catalytically induced the oxidation of I^- by V^V, and that I_3^- formation stopped at the time when the added V^V completely disappeared; further, the formation rate of I_3^- was independent of the time to add V^V (see Fig. 1B). The net concentrations of I_2 (or I_3^-) formed by the copper(II)-catalyzed reactions were equivalent to half of the added V^V. Accordingly, the stoichiometry of the catalyzed reaction could be described as:

$$2I^-+2V^V \longrightarrow I_2+2V^{IV} \tag{2}$$

As further evidence of an efficient catalysis, when the copper(II) ion concentrations were less than 5.0×10^{-7} M, the formation of I_3^- was hardly appreciable in the absence of V^V, but it could be obviously found by adding small amounts of

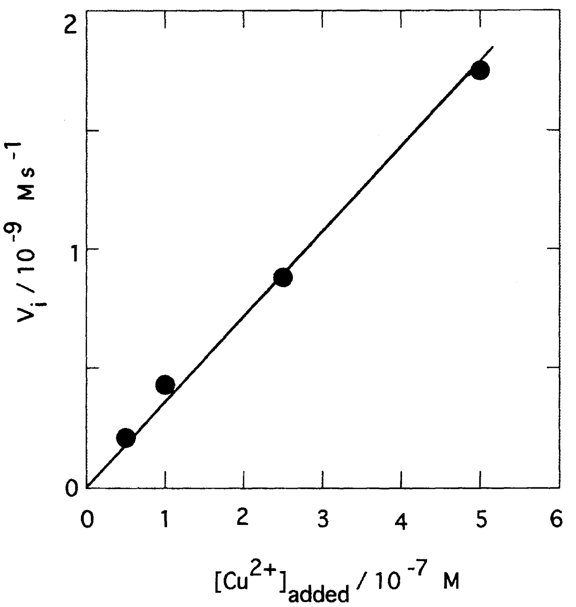

Fig. 3. Dependence of the copper(II) concentrations.
The initial rate (V_i) was obtained from the slope in Fig. 2.

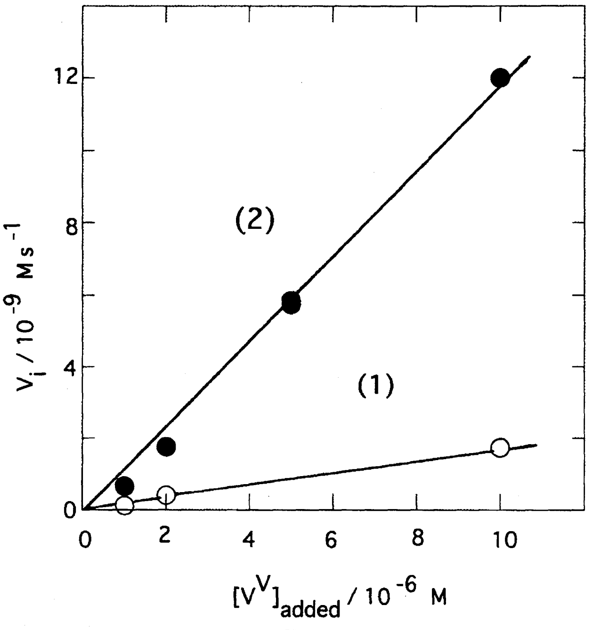

Fig. 4. Dependence of the V^V concentration.
Lines (1) and (2) indicate the cases of 5.0×10^{-7} and 4.4×10^{-6} M in $CuSO_4$, respectively. The V_i values were determined from the slope in plots of [I_3^-] vs. t after V^V was added at $t = 30$ min. The other conditions were the same as those in Fig. 1.

V^V (see Fig. 2).

