Kinetics and Mechanisms of the Copper(II)-Catalyzed Oxidation of Iodide Ion in the Presence of Molecular Oxygen in Aqueous Acid Media

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Traces of copper(II) ion in 10^{-7}—10^{-5} M (M=mol dm^{-3}) catalytically accelerated the oxidation reactions of iodide ion to iodine in relatively strong acid solutions (pH≦2) in the presence of molecular oxygen under conditions containing relatively high concentrations of I^-. When a copper(II) solution was mixed with an iodide solution, after a rapid formation of iodine, it gradually increased according to the reaction times. For about 5 min after mixing, plots of $[I_3^-]_{\text{formed}}$ vs. t showed a good straight line; the formation rate of I_2 (or I_3^-) increased proportionally with increasing concentrations of copper(II) ion and oxygen, with increasing concentrations of hydrogen ion and iodide ion, and with increasing temperature and with decreasing the ionic strength in the reaction solution. The formation rate of I_2 was extremely inhibited by the presence of either radical scavengers or ethylenediaminetetraacetic acid (EDTA). A chain mechanism is presented to account for the obtained results.

In general, copper(II) ion reacts quantitatively with iodide ion in accordance with the following overall equation, precipitating CuI (or Cu_2I_2):

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2. \qquad (1)$$

However, this reaction does not occur quantitatively under the condition of low concentrations of copper(II) ion (refer to Figs. 2 and 4), and no precipitation is found. This is probably due to either the slow coagulation of the CuI molecule or fast oxidations of CuI by $I^{\bullet}$ (backward reaction in Eq. 5) and molecular oxygen (Eq. 9). 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:

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

Although the reaction is slow, its rate increases along with an increase in the acid concentration. The air (or O_2) oxidation of the iodide ion is promoted by either the irradiation of light or by some catalytic substances in the solution.[1)] The mechanisms of the catalyzed reactions in the presence of oxygen have not been well investigated. We previously investigated the nitrous acid catalyst for the oxidation of the iodide ion in the presence of oxygen.[2)] In this work we found that traces of the copper(II) ion catalytically accelerated the oxidation reactions of iodide ion to iodine in the presence of oxygen. We now report on the reaction mechanism to account for the obtained results.

Experimental

Materials. Potassium iodide, copper(II) sulfate, and the other chemicals used were of guaranteed grade of Wako Pure Chemical Industries, Ltd.

Procedure. The reaction was started by mixing a copper(II) solution with an iodide solution; the absorbance of the formed I_3^- was measured using a Shimadzu UV-150-02 spectrophotometer. The temperature of the reaction solutions was controlled to within 0.1 °C. Each solution containing Cu^{2+} or I^- was separately saturated by bubbling a gas of oxygen, air, or nitrogen through the solution before mixing the Cu^{2+} with I^- solution. Each gas was then continuously supplied to the surface of the reacting solution during the reaction.

Aliquot solutions were taken out at appropriate time intervals in order to measure the concentrations of iodine formed; iodine (I_2) formed during the reaction was rapidly converted to the triiodide ion (I_3^-) in the presence of the iodide ion:

$$I_2 + I^- \rightleftarrows I_3^-, \qquad (3)$$

were $k_3=5.6\times10^9$ M^{-1} s^{-1} and k_3/k_{-3}(orK_3)=710 M^{-1}.[3,4)] The I_3^- ion has large absorption coefficients of 3.82×10^4 and 2.5×10^4 M^{-1}cm^{-1} at 288 and 350 nm,[5)] respectively. The concentrations of I_3^- were proportional to those of I_2 in the presence of I^- in large excess. Thus, the absorbance of I_3^- at 350 nm (or 288 nm) could be used as a monitor for the kinetic measurements in this work. All of the kinetic runs were carried out under conditions that the I^- ion was in at least 1000-fold excess over the I_2 formed by the reaction.

Results and Discussion

Figure 1 shows plots of the absorbance of I_3^- at 350 nm against the reaction time for a solution saturated with air at different pH's. The intercept values extrapolated to t=0 were independent of the pH and O_2 concentration, and were proportional to the iodide-ion concentration added (refer to Figs. 1 and 2).

