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Kinetics and Mechanism of the Copper(II)-Catalyzed Oxidation of the Iodide Ion by Chromate(VI) Ion in an Aqueous Solution

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Although the chromate(VI) ions, CrO_4^{2-} and $HCrO_4^-$, which are described as Cr^{VI} herein, could hardly oxidize the iodide ion to iodine above pH 3.0, it was catalytically oxidized by adding traces of copper(II) ion. When a copper(II) solution of 10^{-7}—10^{-5} mol dm^{-3} was mixed with an iodide solution, after a fast formation of iodine, the iodine concentration remained constant. After such an iodine formation had occurred, if a chromate solution was added into the reacting mixture, the iodine began to form again in accordance with a rate law of $2/3(d[I_2]/dt) = -d[Cr^{VI}]/dt = k[CuI][Cu^{VI}]$, in which [CuI] is the steady-state concentration in the chain cycle CuI^+/CuI. The rate of the chain reaction was independent of the time to add chromate, and the formation of iodine I_2 (or triiodide ion I_3^-) stopped at the time when all of the chromate was consumed by the chain reaction. The stoichiometry was $3I^- + Cr^{VI} \rightarrow 1.5I_2 + Cr^{III}$. The iodine formation was extremely inhibited by the presence of either radical scavengers or complex-forming reagents as well as by increasing pH. Although addition of alcohols to the reaction mixture extremely accelerated the iodine formation before adding chromate, it hardly affected on this process after the addition of chromate. The reaction mechanisms are presented in order to account for the observed results.

The copper(II) ion reacts with the iodine ion in accordance with the following overall equation:

$$4I^- + 2Cu^{2+} \rightarrow I_2 + 2CuI \text{ (or } Cu_2I_2) \tag{1}$$

In general, this reaction is thought to be a quantitative precipitation reaction of CuI (or Cu_2I_2) with forming iodine. However, no precipitations were found under the conditions of low concentrations of copper(II). Our previous study[1] showed that iodine formation was extremely accelerated by the presence of molecular oxygen (O_2) under the conditions of pH's less than 2, comprising a chain cycle of the CuI^+/CuI (or Cu^{II}/Cu^{I}). In this work we found that such a cycle of Cu^{II}/Cu^{I} could occur efficiently by the addition of even trace amounts of chromate(VI) ion under the conditions of pH's larger than 3. We herein report on the reaction mechanism to account for the obtained results.

Experimental

Chemicals. Potassium iodide, copper(II) sulfate, potassium chromate(VI), and the other chemicals used 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 chromate(VI); in some runs a chromate(VI) 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. Preliminary experiments showed that the dissolved oxygen did not seriously affect the formation rate of I_3^- under the conditions in the present study; thus, unless otherwise stated, the dissolved air was not removed. Aliquot solutions were taken out at appropriate time intervals in order to measure the concentration of iodine formed; the formed iodine (I_2) during the reactions was rapidly converted to the triiodide ion (I_3^-) in the presence of the iodide ion:

$$I_2 + I^- \rightleftarrows I_3^-, \tag{2}$$

where $k_2 = 5.6\times10^9$ M^{-1} s^{-1} and k_2/k_{-2} (or K_2) = 710 M^{-1} (M = mol dm^{-3}).[2,3]

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.[4] 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 the kinetic measurements. 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. The formation constants of $HCrO_4^-$ and $Cr_2O_7^{2-}$ are $10^{6.49}$ M^{-1} [5] for $[HCrO_4^-]/[CrO_4^{2-}][H^+]$ and 98 M^{-1} [6] for $[Cr_2O_7^{2-}]/[HCrO_4^-]^2$, respectively. Thus, the CrO_4^{2-} and $Cr_2O_7^{2-}$ species remain negligible under the conditions of low concentrations of 10^{-7}—10^{-5} M chromate at pH's lower than 4.5, and the predominant species is thought to be $HCrO_4^-$. The maximum molar absorption coefficient of $HCrO_4^-$ was 1.6×10^3 M^{-1} cm^{-1} at 350 nm. Thus, the absorption at 350 nm due to I_3^- after the addition of chromate was corrected by the following equations:

