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Kinetic Studies of the Oxidation of L-Ascorbic Acid by the Peroxodisulfate Ion, and of Copper(II)-catalysis

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Kinetic studies of the oxidation reaction of L-ascorbic acid by the peroxodisulfate ion($S_2O_8^{2-}$) are carried out in an aqueous solution over the pH range of 3.4—4.6 at various ionic-strengths from 0.071 to 1.07 M (1 M= 1 mol dm^{-3}) with $NaClO_4$, and at four temperatures between 15 and 30 °C, at an ionic-strength of 1.07 M. The variations in the rate of the oxidation with the hydrogen-ion concentrations are consistent with the reaction schemes involving two pH-related species; ascorbic acid H_2A ($k_1=0.032$ M^{-1} s^{-1} at 25 °C, $\Delta H_1^{\ddagger}=17$ kJ mol^{-1}, $\Delta S_1^{\ddagger}=-220$ J deg^{-1} mol^{-1}) and the ascorbic anion HA^- ($k_2=0.43$ M^{-1} s^{-1} at 25 °C, $\Delta H_2^{\ddagger}=45$ kJ mol^{-1}, $\Delta S_2^{\ddagger}=-102$ J deg^{-1} mol^{-1}). A relationship of $\log k_2=-1.47+2.17\, I^{1/2}/(1+I^{1/2})$ is found with the ionic-strength (I) at 25 °C. The reaction rate is greatly catalyzed by the presence of trace amounts of the copper(II) ion; the mechanisms of the copper(II)-catalyzed reaction are discussed.

The peroxodisulfate ion is known as a powerful two-electron oxidizing agent, and its reactions with organic and inorganic substrates have been extensively studied by many researchers and reviewed by several authors.[1–4)] Previously, we studied the kinetics of the oxidation reactions of oxalic acid,[5)] formic acid,[6)] the thallium ion,[7)] and the silver(I) ion[8)] by the peroxodisulfate ion in an aqueous solution. The present paper intends to propose a reaction mechanism and the kinetic parameters for the reaction between L-ascorbic acid and the peroxodisulfate ion in an acidic aqueous solution, and also to propose the kinetic properties of the copper(II) ion-catalyzed reaction for this reaction system.

Experimental

Reagents. Reagent-grade potassium peroxodisulfate was recrystallized twice from redistilled water and dried at 25 °C in a vacuum desiccator. L-ascorbic acid of a guaranteed-reagent grade of the Wako Pure Chemical Co., Ltd., was used without further purification. Solutions of peroxodisulfate and L-ascorbic acid were prepared just before each use. The sodium perchlorate used for adjusting the ionic-strength was purified by filtering the aqueous solution through filter-paper coated with activated carbon[9)] and then recrystallized twice from redistilled water. The redistilled water was prepared from the deionized water by successive distillation of solutions with and without permanganate in a glass still. All the other chemicals used were guaranteed reagents of the Wako Pure Chemical Co., Ltd.

Reaction Solution. Preliminary experiments showed that (1) the rate of reaction decreased with a decrease in the pH in the reacting solution, and thus gradually became slow by the pH decrease, according to the progress of the reaction in an unbuffered solution for pH (refer to Table 1), and that (2) the rate of reaction was greatly catalyzed by a trace amount of the copper(II) ion (see Table 4 and Fig. 5); it seemed that the rate was slightly accelerated by the trace impurity of the copper(II) ion present in the reagents used (see line(2) in Fig. 3), and such a catalytic effect of the copper(II) ion was masked by the presence of ethylenediaminetetraacetate (EDTA) (see a closed mark (●) in Fig. 3 and also Table 4). Thus, we used pH buffer solutions of acetate-acetic acid involving 0.05 M in sodium acetate, and 0.005 M in disodium dihydrogen ethylenediaminetetraacetate (EDTA), as masking agents against the copper(II)-catalysis.