The intercept is accounted for by the following elementary reactions:

$$Cu^{2+} + I^- \rightleftarrows CuI^+ \qquad (4)$$

$$CuI^+ + I^- \rightleftarrows CuI + I^{\bullet} \qquad (5)$$

$$I^{\bullet} + I^- \rightleftarrows I_2^{-\bullet} \quad [K = 1.04\times10^4\ \mathrm{M}^{-1}]^{7)} \qquad (6)$$

$$2I_2^{-\bullet} \rightarrow I_2 + 2I^- \qquad (7)$$

$$2I^{\bullet} \rightarrow I_2 \qquad (8)$$

The equilibrium constant for the reaction $Cu^+ + I^- \rightleftarrows CuI$ is 9.1×10^{11} M^{-1}.[6)] Reaction 1 is a grand total of the above elementary reactions, being described as

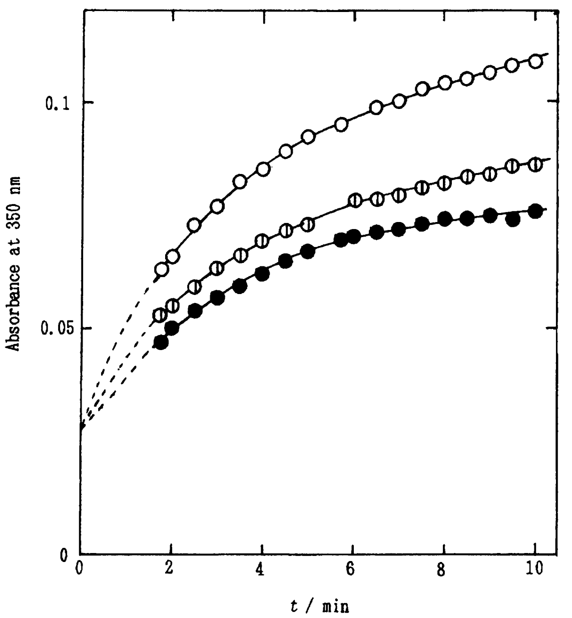


Fig. 1. Plots of absorbance of I_3^- against t ($t \leq 10$ min). Conditions: 0.1 M KI, $[\mathrm{CuSO_4}]_{\mathrm{added}}=1\times10^{-5}$ M, Air-sat., 25 °C, and Dark. pH=5.33 (●), 2.87 (◐), and 1.82 (○).

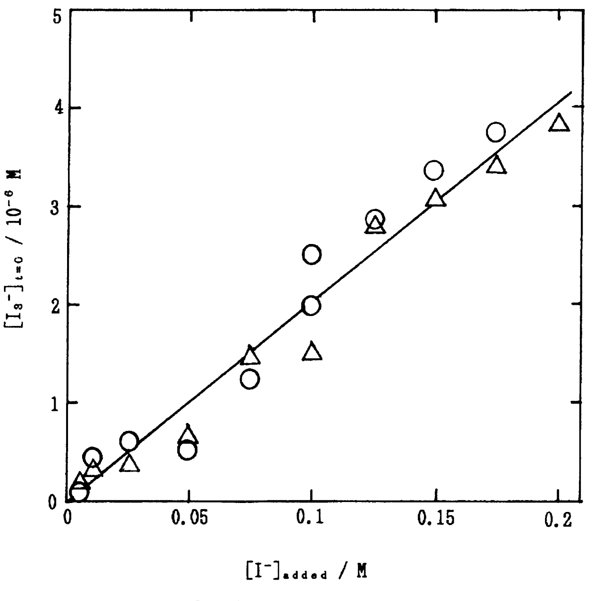


Fig. 2. Plots of $[I_3^-]_{t=0}$ vs. $[I^-]_{\mathrm{added}}$. Conditions: $[\mathrm{CuSO_4}]_{\mathrm{added}}=1\times10^{-5}$ M, 0.01 M H_2SO_4, Air-sat. (△) and O_2-sat. (○). The other conditions are as in Fig. 1. $[I_3^-]_{t=0}$ were obtained by the extrapolation to $t=0$ using plots at $t=2$—5 min.