$$\varepsilon_1 l[HCrO_4^-]_t + \varepsilon_2 l[I_3^-]_t = A_t, \tag{3}$$

$$[HCrO_4^-]_t = [Cu^{VI}]_{added} - 1.5[I_3^-]_t, \tag{4}$$

where subscript t indicates the reaction times: A_t, the observed absorbance at t and 350 nm; l, the optical cell length (1 cm); ε_1 and ε_2 are 1.6×10^3 and 2.5×10^4 M^{-1} cm^{-1}, respectively. The coefficient of 1.5 in Eq. 4 comes from the overall stoichiometry in the iodide oxidation by chromate ion in the copper(II)-catalyzed reaction (see Eq. 5).

Results and Discussion

Evidence of Induced-Catalysis. Figure 1 shows plots of the concentrations of I_3^- formed against the reaction times for a solution at pH 3.57. We can recognize from Fig. 1 that traces of the copper(II) ion induced catalytically the oxidation of I^- by chromate(VI), and that the I_3^- formation stopped at the time when the added chromate(VI) completely disappeared. The net concentrations of I_3^- formed by the copper(II)-catalyzed reactions were 1.5-fold of those of the added chromate. Accordingly the stoichiometry of the catalyzed reaction can be described as

$$3I^- + Cu^{VI} \rightarrow 1.5I_2 + Cu^{III}. \qquad (5)$$

As further evidence of an efficient catalysis, when the copper(II) concentration was 1.0×10^{-7} M, the formation of I_3^- was hardly appreciable in the case without adding chromate (see plots ○ in Fig. 2), but could be obviously observed by the addition of the chromate(VI) ion (see Fig. 2).

Stability (or Instability) of CuI. At some times later than having mixed (or added) the iodide solution into a copper(II) solution, the chromate(VI) solution was added into the reacting solution. Figure 3 shows that the formation rate of I_3^- was independent of the times to add the chromate(VI) ion. Therefore, the rapidly formed CuI (see plots ● in Fig. 3) must be rather stable, and the disproportionation reaction $2CuI \rightarrow CuI^+ + Cu + I^-$ (or $2Cu^+ \rightarrow Cu^{2+} + Cu$) did not occur appreciably under the present conditions.

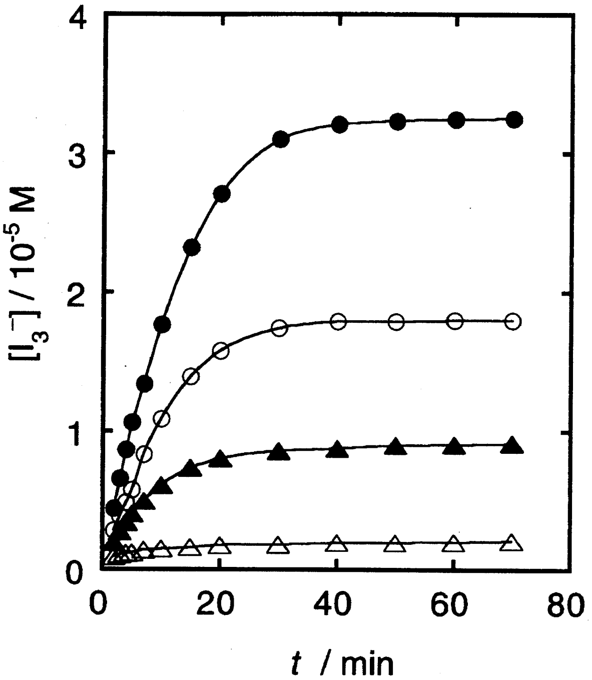

Fig. 1. Evidence of the copper(II)-catalyzed reaction: plots of $[I_3^-]$ vs. t. Plots of △, ▲, ○, and ● indicate those in the presence of 5.0×10^{-6} M $CuSO_4$ with K_2CrO_4 of zero, 5.0×10^{-6}, 1.0×10^{-5}, and 2.0×10^{-5} M, respectively. The other conditions are 0.10 M KI, 5.0×10^{-2} M CH_3COOH, 5.0×10^{-3} M CH_3COONa, pH 3.57, and 25.0 °C.