Dependence of Copper(II) Concentrations. When the Cu(II) concentrations were less than 5.0×10^{-7} M, the I_3^- formations, such as the plots ● in Fig. 1, were hardly appreciable without adding V^V; however, in the case that V^V was added, after an induction period the I_3^- ion increased linearly (Fig. 2). Such an induction period could appear only under the condition $[Cu(II)]_{added} \leqq 5.0\times10^{-7}$ M, and became longer at lower concentrations of the copper(II) ion (see Fig. 2A). Further, the induction period as well as the I_3^- formation rate was not influenced by the addition of alcohol (see ▲ in Fig. 2A), and also by the addition time of V^V (see △ and ● in Fig. 2B). The slope in the linear line after the induction period was proportional to the concentration of the added copper(II) sulfate (see Fig. 3).

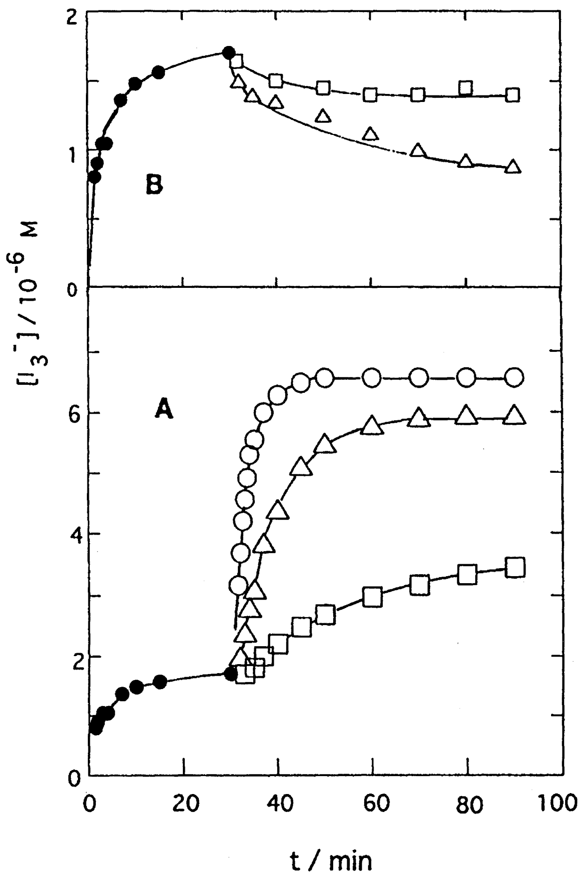

Fig. 5. pH effect on the I_3^- formation reaction, and on the I_3^- decrease by the addition of V^V.
Plots ● indicate the I_3^- formation curves by the reaction between 0.10 M I^- and 4.4×10^{-6} M Cu^{2+}.
A: 1.0×10^{-5} M V^V was added at $t = 30$ min into the reacting solution of the plots ●, where the pH values were 2.80 (○), 3.73 (△), and 4.15 (□), respectively.
B: 1.0×10^{-5} M V^{IV} was added at $t = 30$ min into the reacting solution of ●, where the pH values were 2.80 (□) and 4.25 (△), respectively. The other conditions are the same as in Fig. 1.

Dependence of Vanadium(V) Concentration. As can be seen from Fig. 1B, the plots of log $\{[I_3^-]_{t=\infty} - [I_3^-]_{t=t}\}$ vs. t are rectilinear. This means that the reaction is first order with respect to the V^V concentration, and that the rate-determining step is the oxidation reaction of CuI to CuI^+ by V^V, maintaining a constant concentration of CuI (refer to Eqs. 7, 8, and 9). Even when the V^V concentrations were low, the initial rate of the reaction (V_i) could be obtained with good accuracy, e.g., the relative standard deviation or the coefficient of variation for 10 runs was 1.8%; $V_i = (5.7\pm0.1)\times10^{-9}$ M s^{-1} at $[V^V]_{added} = 5.0\times10^{-6}$ M in the case of plots (2) in Fig. 4. The plots of V_i ($= \Delta[I_3^-]/\Delta t$)