(1)=2(4)+2(5)+2(6)+(7), where (8)=2(6)+(7). All of these reactions are thought to be rapid, and the amount of I_2 formed is dependent on the $\mathrm{CuI^+}$ concentration, which is described as $[\mathrm{CuI^+}]=K_4[\mathrm{Cu^{2+}}]_{\mathrm{added}}\times[I^-]/(K_4[I^-]+1)$. Consequently, the intercept at $t=0$ in Fig. 1 and $[I_3^-]_{t=0}$ in Fig. 2 are independent of the pH and O_2, but dependent on $[\mathrm{Cu^{2+}}]_{\mathrm{added}}$ and $[I^-]_{\mathrm{added}}$. The proportional line in Fig. 2 indicates that $K_4[I^-]\ll 1$.8) As far as the $\mathrm{Cu^{2+}}$ ion dependence is concerned, the results of Fig. 5 can be referred to as well. It is noted here that the intercept in Fig. 3, i.e. $[I_3^-]_{t=0}$ in Fig. 5, is also dependent on the concentrations of $\mathrm{CuI^+}$, which is due to the equilibrium reaction (vide infra). As can be seen from Fig. 3, plots of the absorbance of I_3^- at 350 nm against t after 5 min were rectilinear, and, thus, the formation rate of I_2 (or I_3^-), i.e., $=\mathrm{d}[I_2]/\mathrm{d}t=\mathrm{d}[I_3^-]/\mathrm{d}t$, could be obtained with good accuracy. For example, the coefficient of variation for 10 runs was 0.8%, i.e., $V=(5.29\pm0.04)\times10^{-9}$ M s^{-1} at 1×10^{-5} M $\mathrm{CuSO_4}$ under the conditions of plots ○ in Fig. 3.

Dependence of the Concentrations of $\mathrm{Cu^{2+}}$ and O_2. The formation rate (V) increased proportionally to the concentrations of the copper(II) ion added, as well as O_2 dissolved (see Figs. 3 and 4). Thus, this reaction is applicable to the determination of traces of the copper(II) ion or the O_2 concentrations in aqueous media.

Effect of Acidity. The formation rate of I_2 (or I_3^-) is extremely affected by the acid concentration. As can be seen in Table 1, V increased greatly with increasing concentrations of acid; simultaneously, the noncatalytic reaction rate (V_0 in Table 1) increased as well. The values of ($V-V_0$) correspond to the copper(II)-catalyzed reaction, and increased with increasing acidity. The noncatalytic reaction corresponding to Eq. 2 showed straight lines as well in the plots of $[I_3^-]_{\mathrm{formed}}$ vs. t (see Fig. 7). The intercept at $t=0$ might be caused by a copper(II) ion impurity in hydrochrolic acid.

Effect of Concentration of I^-. As can be seen

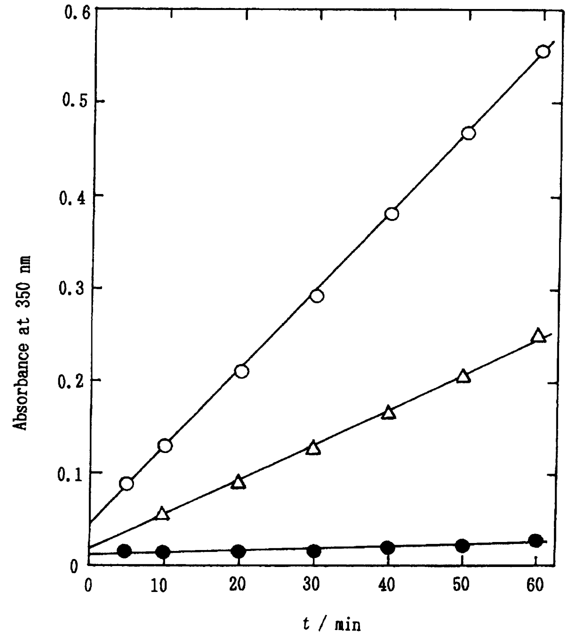


Fig. 3. Plots of absorbance of I_3^- against t. Conditions: 0.01 M H_2SO_4 (pH 1.85), O_2-sat. $[\mathrm{Cu^{2+}}]_{\mathrm{added}}=$ 0 (●), 4×10^{-6} (△), and 1×10^{-5} M (○). The other conditions are the same as in Fig. 1.