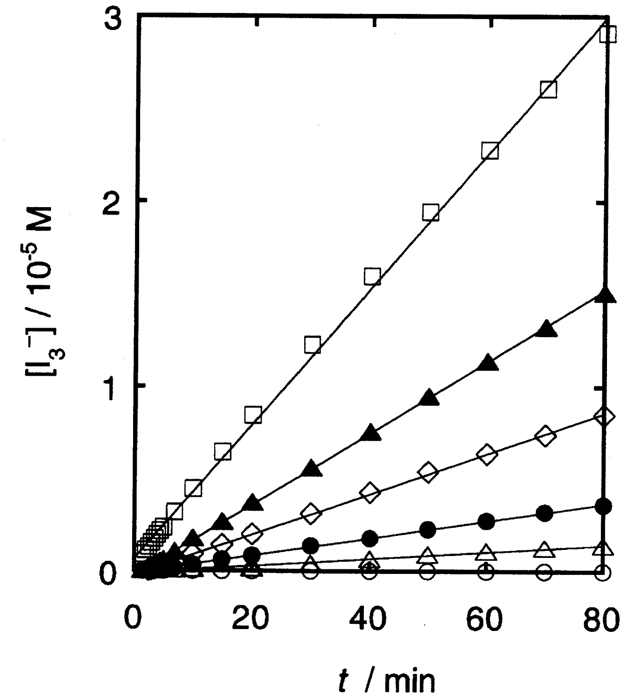

Fig. 2. Effect of concentration of chromate: plots of $[I_3^-]$ vs. t. Plots ○, △, ●, ◇, ▲, and □ indicate $[K_2CrO_4]_{added}$ = 0.0, 4.0×10^{-6}, 1.0×10^{-5}, 4.0×10^{-5}, 8.0×10^{-5}, and 1.0×10^{-4} M, respectively. The other conditions but 1.0×10^{-7} M $CuSO_4$ are the same as in Fig. 1.

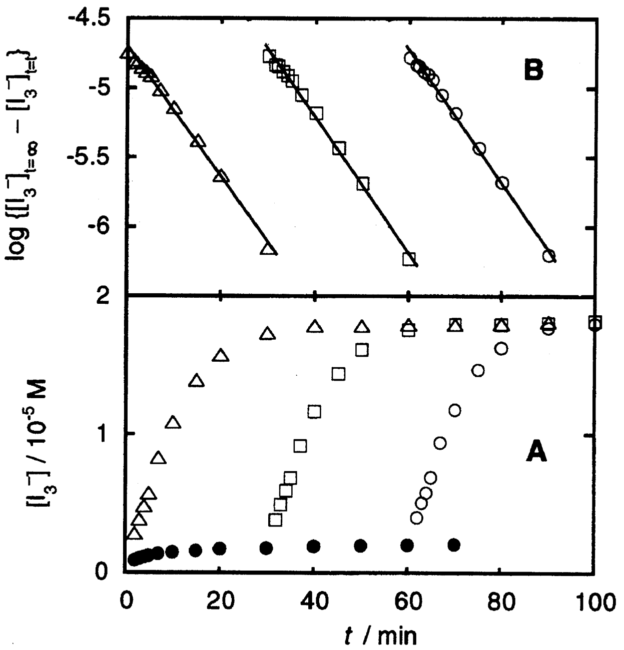

Fig. 3. Stability of CuI. A and B indicate plots $[I_3^-]$ vs. t and $\log\{[I_3^-]_{t=\infty} - [I_3^-]_{t=t}\}$ vs. t, respectively. Plots ● indicate cases of 5.0×10^{-6} M $CuSO_4$ without adding chromate, and △, □, and ○, the cases having added 1.0×10^{-5} M K_2CrO_4 at t = 0, 30, and 60 min, respectively. The other conditions are the same as in Fig. 1.

Dependence of Chromate(VI) Concentrations. As can be seen in Fig. 2, when the copper(II) concentrations were low, the initial rate of reaction (V_i) could be accurately obtained. The initial rate of $V_i=\Delta[I_3^-]/\Delta t$ increased with increasing concentrations of the chromate(VI) ion. Plots of V_i vs. $[Cr^{VI}]_{added}$ were rectilinear (Fig. 4). Further, the plots of log $\{[I_3^-]_{t=\infty}-[I_3^-]_{t=t}\}$ vs. t were also rectilinear (see B in Figs. 3 and 7). This means that this reaction is of first order with respect to chromate concentrations, being a rate-determining step in a chain reaction comprizing CuI^+/CuI (refer to the reaction mechanism in Eqs. 6, 7, 8, 9, 10, 11, and 12 with rate law of Eqs. 13 and 14).