Kinetic Measurements. The reaction was started by mixing the peroxodisulfate solution with an L-ascorbic acid solution containing the pH buffer, EDTA, and sodium perchlorate. The pH value, ionic strength, and temperature of the reaction solution were kept constant at a given value. The reaction vessel was covered with black adhesive-plastic tape to ensure darkness and placed in a thermostat bath. Aliquot samples were withdrawn at appropriate times, and the concentration of the peroxodisulfate ion remaining was measured at 0.15 V *vs.* SCE (a saturated calomel electrode) by means of polarography in a solution of 0.05 M perchloric acid, 0.1 M sodium perchlorate, and 0.01% gelatin at 25 °C, essentially as has been described previously.[5–8)] The gelatin was used as a maximum suppressor. Preliminary experiments showed that the rate of reaction between L-ascorbic acid and peroxodisulfate was so slow in a perchloric acid solution of 0.05 M that the loss of both the reactants during the period of about 5 min. needed for the measurement of the polarogram was, in practice, negligible. Since the reaction rate was not affected by the oxygen dissolved in a solution, the kinetic runs were carried out in solutions without removing the dissolved air, unless otherwise stated. The pH of the reacting solution was measured for the aliquot samples by the use of a Hitachi-Horiba M-5 pH meter. Sodium chloride was used instead of potassium chloride as the electrolyte in the reference electrode of the pH meter. The ionic strength was adjusted by the addition of sodium perchlorate. The activity coefficients f_i at varying ionic strengths (I) were obtained by using $\log f_i=-0.358\times Z_i^2 I^{1/2}/(1+10^8 a_i\times 0.2325 I^{1/2})$ with $a_i=900$ pm and $Z_i=1$.[10)] The activity coefficients used in this paper were 0.88 (0.071), 0.83 (0.2), 0.79 (0.47), and 0.77 (1.07), with the ionic strength in parentheses.

Results and Discussion

Stoichiometry. With concentration of 5.0×10^{-3} M for each reactant of peroxodisulfate and L-ascorbic acid, the concentrations of the reactants disappearing according to the reaction were determined at the reaction times. The results are shown in Table 1. The concentrations of peroxodisulfate and L-ascorbic acid were measured at 0.15 V *vs.* SCE and 0.375 V *vs.* SCE, respectively by means of polarography in a solution of 0.05 M perchloric acid, 0.1 M sodium perchlorate, and 0.01% gelatin at 25 °C. Under these conditions, only the reduction current of the peroxodisulfate ion was measured at 0.15 V, while the total

Table 1. Stoichiometry[a)]

Reaction time / h	pH	$10^3[S_2O_8^{2-}]_{disapp.}$ / M	$10^3[AA]_{disapp.}$ / M	$\frac{[S_2O_8^{2-}]_{disapp.}}{[AA]_{disapp.}}$
0	4.06	—	—	—
1	3.36	1.30	1.32	0.98
2	3.10	1.63	1.65	0.99
3	2.99	1.75	1.78	0.98
4	2.88	1.91	1.96	0.97
5	2.81	2.07	2.09	0.99
				Av. 0.98

a) The initial concentrations are: $[S_2O_8^{2-}]_i = [AA]_i = 5.0 \times 10^{-3}$ M. Unbuffered solutions at an ionic strength of 0.02 M at 25 °C and in the dark.

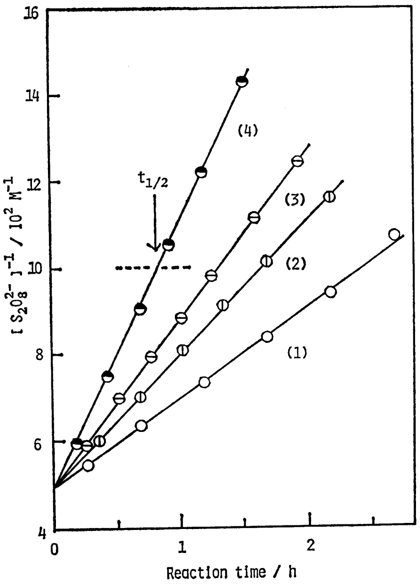


Fig. 1. Examples of plots of $[S_2O_8^{2-}]^{-1}$ *vs.* t (Eq. 1). The pH values are 3.50, 3.71, 3.90, and 4.40 for lines (1), (2), (3), and (4), respectively. Other conditions are the same as those of a) in Table 2 at an ionic strength of 0.47 M.