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

Concn of acid added	$V/10^{-9}\,M\,s^{-1}$			$V_0\,/10^{-9}\,M\,s^{-1}$ [b)]		$(V-V_0)\,/10^{-9}\,M\,s^{-1}$	
0 (pH 4.5—6.8)	0.00[c)]			0.00[c)]		0.00	
0.01 M H_2SO_4 (pH 1.85)	5.70[c)]			0.17[c)]		5.53	
0.016 M HCl (pH 1.9)	5.30[c)]			—		5.30	
0.02 M HCl	7.40[c)]			0.35[c)]		6.95	
0.02 M H_2SO_4	12.2[c)]			0.29[c)]		11.9	
0.05 M HCl	11.6[c)]			0.7[c)]		10.9	
0.05 M H_2SO_4	15.5[c)]			1.2[c)]		13.2	
0.10 M HCl	17.8[c)]	13.7	3.41[d)]	2.0[c)] 2.7	0.59[d)]	15.8 11.0	2.82[d)]
0.10 MH_2SO_4	24.7			2.5		22.2	
0.20 M HCl	23.3	6.18[d)]		3.9	0.32[d)]	19.4	5.86[d)]
0.50 M HCl	44.1	11.3[d)]		14.9	1.9[d)]	29.2	9.4[d)]
0.80 M HCl	63.5	15.4[d)]		25.5	3.2[d)]	38.0	12.2[d)]
1.0 M HCl		17.3[d)]			4.8[d)]		12.5[d)]

a) 0.1 M KI, 1×10^{-5} M $CuSO_4$, O_2-sat., dark, 25 °C, $\mu=1.0$ M. b) No copper(II) added; the other conditions are the same as in a). c) $\mu=0.1$ M; the other conditions are the same as in a) or b). d) Air-sat., and the other conditions are the same as in a) or b).

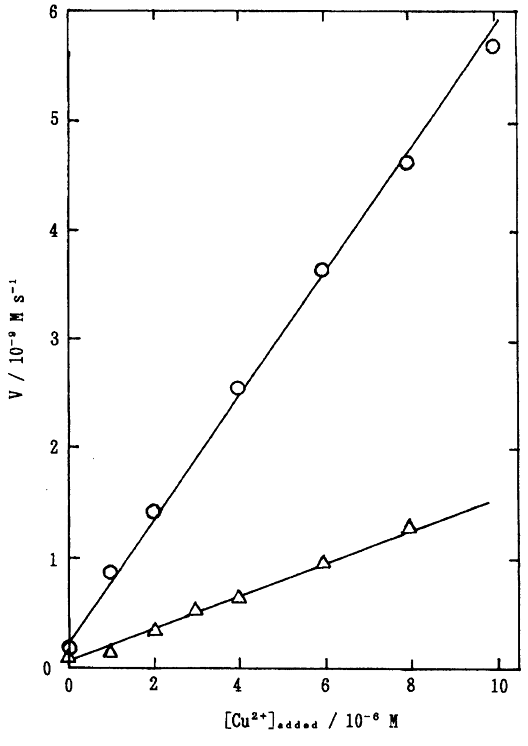


Fig. 4. Plots of V vs. $[Cu^{2+}]_{added}$. Conditions are the same as in Fig. 3; except for the air-saturated (△) and the oxygen-saturated (○).