Dependence of Copper(II) Concentrations. The initial rates (V_i) in a concentration of chromate were proportional to the concentrations of the initially added copper(II) ion (see Fig. 5), indicating that concentrations of CuI at the steady-states are also proportional to $[CuSO_4]_{added}$. This would be probable from considering reactions (6), (7), and (10).

Effect of Iodide Concentration. The I_3^- concentrations formed at $t = 30$ min in the reaction between I^- and Cu^{2+} increased according to the increase in the iodide concentrations in the range 0.020—0.10 M, and remained constant at $[I^-] \geqq 0.10$ M (see B in Fig. 6). On the other hand, when the chromate(VI) ion was added into the reacting solution of I^- with Cu^{2+} at $t = 30$ min, the rate (V_i) increased by $[I^-] = 0.10$ M, and then began to decrease with increasing the iodide ion concentrations (see A in Fig. 6). This is thought to have been due to the formation of less inactive species, CuI_2^-, for the oxidation. Considering that the formation constants of CuI and CuI_2^- are 9.0×10^{11} M^{-1} for $[CuI]/[Cu^+][I^-]$

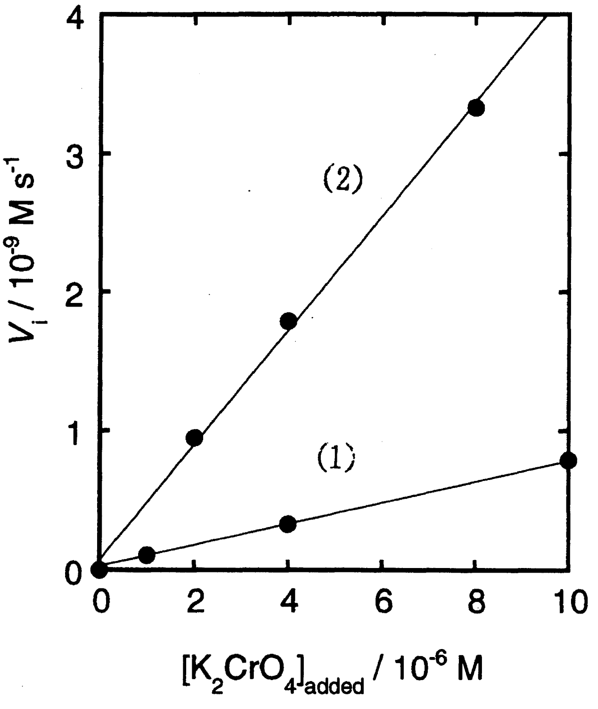

Fig. 4. Dependence of chromate concentrations: V_i vs. $[K_2CrO_4]_{added}$. Lines (1) and (2) indicate 1.0×10^{-7} and 5.0×10^{-7} M $CuSO_4$, respectively. The other conditions are the same as in Fig. 1.