currents of reduction of the peroxodisulfate ion and of the oxidation of L-ascorbic acid were measured at 0.375 V. The results in Table 1 may indicate the stoichiometry to be 1:1. This stoichiometry was confirmed by kinetic experiments such as those illustrated in Fig. 1.

Kinetics of Reaction. The kinetic runs were carried out over the pH range from 3.3 to 4.6. In this pH range, the thermal decomposition of both peroxodisulfate and L-ascorbic acid was so slow that it could be neglected. When the reaction was started at the same concentrations for both reactants, the plots of $[S_2O_8^{2-}]^{-1}$ *vs.* t were rectilinear; some examples of the plots are given in Fig. 1. Thus, the empirical rate law may be written as follows:

$$-d[S_2O_8^{2-}]/dt = -d[AA]/dt = k_0[AA][S_2O_8^{2-}] \quad (1)$$

where k_0 is the observed second-order rate constant and where [AA] indicates the total concentration of all the forms of L-ascorbic acid and can be set as $[H_2A]+[HA^-]$ in the present pH range. The rate constants (k_0) were determined by treating plots of $[S_2O_8^{2-}]^{-1}$ *vs.* t with a least-squares method. The values of k_0 obtained are given in Table 2. The plots of k_0 *vs.* $K_1/(K_1+[H^+])$ showed a straight line with an intercept; some examples of the plots are given in Fig. 2. Thus, the relationship of the k_0 with $[H^+]$ is accounted for by Eq. 2, consistent with the reaction mechanisms (*v.i.*):

$$k_0 = k_1 + (k_2 - k_1)\frac{K_1}{[H^+]+K_1}, \quad (2)$$

where K_1 is the first acid-dissociation constant of L-ascorbic acid of Eq. 3. The rate constants, k_1 and k_2, were determined by treating plots of k_0 *vs.* $K_1/([H^+]+K_1)$ with a least-squares method; they are listed in Table 3. The values of K_1 were necessary for making the plots such as in Fig. 2. Recently,[11)] we determined the K_1 values by the pH titration of L-ascorbic acid under various conditions. The values of pK_1 used in this work are as follows: at an ionic strength of 1.07 M (with the temperature (°C) in parentheses): 4.04 (15), 4.00 (20), 3.95 (25), and 3.90 (30), and at 25 °C (with the ionic strength in parentheses): 4.09 (0.071), 4.00 (0.2), and 3.96 (0.47).

Mechanisms of Reaction. The following three schemes can be presented to account for the empirical results:

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \quad (3)$$

Scheme 1:

$$H_2A + S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{2-} + A + 2H^+ \quad (4)$$

$$HA^- + S_2O_8^{2-} \xrightarrow{k_2} 2SO_4^{2-} + A + H^+ \quad (5)$$

Scheme 2:

$$H_2A + S_2O_8^{2-} \xrightarrow{k_1} (H_2A^{\dot{+}} + SO_4^{\dot{-}} + SO_4^{2-}) \xrightarrow{\text{fast}} 2SO_4^{2-} + A + 2H^+ \quad (6)$$

$$HA^- + S_2O_8^{2-} \xrightarrow{k_2} (HA\cdot + SO_4^{\dot{-}} + SO_4^{2-}) \xrightarrow{\text{fast}} 2SO_4^{2-} + A + H^+ \quad (7)$$