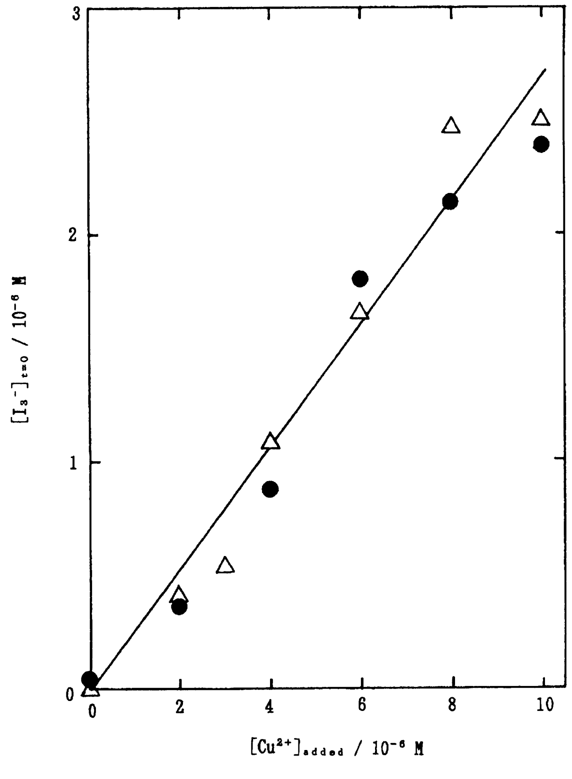


Fig. 5. Plots of $[I_3^-]_{t=0}$ vs. $[Cu^{2+}]_{added}$. $[I_3^-]_{t=0}$ were obtained from the intercept of straight lines in the plots of $[I_3^-]_{formed}$ vs. t at t=5—60 min. Plots △ and ● indicate air-sat. and N_2-sat., respectively. Other conditions are the same as in Fig. 3.

in Table 2, V has a maximum at around 0.075—0.1 M of I^-. The decrease in V at higher concentrations of I^- might have been caused by the formation of more inactive species, such as CuI_2 or CuI_2^- which may be formed under conditions of the higher concentrations of I^-.

Ionic Strength Dependence. The formation rate of I_2 (or I_3^-) is dependent on the ionic strength (μ) of the reacting solutions, and the plots of log V vs. $\mu^{1/2}/(1+\mu^{1/2})$ are rectilinear with a slope value of -1 (see Fig. 6).

Temperature Dependence. The temperature dependence on the rate was examined under conditions of the plots ○ in Fig. 3. The values of $V/10^{-9}$ M s^{-1} are 0.62, 1.09, 1.43, 2.19, 3.40, 5.29, 6.11, and 7.79 at 0, 5, 10, 15, 20, 25, 30, and 35 °C, respectively. Plots

Table 2. Effects of Concentrations of the Iodide Ion on the Rate[a)]

$[I^-]$ added	$V/10^{-9}$M s^{-1}	
M	Air-sat.	O_2-sat.
0.01	0.00	0.00
0.025	0.00	0.05
0.05	1.40	3.30
0.075	1.50	5.30
0.10	1.40	5.15 5.70[b)]
0.125	0.90	4.20
0.15	0.73	3.10
0.175	0.52	2.75

a) 0.01 M H_2SO_4 and $\mu=0.2$ M; the other conditions are the same as in Table 1. b) $\mu=0.1$ M; the other conditions are the same as in a).

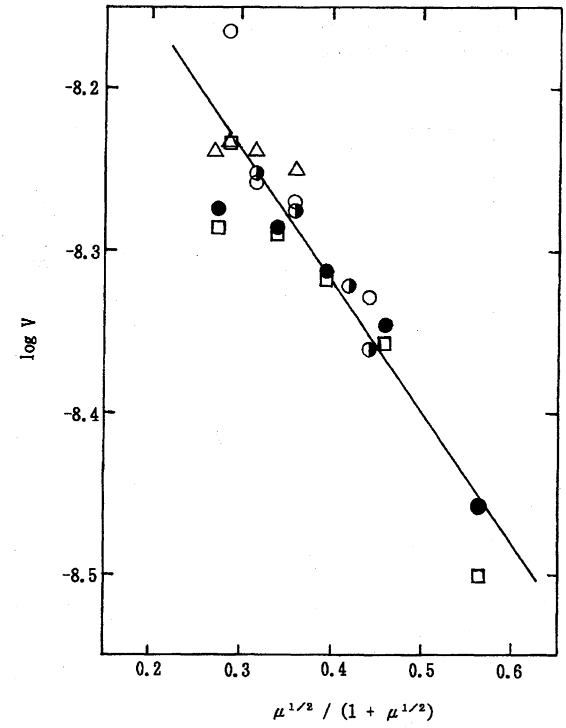


Fig. 6. Plots of log V vs. $\mu^{1/2}/(1+\mu^{1/2})$. The ionic strengths (μ) are adjusted by adding KCl (○), KNO_3 (◑), $NaClO_4$ (△), $MgCl_2$ (□), and $CaCl_2$ (●). 0.01 M H_2SO_4 (pH 1.6—1.9), 1×10^{-5} M $CuSO_4$. The other conditions are the same as in Fig. 3.