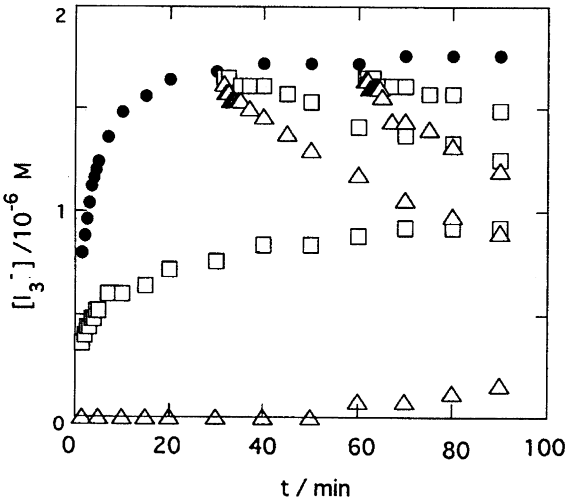

Fig. 6. Effect of the addition time of V^{IV}.
Plots ● indicate the same as those (●) in Fig. 1. The plots △ and □ indicate the V^{IV} concentrations of 5.0×10^{-5} and 1.0×10^{-5} M, respectively, which were added at $t = 0$, 30, or 60 min. The other conditions but pH 3.92 are the same as in Fig. 1.

vs. $[V^V]_{\text{added}}$ were rectilinear (Fig. 4), again indicating the first order with respect to the V^V concentration.

Effect of Acidity together with the Retardation Effect. As can be seen from Fig. 5A, the catalyzed reaction rate began to decrease at larger pH's. Figure 5B indicates that such a retardation could arise from the presence of V^{IV}, which is a reaction product. Figure 6 shows that such a retardation appeared much more strongly when V^{IV} was added at $t = 0$, and appeared more weakly when it was added at $t = 30$ and 60 min, being independent of the time to add (see △ and □ in Fig. 6); even in the case of weak retardation due to addition at 30 and 60 min, the formation of I_3^- was scarcely found by addition at $t = 0$ min (see the plots △ in Fig. 6). Such an efficient retardation effect at the zero-time addition of V^{IV}, indicates that the radical species of $I_2^{-\bullet}$ is constantly forming from the starting time of the reaction, and could efficiently oxidize V^{IV} (refer to Eq. 12). As can be seen from Fig. 7, the retardation by V^{IV} began to appear at pH > 3.6. Although the retardation by V^{IV} was very sensitive at a larger pH region, it was hardly found at lower pH's (see Fig. 8).

Discussion

Mechanism of Reaction. The results shown in Fig. 1 are accounted for by the following mechanism:

$$Cu^{2+} + I^- \rightleftarrows CuI^+ \tag{3}$$

$$CuI^+ + I^- \rightleftarrows CuI + I^\bullet$$
$$\{[CuI]/[Cu^+][I^-] = 9.1\times10^{11}\ M^{-1}\}^{7)} \tag{4}$$

$$I^\bullet + I^- \rightleftarrows I_2^{-\bullet}$$
$$\{[I_2^{-\bullet}]/[I^\bullet][I^-] = 1.04\times10^{4}\ M^{-1}\}^{8)} \tag{5}$$