Scheme 3:

$$H_2A + S_2O_8^{2-} \xrightarrow{k_1} H_2A^{\dot{+}} + SO_4^{\dot{-}} + SO_4^{2-} \quad (8)$$

$$H_2A + SO_4^{\dot{-}} \longrightarrow H_2A^{\dot{+}} + SO_4^{2-} \quad (9)$$

$$S_2O_8^{2-} + H_2A^{\dot{+}} \longrightarrow SO_4^{\dot{-}} + SO_4^{2-} + A + 2H^+ \quad (10)$$

TABLE 2. THE OBSERVED SECOND-ORDER RATE CONSTANTS, k_0, OF Eq. 1[a)]

Ionic strength (I) M	Temp °C	pH	$10^2 k_0$ $M^{-1} s^{-1}$
1.07	15	3.72	7.59
		3.73	7.72
		3.93	9.90
		4.12	12.4
		4.21	13.3
		4.39	14.8
1.07	20	3.49	7.69
		3.67	10.9
		3.91	13.7
		4.11	17.1
		4.39	20.6
1.07	25	3.45	10.7
		3.69	15.5
		3.88	19.8
		4.08	23.6
		4.13	24.7
1.07	30	3.43	14.8
		3.44	15.1
		3.67	20.9
		3.87	27.2 27.3
		4.07	33.0
		4.08	33.5
0.47	25	3.50	5.88
		3.71	8.50
		3.90	10.8
		4.40	17.4
0.20	25	3.58	3.68
		3.80	5.48
		4.00	7.07
		4.01[b)]	6.68[b)]
		4.22[b)]	8.55[b)]
		4.47	11.1
		4.51[b)]	10.5[b)]
0.071	25	3.70	2.47
		3.88	3.68
		3.90[d),c)]	3.56[d)] 4.50[c)]
		4.10	4.76
		4.15[c)]	5.95[c)]
		4.31[c)]	6.88[c)]
		4.40[c)]	7.37[c)]
		4.60	7.14

a) The initial concentrations are 2.0×10^{-3} M for potassium peroxodisulfate and L-ascorbic acid, 5×10^{-3} M in disodium dihydrogen ethylenediaminetetraacetate (EDTA), 0.05 M in sodium acetate, and the given concentrations of acetic acid and sodium perchlorate. b) In the presence of 1% acrylonitrile; the other conditions are the same as those in a). c) In the absence of EDTA; the other conditions are the same as those in a). d) In the presence of 1×10^{-6} M in copper(II) sulfate; the other conditions are the same as those in a).

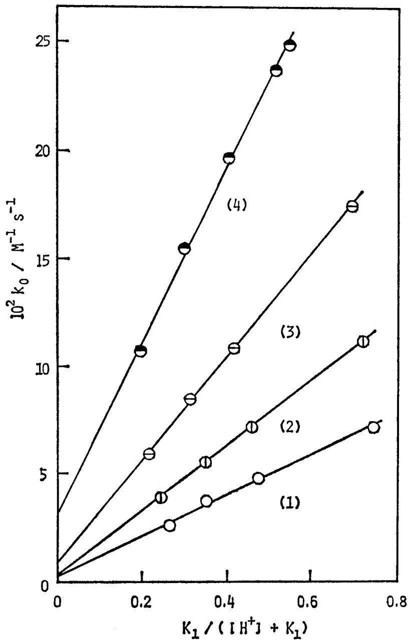


Fig. 2. Examples of plots of K_0 vs. $K_1/([H^+]+K_1)$ (Eq. 2).

Ionic strengths are 0.071, 0.20, 0.47, and 1.07 M for lines (1), (2), (3), and (4), respectively. Other conditions are the same as those of a) in Table 2 at 25 °C.