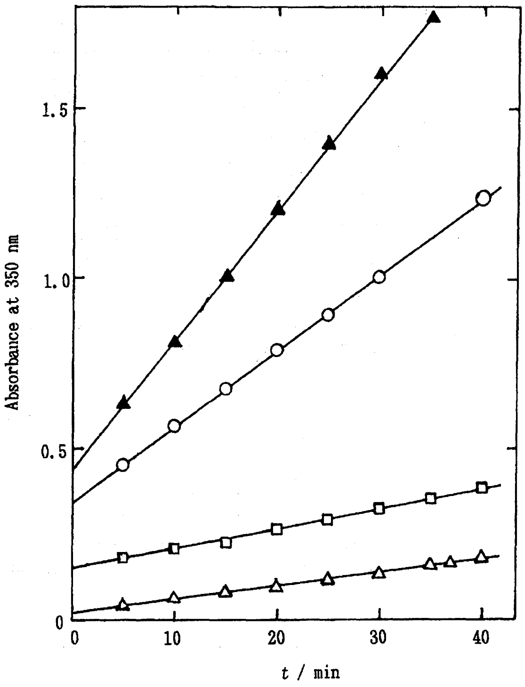


Fig. 7. Formation of I_2 (or I_3^-) by the molecular oxygen at $[Cu^{2+}]_{added}=0$. Conditions are the same as in b) of Table 1. Concentrations of HCl are 0.1 M (△), 0.2 M (□), 0.5 M (○), and 0.8 M (▲).

Table 3. Effect of Radical Scavengers and the Chelating Reagent EDTA on the Rate[a)]

Substances added	$V/10^{-9}$ M s^{-1}
None	5.30
Acrylamide	
0.5 (w/w) %	3.90
1.5 (w/w) %	3.45
Acrylonitrile	
0.5 (v/v) %	3.40
1.0 (v/v) %	3.75
5×10^{-6} M EDTA	2.47
1×10^{-5} M EDTA	1.01
2×10^{-5} M EDTA	0.32

a) 0.016 M HCl, $\mu=0.1$ M, and substances added; the other conditions are the same as in Table 1.

of log V vs. T^{-1} are rectilinear with 50 kJ mol^{-1} as an activation energy.

Effect of Radical Scavengers and Chelate Reagents. Although acrylamide and acrylonitrile did not seriously affect the formation rate of iodine, the rate decreased remarkably upon the addition of ethylenediaminetetraacetic acid, which is capable of complex-forming with the copper(II) ion (see Table 3). It is noted that not only the slope (i.e., V), but also the intercept in plots of $[I_3^-]_{formed}$ vs. t decreased upon the addition of ethylenediaminetetraacetic acid, which efficiently masks the copper(II) ion to inhibit the formation of CuI^+ by the reaction of $CuI^+ + EDTA \rightarrow [Cu(edta)]^{2-} + I^-$.

Mechanism of Reaction. All of the results obtained at $t \geqq 5$ min are accounted for by the following mechanism together with reactions 3—8:

$$CuI + O_2 \rightleftarrows CuI^+ + O_2^{-\cdot} \quad [\text{slow}] \tag{9}$$

$$O_2^{-\cdot} + H^+ \rightleftarrows HO_2^{\cdot} \quad [pK_a = 4.8]^{9)} \tag{10}$$

$$CuI + HO_2^{\cdot} + H^+ \rightarrow CuI^+ + H_2O_2 \tag{11}$$

$$2I^- + 2H^+ + H_2O_2 \rightarrow I_2 + 2H_2O \quad [\text{slow}] \tag{12}$$

$$I_2^{-\cdot} + O_2 + H^+ \rightarrow I_2 + HO_2^{\cdot} \tag{13}$$

$$I^- + H^+ + O_2 \rightarrow I^{\cdot} + HO_2^{\cdot} \quad [\text{slow}] \tag{14}$$