$$2I_2^{-\bullet} \longrightarrow I_3^- + I^- \tag{6}$$

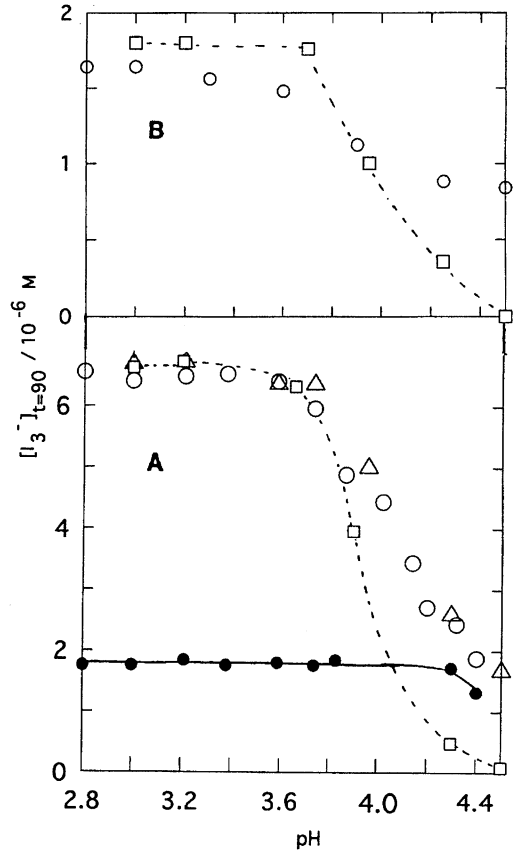

Fig. 7. pH dependence on the I_3^- formation and on the retardation effect together with the effect of the addition time of V^V or V^{IV}.
A: Plots ● indicate the same as those (●) in Fig. 1 at varied pH's; the plots ○ and △ indicate 1.0×10^{-5} M V^V added at $t = 0$ and 30 min, respectively; □, 1.0×10^{-5} M V^V and 1.0×10^{-5} M V^{IV} added together at $t = 0$ min.
B: Plots □ and ○ indicate 1.0×10^{-5} M V^{IV} added at $t = 0$ and 30 min, respectively. The other conditions were the same as those in Fig. 1.

$$CuI + V^V \longrightarrow CuI^+ + V^{IV} \tag{7}$$

The reaction without adding V^V in Fig. 1 (plots ●) is due to reactions (3)—(6), and the overall reaction is $2Cu^{2+} + 5I^- \rightarrow 2CuI + I_3^-$, which is the same as $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ plus $I_2 + I^- \rightarrow I_3^-$. The reactions in the case of the addition of V^V in Fig. 1 (△, ○, and □) could occur by the reactions of Eqs. 4, 5, 6, and 7, in which reaction (7) is an initiating reaction and is also a rate-determining step in order to constitute a chain cycle of CuI^+/CuI; the catalyzed reaction in Eqs. 4, 5, 6, and 7 is $3I^- + 2V^V \rightarrow I_3^- + 2V^{IV}$ as an overall reaction or the stoichiometric equation. Therefore, the following rate law can be derived:

$$-d[V^V]/dt = k_7[CuI][V^V]$$
$$= k_{\text{obsd}}[V^V], \tag{8}$$

$$\ln\,[V^V]_{t=t} = -k_{\text{obsd}}\,t + \ln\,[V^V]_{t=0}, \tag{9}$$

where $k_{\text{obsd}} = k_7[CuI]$ and $[V^V]_{t=t} = 2\{[I_3^-]_{t=\infty} - [I_3^-]_{t=t}\}$. The above rate law with the stoichiometry could be verified