TABLE 3. THE SECOND-ORDER RATE CONSTANTS, k_1 AND k_2 IN Eq. 2, AND THE KINETIC PARAMETERS FOR EACH REACTION PATH[a)]

Temp °C	Ionic strength(I) M	$10^2 k_1$ $M^{-1} s^{-1}$	$10 k_2$ $M^{-1} s^{-1}$
15	1.07	2.2±0.4	2.3±0.1
20	1.07	2.8±0.6	3.1±0.2
25	1.07	3.2±0.7	4.3±0.2
30	1.07	3.3±0.4	6.0±0.1
25	0.07_1	0.2±0.3	1.0±0.1
25	0.20	0.0±0.1	1.57±0.04
25	0.47	0.9±0.3	2.5±0.08

$\Delta H_1^{\ast} = 17\pm5$ kJ mol^{-1} $\quad \Delta S_1^{\ast} = -220\pm20$ J deg^{-1} mol^{-1}

$\Delta H_2^{\ast} = 45\pm1$ kJ mol^{-1} $\quad \Delta S_2^{\ast} = -102\pm4$ J deg^{-1} mol^{-1}

a) The conditions are the same as those of a) in Table 2.

$$H_2A^{\dot{+}} + SO_4^{\dot{-}} \xrightarrow{\text{fast}} SO_4^{2-} + A + 2H^+ \quad (11)$$

$$HA^- + S_2O_8^{2-} \xrightarrow{k_2} HA\cdot + SO_4^{\dot{-}} + SO_4^{2-} \quad (12)$$

$$HA^- + SO_4^{\dot{-}} \longrightarrow HA\cdot + SO_4^{2-} \quad (13)$$

$$S_2O_8^{2-} + HA\cdot \longrightarrow SO_4^{\dot{-}} + SO_4^{2-} + A + H^+ \quad (14)$$

$$HA\cdot + SO_4^{\dot{-}} \xrightarrow{\text{fast}} SO_4^{2-} + A + H^+, \quad (15)$$

where A represents dehydroascorbic acid; dehydroascorbic acid is known as the final product in the oxidation of L-ascorbic acid by many oxidizing agents;[12)] the presence of free radicals of $H_2A^{\dot{+}}$ and HA· in the oxidation of L-ascorbic acid has been confirmed by ESR measurements and kinetic investigations by many researchers.[12)] Every one of the above three schemes is consistent with the empirical rate law of Eqs. 1 and 2. For the purpose of examining whether or not the reaction occurs *via* a successive one-electron transfer involving the free radicals, as in schemes 2 and 3, the acrylonitrile of a radical scavenger was added to the reaction solution at the initiation of the reaction. The results are given in Table 2 and Fig. 3; the polyacrylonitriles were not found in the reacting solution, and the reaction rate appeared to be a little slower than that in the absence of acrylonitrile. In most of the previous works on peroxodisulfate reactions,[5-8] the acrylonitrile was a strong retarder of the reaction rate, forming polyacrylonitrile as a white sediment. Thus, the acrylonitrile effect obtained in this work was extraordinarily different from most cases of peroxodisulfate reactions; this may indicate, at least apparently, a two-electron transfer reaction without forming radicals, *i.e.*, Scheme 1. Scheme 2 will be not very sensitive to the presence of a radical scavenger, while Scheme 3 is probably very sensitive to such a scavenger for radicals.

Temperature Dependence. The activation parameters corresponding to the specific rate constants are shown in Table 3. The values of both ΔH^{*}_{1} and ΔS^{*}_{1} are smaller than those of ΔH^{*}_{2} and ΔS^{*}_{2}. Although the k_1 values were much smaller than the k_2 values over the temperature range of 15—30 °C, the k_1 should become larger than the k_2 at temperatures lower than −36 °C, which is obtained as the isokinetic temperature by using the kinetic parameters. In most of the oxidation reactions of L-ascorbic acid, the values of k_1 are much smaller than those of k_2. For example, the k_2/k_1 ratio at 25 °C (with the oxidizing agent in parentheses) is 13 (peroxodisulfate) at $I=1.07$ M in this work, 34 (tris(oxalato)cobaltate(III)),[11] 3.7×10^3 (tris(1,10-phenanthroline)iron(III),[11] 6×10^2 (thioureapentacyanoferrate(III)),[13] and 1.3×10^3 (hexacyanoferrate(III)).[14] The trend toward less negative ΔS^{*} values on going from H_2A to HA^- is similar to that ($\Delta S^{*}_{1}=-192$ J deg^{-1} mol^{-1}; $\Delta S^{*}_{2}=-134$ J deg^{-1} mol^{-1}) found in the reaction of L-ascorbic acid with thioureapentacyanoferrate(III).[13] The larger ΔH^{*}_{2} values than ΔH^{*}_{1} indicate the stronger hydration for HA^- than that for H_2A.