$$I^- + H^+ + HO_2^{\bullet} \rightarrow I^{\bullet} + H_2O_2 \qquad (15)$$

The overall reaction 2 is described by these reactions i.e., (2) = 2(5) + 3(6) + (8) + (9) + (10) + (11) + 5(12) + 3(13)+(14)+4(15) in the presence of copper(II) ion and (2)=(6)+(8)+2(12)+(13)+(14)+2(15) in the absence of copper(II) ion. The former case corresponds to the copper(II)-catalyzed reaction, which is represented by V as its rate, and the latter one to the noncatalyzed reaction, which is V_0 in Table 1. This relationship indicates that the copper(II) ion is a homogeneous catalyst for reaction 2, comprising the Cu(I)/Cu(II) cycle being initiated by CuI^+ with Eq. 4. All of the reactions, except for the forward reactions 9, 12, and 14, may be fast, and forward reactions 9 and 14 are thought to be the rate-determining step in the catalyzed and uncatalyzed reaction, respectively.

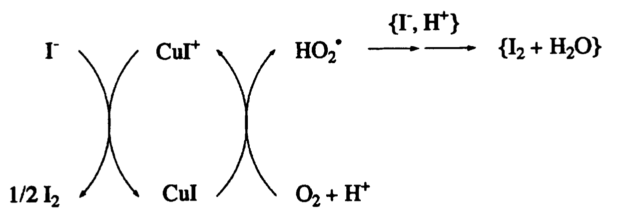
When the equilibrium reaction 4 is so fast as to maintain equilibrium while carrying out all other reactions under the given conditions, the formation rate of I_2 (or I_3^-) should be determined by the concentrations of CuI^+, keeping the CuI/CuI^+ cycle with the relationship $k_5[CuI^+][I^-]=k_9[CuI][O_2]$. It is thus described as:

$$\begin{aligned} d[I_2]/dt &= d[I_3^-]/dt \equiv V = k_9[CuI][O_2] = k_5[CuI^+][I^-] \\ &= k_5K_4[Cu^{2+}]_{added}[I^-]^2/(K_4[I^-]+1). \qquad (16) \end{aligned}$$

The right-hand side of Eq. 16 should be constant under conditions with $[I_2]_{formed} \ll [I^-]_{added}$, being in agreement with the results obtained in Figs. 3 and 4. The results given in Table 2 might deviate from Eq. 16. This deviation might be due to the formation of CuI_2^-, depending on the larger concentrations of I^-. The ionic-strength dependence in Fig. 6 with a slope of −1 might be due to a counterbalance effect on K_4 and k_{-9}, which can change the steady-state concentration of CuI^+.

Considering the following redox potentials,[6] all of the above reactions are likely to occur to the right-hand side in the stronger acid solutions containing higher concentrations of I^-; i.e., these data suggest that reaction 5 can occur without an appreciable activation energy, and that reaction 13 can also occur easily in large concentrations of H^+.

For brevity, an essential scheme of a reaction containing the CuI^+/CuI cycle can be described as follows (Scheme 1):



Scheme 1.

$$I_2 + 2e^- \rightleftarrows 2I^- \quad [E^\circ = 0.54\ V] \qquad (17)$$

$$I_2 + e^- \rightleftarrows I_2^{-\bullet} \quad [E^\circ = 0.11\ V] \qquad (18)$$

$$Cu^{2+} + I^- + e^- \rightleftarrows CuI \quad [E^\circ = 0.86\ V] \qquad (19)$$

$$Cu^{2+} + e^- \rightleftarrows Cu^+ \quad [E^\circ = 0.15\ V] \qquad (20)$$

$$HO_2^{\bullet} + H^+ + e^- \rightleftarrows H_2O_2 \quad [E^\circ = 1.50\ V] \qquad (21)$$

$$O_2 + H^+ + e^- \rightleftarrows HO_2^{\bullet} \quad [E^\circ = -0.13\ V] \qquad (22)$$

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