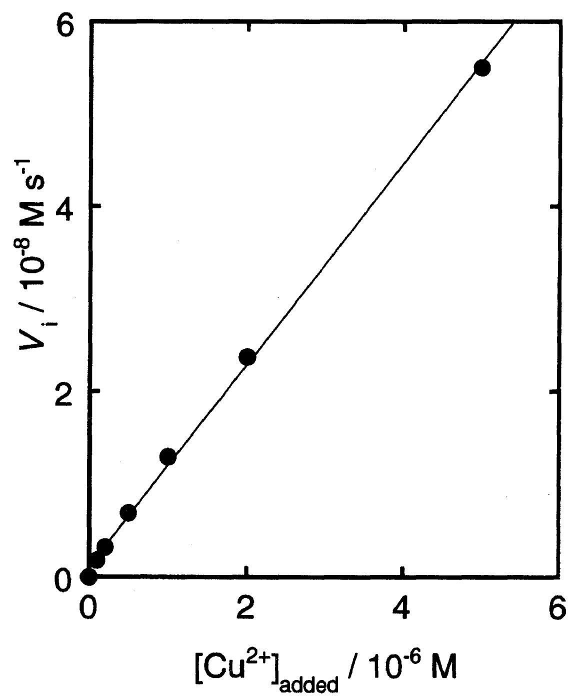

Fig. 5. Dependence of copper(II) concentration: V_i vs. $[CuSO_4]_{added}$. 4.0×10^{-5} M of chromate(VI) was added at $t = 30$ min at varied concentrations of copper(II). The other conditions are the same as in Fig. 1.

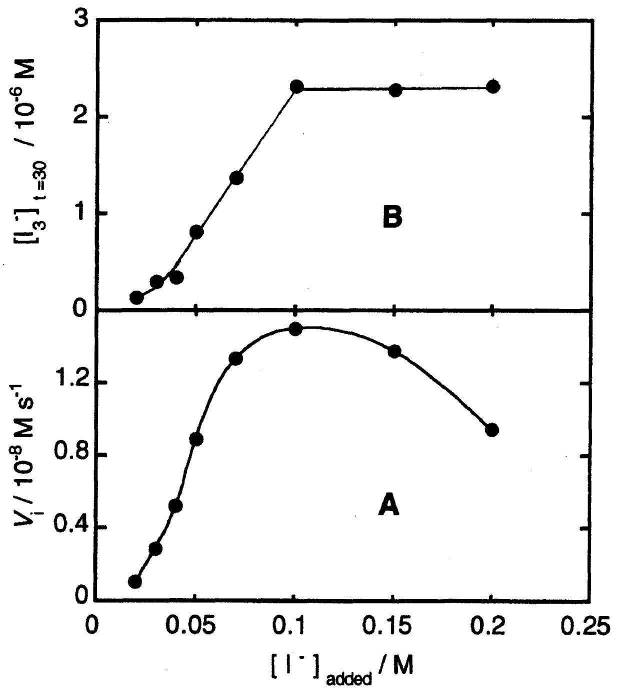

Fig. 6. Effect of the iodide concentration: plots V_i vs. $[I^-]_{added}$ and $[I_3^-]_{t=30}$ vs. $[I^-]_{added}$. In case of A, 1.0×10^{-5} M chromate(VI) was added at $t = 30$ min to measure V_i. In case of B, the triiodide concentration at $t = 30$ min were measured without adding chromate. The ionic strength was adjusted to 0.20 M with KCl. The other conditions are the same as in Fig. 1.

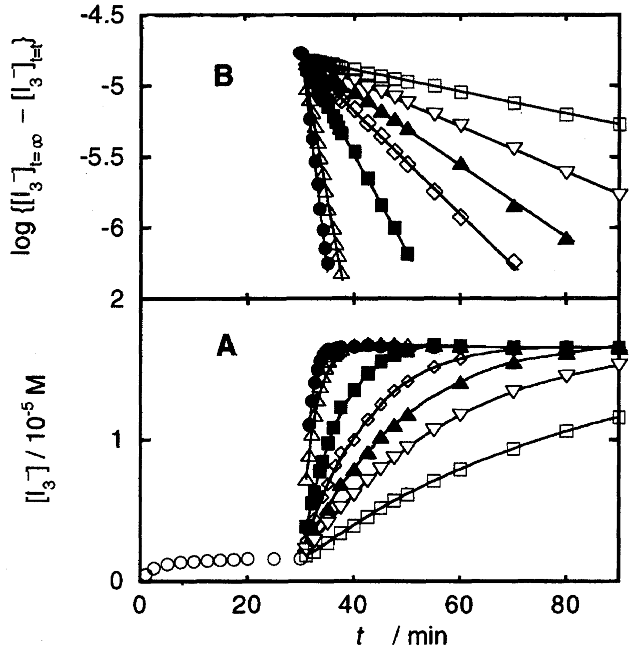

Fig. 7. Effect of acidity on the catalyzed reaction rate. Plots ○ indicate results without adding chromate, and □, ▽, ▲, ◇, ■, △, and ●, at pH = 4.47, 4.13, 3.19, 3.64, 3.37, 2.67, and 2.38, respectively, with adding 1.0×10^{-5} M K_2CrO_4 at $t = 30$ min at varied pH's which were adjusted with sulfuric acid from 1×10^{-4} to 1×10^{-2} M. All reactions were carried out in an N_2-saturated solution. The other conditions are the same as in Fig. 1. The case B is a plot for Eq. 14, being based on the data in Fig. 7A.