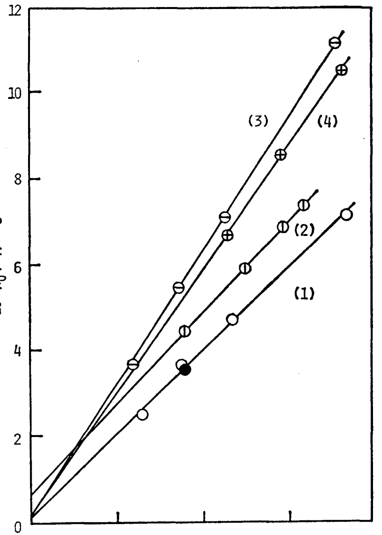


Fig. 3. Effects of acrylonitrile, EDTA, and copper(II) ion (as an impurity) on the rate constant k_0 in Eq.1 at an ionic strength 0.07 M and at 25 °C.
Line (1) indicates the results in the presence of 5×10^{-3} M in disodium dihydrogen ehthenediaminetetraacetate (EDTA); line (2) indicates the results in the absence of EDTA under the other conditions same as those in line (1); line (3) indicates the results at an ionic strength 0.2 M under the other conditions same as those in line (1); line (4) indicates the results in the presence of 1% acrylonitrile under the other conditions same as those in line (3); a plot ● in line (1) indicates a result in the presence of 1×10^{-6} M in copper(II) sulfate under the conditions same as those in line (1).

Ionic Strength Dependence. Although the ionic-strength values employed in this work lie outside the Debye-Hückel region, plots of $\log k_2$ *vs.* $I^{1/2}/(1+I^{1/2})$ showed a straight line, with a relationship of $\log k_2 = -(1.47\pm0.02)+(2.17\pm0.04)I^{1/2}/(1+I^{1/2})$. This dependence is as expected for the reaction between two ions of a like sign; the positive value of 2.17 is in good agreement with that of 2.04 which is obtained from the theoretical term of $1.02Z_aZ_b\times I^{1/2}/(1+I^{1/2})$ with $Z_a=-1$ for HA^- and $Z_b=-2$ for $S_2O_8{}^{2-}$.

Effect of the Copper(II) Ion. When the reaction solution did not contain EDTA, the k_0 values increased to some extent (see line(2) in Fig. 3). However, such an increase in k_0 was depressed by the presence of EDTA (see line(1) in Fig. 3) and thus, was thought to be due to the copper(II) ion present as an impurity in the reaction solution; most of the copper(II)-ion impurity may come from the acetate-buffer solutions used. Moreover, it was found that the rate of reaction between L-ascorbic acid and peroxodisulfate was greatly accelerated by the presence of trace amounts of the copper(II) ion, and that the copper(II)-catalyzed reaction rate was: (1) indifferent to the presence or absence of oxygen, (2) retarded completely by the