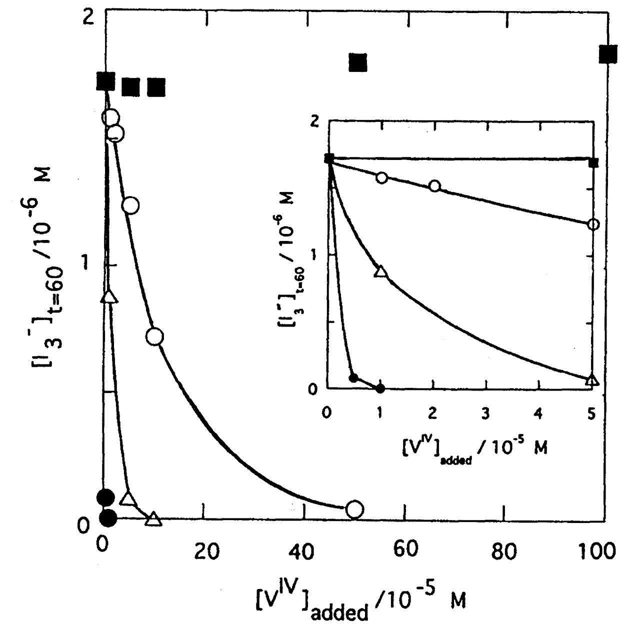

Fig. 8. Effects of the V^{IV} concentration at given pH's.
The V^{IV} ion was added at $t = 0$ min into the solution of Cu^{2+} with I^-. Plots ●, △, ○, and ■ indicate the cases of pH 4.63, 3.92, 3.60, and 3.00, respectively. The other conditions are the same as in Fig. 1.

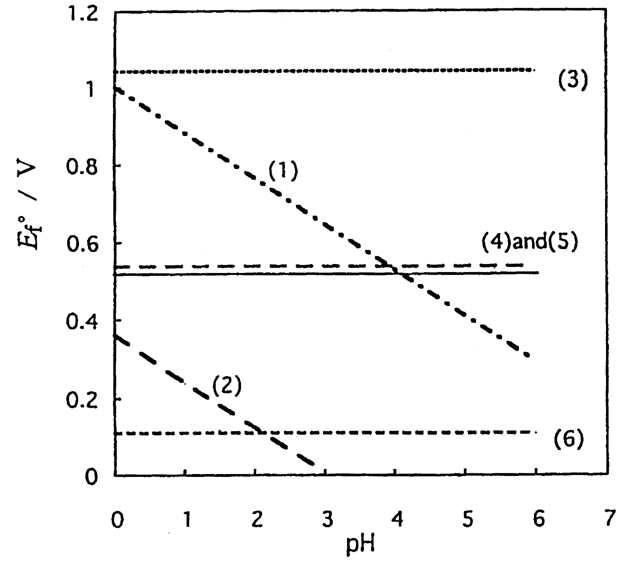

Fig. 9. Profile of the formal standard-redox potentials (E_f°) against pH.
Lines (1), (2), (3), (4), (5), and (6) indicate for the redox couples of VO_2^+/VO^{2+} (Ref. 7), VO^{2+}/V^{3+} (Ref. 7), $I_2^{-\bullet}/2I^-$ (Ref. 11), $I_2/2I^-$ (Ref. 7), $I_3^-/3I^-$ (Ref. 7), and $I_2/I_2^{-\bullet}$ (Ref. 10), respectively.

by Figs. 1A and 1B. When the steady-states' concentration of CuI in Eq. 8 could be assumed to be 2-fold of the triiodide ion concentration at $t = \infty$ in the case of Fig. 1, the relationship is $[CuI] = 2[I_3^-]_{t=30} \fallingdotseq 0.8[Cu^{2+}]_{added}$ and the rate constants (k_7) were obtained from the slope of the linear plots in Fig. 1B to be $(5.1\pm0.1)\times10^2$, $(5.0\pm0.1)\times10^2$, and $(5.1\pm0.1)\times10^2$ $M^{-1}\,s^{-1}$ for plots △, ○, and □ in Fig. 1B at pH 3.60, respectively. The values of k_7 at the other pH's, which were obtained from the same plots as those in Fig. 1B, were $(9.9\pm0.2)\times10^2$ and $(16\pm3)\times10^2$ $M^{-1}\,s^{-1}$ at pH 3.02 and 2.80, respectively. On the other hand, the initial rate (V_i) in Figs. 2, 3, and 4 can be described as $V_i = k_7[CuI]_i[V^V]_i$. If it is assumed to be $[CuI]_i = 0.8[Cu^{2+}]_{added}$ and $[V^V]_i = [V^V]_{added}$, the k_7 values can be obtained to be $(4.4\pm0.3)\times10^2$, $(4.4\pm0.3)\times10^2$, and $(3.4\pm0.3)\times10^2$ $M^{-1}\,s^{-1}$ from Fig. 3, (1) and (2) in Fig. 4, respectively. These values are mutually in good agreement.