and 1.6×10^3 M^{-1} for $[CuI_2^-]/[CuI][I^-]$, respectively,[7] the formation of CuI_2^- would be probable at higher iodide concentrations. A great decrease in both V_i and $[I_3^-]_{t=30}$ at $[I^-] \leqq 0.05$ M in Fig. 6 is thought to be due to a slowdown of the foreward reaction in Eqs. 6 and 7.

Effect of Acidity. Under the same conditions as the plots ○ in Fig. 7A, i.e., in the case without any addition of chromate, the values of $[I_3^-]_{t=30}/10^{-6}$ M were 1.94, 1.90, 1.90, 1.92, 1.92, 1.98, 1.84, 1.36, 0.84, 0.32, and 0.00 at pH = 1.33, 1.97, 2.28, 2.99, 3.47, 3.82, 4.64, 5.73, 6.67, 7.23, and 8.81, respectively. This indicates that the amounts of I_2 (or I_3^-) formation or CuI formation were constant at pH $\leqq$ 4.0, and then decreased at pH $\geqq$ 4.6. On the other hand, the rate of the copper(II)-catalyzed reaction decreased extremely with increasing pH (see Fig. 7). Namely, although the reaction between Cu^{2+} and I^- was not affected at pH $\leqq$ 4.0, the catalyzed reaction after adding chromate was greatly dependent on the pH within the same pH range. Accordingly, the retarding effect due to a pH increase on the catalyzed-reaction in Fig. 7 could be caused by a decrease in the oxidation capability of chromate, in accordance with changing $HCrO_4^-$ into CrO_4^{2-}. However, a decrease in I_3^- at pH $\geqq$ 4.6 is thought to have arisen from the occurrence of a hydrolysis reaction with forming such a species of $Cu(OH)^+$, which could inhibit the CuI^+ formation by Eq. 6, which is necessary to from the triiodide ion (I_3^-) together with CuI, $I^\bullet$, and $I_2^{-\bullet}$ by Eqs. 7, 8, and 9.

Effect of Radical Scavengers and Chelate Reagents. The initial rate of iodine in the copper(II)-catalyzed reaction, i.e., $V_i/10^{-9}$ M s^{-1}, was 4.44 in the case of the addition of 1.0×10^{-5} M chromate at $t = 30$ min under the conditions of 1.0×10^{-6} M $CuSO_4$ and 0.10 M KI at 25 °C and pH 3.57. Under the same conditions, the values of $V_i/10^{-9}$ M s^{-1} were 2.62 and 0.14 in the presence of 1.0 (v/v)% acrylamide and 1.0×10^{-6} M ethylenediaminetetraacetic acid (EDTA), respectively. However, under the same conditions, but with $[Cu^{2+}] = 1.0\times10^{-5}$ M, and without adding chromate, the values of $[I_3^-]_{t=30}/10^{-6}$ M were 4.16, 3.36, 3.12, 1.88, 0.64, and 0.00 at $[EDTA]/10^{-6}$ M = 0.0, 1.0, 2.0, 5.0, 8.0 and 10, respectively, indicating the quantitative masking-effect of EDTA on Cu^{2+}; thus, no formation of I_3^- was found at $[EDTA]_{added} = [Cu^{2+}]_{added} = 1.0\times10^{-5}$ M. Accordingly, the remarkable retardation effect by EDTA on V_i in a catalyzed reaction is also caused by the complex-formation of $[Cu(edta)]^{2-}$, which inhibits the formation of CuI^+ in Eq. 6. The retardation by acrylamide would be due to the capture of radicals $I^\bullet$ or/and $I_2^{-\bullet}$ in the reacting solution (refer to the reaction mechanisms in Eqs. 6, 7, 8, 9, 10, 11, and 12).

Effect of Alcohols. As can be seen from Fig. 8, the I_3^- formation rate before adding chromate i.e., the formation rate of CuI, was extremely accelerated by the presence of alcohols. On the contrary, the formation rate of I_3^- after chromate addition at $t = 30$ min was scarcely affected by the presence of alcohols (see Fig. 9). The decrease in permittivity by the addition of alcohols is favorable to iodine formation by Eqs. 6, 7, 8, and 9, being in agreement with these results in Fig. 8, and is indifferent to the reaction of Eq. 10, containing a neutral species, CuI, being in agreement with the results in

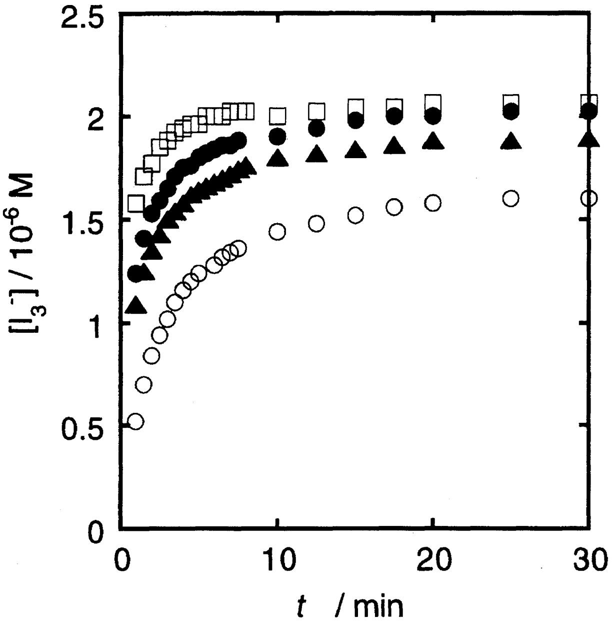

Fig. 8. Effect of alcohols on reaction between I^- and Cu^{2+}. Plots ○, ▲, ●, and □ indicate no alcohol, 10 (v/v)% methanol, 10 (v/v)% ethanol, and 20 (v/v)% ethanol, respectively. Conditions are 0.10 M KI, 5.2×10^{-6} M $CuSO_4$, 25.0 °C, pH 3.2, and N_2-sat.

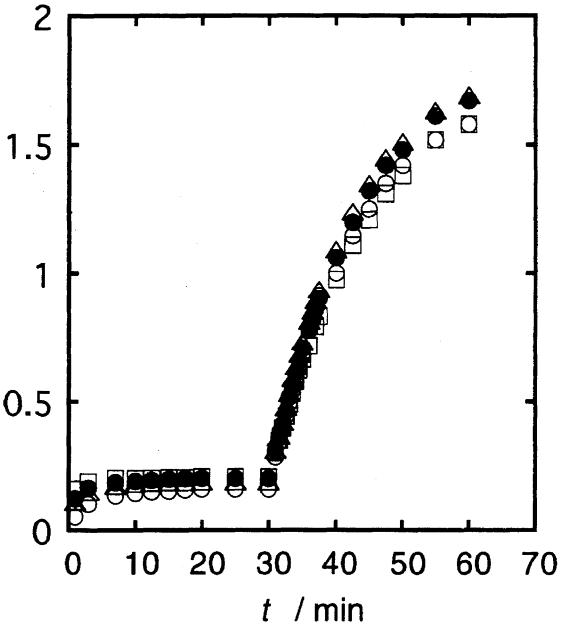

Fig. 9. Effect of alcohols on reaction between Cr^{VI} and CuI. 1.0×10^{-5} M K_2CrO_4 was added at $t = 30$ min into the reacting solutions which correspond to each plot in Fig. 8. The other conditions as well as the symbols are the same as those in Fig. 8.

Fig. 9.