Comparison of the Rate Constants. The rate constant corresponding to k_7 in the case of Cr^{VI} in our previous study[2)] was 5.2×10^2 $M^{-1}\,s^{-1}$ at pH 3.57, which is compared to $(5.1\pm0.1)\times10^2$ $M^{-1}\,s^{-1}$ at pH 3.60, obtained from Fig. 1. These values are almost identical. This is thought to have arisen from the facts that the redox potential E_f° for VO_2^+/VO^{2+} is 0.57 V at pH = 3.60 as can be seen from line (1) in Fig. 9, and that the value for the redox couple Cr^{VI}/Cr^V is 0.55 V,[9)] being almost equivalent to each other.

Mechanisms of the Retardation Effect by V^{IV}. The self-retardation by the reaction product of V^{IV} could appear at pH > 3.60 (see Fig. 5A). It was verified by several facts that such a retardation could arise from the presence of V^{IV} (see Fig. 5B and Figs. 6, 7, and 8). The retardation by V^{IV} is accounted for by the following reactions:

$$CuI + I_3^- \longrightarrow CuI^+ + I_2^{-\bullet} + I^-, \qquad (10)$$

$$CuI^+ + 2I^- \rightleftarrows CuI + I_2^{-\bullet}, \qquad (11) \text{ or } (A)$$

$$V^{IV} + I_2^{-\bullet} \longrightarrow V^V + 2I^-. \qquad (12) \text{ or } (B)$$

It is noted that reaction (10) is comprised in reactions (4) and (5) with (6), and that reaction (11) is equivalent to (4) plus (5). It is interesting that the reversible reaction of Eq. 11 could exist even at $t = 30$ and 60 min (see Fig. 5B and Fig. 6); this would be probable from considerations of the relatively high redox potentials in Eqs. 15 and 18 (vide infra). The equilibrium constant for the reaction of $I_2^{-\bullet} + VO^{2+} \rightleftarrows 2I^- + VO_2^+$, which corresponds to reaction (12), was calculated from the E_f° values to be 5.0×10^6 and 7.9×10^8 M at pH = 3.0 and 4.0, respectively; thus, reaction (12) could occur favorably under the conditions of the larger pH regions. The rate of reaction (12) competes with that of the forward reaction in Eq. 6 and the backward reaction in Eq. 11, overcoming them in order to make such a retardation in Figs. 5, 6, 7, and 8. The overall reaction for Eqs. 10, 11, and 12 is

$$2V^{IV} + I_3^- \longrightarrow 2V^V + 3I^-. \qquad (13)$$

That is, (10)+(11)+2(12) = (13). Accordingly, reaction (13) could occur catalytically by the redox couple of Cu^{II}/Cu^{I}. As can be seen from Fig. 6, the inhibiting effect appeared much more strongly when the V^{IV} ion was added at $t = 0$ min, and appeared to the same extent when it was added at $t = 30$ and 60 min. This indicates that reaction (12) competes with reaction (6), and that the steady states' concentrations of $I_2^{-\bullet}$ after 30 min are constant. When reaction (6) was completely overcome by reaction (12), which corresponds to the plots using △ in the case of $t=0$ in Fig. 6, the overall reaction is described by Eq. 14, where (14) = (3)+(4)+(5)+(12), indicating no formation of I_2 and/or I_3^-

$$\mathrm{Cu^{2+}+I^-+V^{IV}} \longrightarrow \mathrm{CuI+V^V} \qquad (14)$$

In order to discuss the probability for the occurrence of the above reaction mechanisms, the standard redox potentials are given as follows:

$$\mathrm{Cu^{2+}+I^-+e^-} \rightleftarrows \mathrm{CuI} \qquad [E^\circ = 0.86\ \mathrm{V}]^{7)} \quad (15)$$