Mechanism of Reaction. All of the results obtained are accounted for by the following mechanism:

$$Cu^{2+} + I^- \rightleftarrows CuI^+ \tag{6}$$

$$CuI^+ + I^- \rightleftarrows CuI + I^\bullet \tag{7}$$

$$I^\bullet + I^- \rightleftarrows I_2^{-\bullet} \quad [K = 1.04\times10^4 M^{-1}]^{7)} \tag{8}$$

$$2I_2^{-\bullet} \rightarrow I_2 + 2I^- \tag{9}$$

$$CuI + Cr^{VI} \rightarrow CuI^+ + Cr^V \quad \text{[rate determining step]} \tag{10}$$

$$I^- + Cr^V \rightarrow I^\bullet + Cr^{IV} \tag{11}$$

$$I^- + Cr^{IV} \rightarrow I^\bullet + Cr^{III} \tag{12}$$

The overall reaction of Eq. 5 comprises Eqs. 7, 8, 9, 10, 11, and 12, i.e., (5)=(7)+3(8)+1.5(9)+(10)+(11)+(12). Judging from the redox potential diagram,8,9)

$$Cr^{VI} \xrightarrow{0.55\,V} Cr^{V} \xrightarrow{1.34\,V} Cr^{IV} \xrightarrow{2.1\,V} Cr^{III} \xrightarrow{-0.41\,V} Cr^{II}$$

it is assumed that reaction (10) is relatively slow, and that reactions (11) and (12) are rapid or fast. The experimental conditions of $[I^-] \gg [Cu^{2+}]$ (or $[I^-] \gg$[CuI]) employed in the present study were also favorable to reactions (11) and (12) which were much faster than the reaction (10). Further, although the equilibrium constant for the reaction $2Cr^V \rightarrow Cr^{VI} + Cr^{IV}$ is as large as 2.5×10^{13},9) its occurrence could be eliminated from considerations by making the faster reactions of Eqs. 11 and 12. Considering the chromate dependence from Figs. 2 and 4, the rate of reaction (10) is of the rate-determining step in the copper(II) catalyzed reaction involving a chain-cycle of CuI^+/CuI, in which the concentration of CuI and CuI^+ remains constant. This leads to the following rate equations for the catalytic reaction after the reaction between Cu^{2+} and I^- without adding chromate:

$$\begin{aligned} -d[Cr^{VI}]/dt &= k_{10}[CuI][Cr^{VI}] \\ &= k_{obsd}[Cr^{VI}], \end{aligned} \tag{13}$$

$$\log [Cr^{VI}]_{t=t} = -(k_{obsd}/2.303)t + \log [Cr^{VI}]_{t=0}, \tag{14}$$

where $k_{obsd} = k_{10}[CuI]$ and $[Cr^{VI}]_{t=t} = 2/3\{[I_3^-]_{t=\infty} - [I_3^-]_{t=t}\}$. As can be seen from B in Figs. 3 and 7, the above rate law could be verified by the experimental facts. When the steady-states' concentration of [CuI] in Eq. 13 could be assumed to be $2[I_3^-]_{t=30}$ without adding chromate (e.g., this corresponds to the plots ● in Fig. 3), the rate constant (k_{10}) could be obtained from plots of $\log\{[I_3^-]_{t=\infty} - [I_3^-]_{t=t}\}$ vs. t. The k_{10} values from Fig. 3 were obtained to be 5.0×10^2, 5.2×10^2, and 5.1×10^2 $M^{-1}\,s^{-1}$ for plots using △, □, and ○ in Fig. 3B, respectively. On the other hand, the V_i in Figs. 4 and 5 can be described as $V_i = \Delta[I_3^-]_i/\Delta t = 1.5\,k_{10}\times[CuI]_i[Cr^{VI}]_i$. Thus, assuming [CuI] to be equal to $[Cu^{2+}]_{added}$ in Fig. 4, the k_{10} values were obtained to be 5.1×10^2 and 5.5×10^2 $M^{-1}\,s^{-1}$ from (1) and (2) in Fig. 4, respectively. These values, obtained by different ways, are rather in mutual agreement. It is noted here that the concentration of I_3^- formed without adding chromate remained constant for about 20 min after initiating the reaction, and were approximately 40% of the added copper(II), indicating the formed CuI to be ca. 80% of the concentration of added $CuSO_4$ (refer to △ in Fig. 1, or ● in Fig. 3). From the viewpoint of a trace analysis, it is noted that this reaction is extremely sensitive to traces of not only copper(II), but also chromate(VI) (see Figs. 2, 4, and 5).

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