$$\mathrm{VO_2^++2H^++e^-} \rightleftarrows \mathrm{VO^{2+}+H_2O} \qquad [E^\circ = 1.00\ \mathrm{V}]^{7)} \quad (16)$$

$$\mathrm{VO^{2+}+2H^++e^-} \rightleftarrows \mathrm{V^{3+}+H_2O} \qquad [E^\circ = 0.361\ \mathrm{V}]^{7)} \quad (17)$$

$$\mathrm{I_2^{-\bullet}+e^-} \rightleftarrows \mathrm{2I^-} \qquad [E^\circ = 1.04\ \mathrm{V}]^{11)} \quad (18)$$

$$\mathrm{I_2+2e^-} \rightleftarrows \mathrm{2I^-} \qquad [E^\circ = 0.536\ \mathrm{V}]^{7)} \quad (19)$$

$$\mathrm{I_3^-+2e^-} \rightleftarrows \mathrm{3I^-} \qquad [E^\circ = 0.536\ \mathrm{V}]^{7)} \quad (20)$$

$$\mathrm{I_2+e^-} \rightleftarrows \mathrm{I_2^{-\bullet}} \qquad [E^\circ = 0.11\ \mathrm{V}]^{10)} \quad (21)$$

Comparing the redox potentials of Eq. 16 to Eq. 18 or line (3) to (1) in Fig. 9, the occurrence of reaction (12) is thermodynamically favorable under larger pH's. However, reaction (12) was almost overcome by the occurrence of reaction (6) under the conditions of $\mathrm{pH} \leqq 3.60$. It is herein noted that the redox potentials for the couple $I_3^-/3I^-$ (or $I_2/2I^-$) and VO_2^+/VO^{2+} are equivalent at pH 4.0 (see Fig. 9), and thus, that the capability in the occurrence of reactions (7) and (10) might be thermodynamically equivalent at pH 4.0, and that reaction (7) would become more difficult to occur at a larger pH. Actually, as stated above, the rate constant k_7 became smaller at a larger pH. As can be seen from line (1) in Fig. 9, the redox potential becomes smaller at a larger pH, being favorable for the occurrence of reaction (12). These are reasons that the self-retardation in Figs. 5A and 7A appeared only under the conditions $\mathrm{pH} > 3.6$, and that the V^{IV} retardation effect hardly appeared at lower pH (see Figs. 7B and 8). Reaction (12) is equivalent to reaction (B), and is compared to reaction (C), as stated in the introduction section.

Comparing line (2) with (6) in Fig. 9, it is natural that the reaction of Eq. (C) could occur under the condition $\mathrm{pH} \leqq 2.0$ in the previous study.1) As can be seen from Fig. 2, an induction period appeared at concentrations lower than 5.0×10^{-7} M in $CuSO_4$. We know from a previous study2) that reactions (3) and (4) are accelerated by the addition of alcohols, and thus examined the alcohol effect on the induction period. However the induction period could not be shortened by adding alcohol in 10 (v/v)% EtOH (see plots ▲ in Fig. 2A). Further, the induction period could not be shortened by adding V^V at $t = 30$ and 60 min (see Fig. 2B). Thus, such an induction period would not arise from the slowdown of reactions (3) and (4), but would be due to a slowdown in the formation of intermediate species, such as $\mathrm{CuI{\cdot}VO_2^+}$, i.e., the pre-equilibrium reaction for Eq. 12, such as $\mathrm{CuI+V^V} \rightleftarrows \mathrm{CuI{\cdot}V^V}$, was thought to be required in order to constitute a chain cycle of $\mathrm{CuI^+/CuI}$ in Eqs. 3, 4, 5, 6, and 7. In light of the analytical determination of trace amounts of V^V, it should be noted that the reproducibility of the initial rates (V_i) in the present study was good, and that V^V can be determined separately in the presence of even relatively high concentrations of V^{IV} at a lower pH (refer to Fig. 8).

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