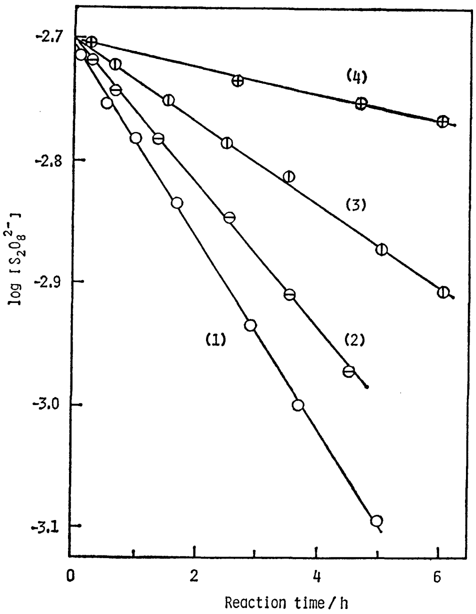


Fig. 4. Examples of plots of log [$S_2O_8{}^{2-}$] *vs.* t (Eq. 16). Initial concentrations of L-ascorbic acid are 0.03, 0.02, 0.01, and 0.002 M for lines (1), (2), (3), and (4), respectively. The catalyser's concentration is 2×10^{-6} M in copper(II) sulfate. Other conditions are the same as those of a) in Table 5.

presence of EDTA, and (3) not retarded by the presence of acrylonitrile; nevertheless, polyacrylonitrile in the forms of a white sediment was obviously found in the reacting solution. These effects are shown in Table 4. When pseudo first-order conditions were satisfied, the plots of log $[S_2O_8^{2-}]$ *vs.* t were rectiliniear up to at least the half-time ($t_{1/2}$) of reaction. Some examples are given in Fig. 4. The rate constants, $k_{cat.}$, in Eq. 16 were obtained under various conditions. The results are given in Table 5. Plots of both $k_{cat.}$ *vs.* $[Cu(II)]_i$ and $k_{cat.}$ *vs.* $[AA]_i$ showed straight lines with intercepts. Some examples of plots of $k_{cat.}$ *vs.* $[Cu(II)]_i$ are given in Fig. 5. These relationships can be described by Eqs. 16 and 17:

$$-d[S_2O_8^{2-}]/dt = k_{cat.}[S_2O_8^{2-}] \qquad (16)$$

$$k_{cat.} = k_a[Cu(II)]_i + (k_b + k_c[Cu(II)]_i)[AA]_i$$
$$= k_b[AA]_i + (k_a + k_c[AA]_i)[Cu(II)]_i, \qquad (17)$$

where $[\ \ ]_i$ indicates the concentration at the initial stage of reaction. The values of k_a ($M^{-1}\,s^{-1}$), k_b ($M^{-1}\,s^{-1}$), and k_c ($M^{-2}\,s^{-1}$) were determined at 25 °C to be: $k_a=2.0$, $k_b=5.5\times10^{-4}$, $k_c=5.6\times10^2$ at pH 2.1, and $k_a=1.5\times10^2$, $k_b=5.0\times10^{-2}$, $k_c=7.1\times10^5$ at

TABLE 4. EFFECTS OF OXYGEN, ACRYLONITRILE (AN), AND EDTA ON THE RATE OF THE COPPER(II)-CATALYZED REACTION

t/min	$10^3[S_2O_8^{2-}]_{disapp.}$/M					
			Air-sat.[c]	N_2-sat.[c]	0.5% AN[d]	1% AN[d]
5	—	—	0.30	0.29	0.52	0.66
10	0.10[a]	—	—	0.56	1.01	0.92
15	0.15[a]	0.16[b]	0.84	0.83	1.28	1.07
20	0.20[a]	—	1.03	1.03	1.44	1.17
25	—	—	1.18	1.19	1.53	1.26
30	0.28[a]	0.24[b]	1.34	1.34	1.61	1.33
60	0.55[a]	0.42[b]	—	—	—	—
90	0.75[a]	0.60[b]	—	—	—	—
120	—	0.70[b]	—	—	—	—

a) The conditions are: 2.0×10^{-3} M for potassium peroxodisulfate and L-ascorbic acid; an ionic strength of 0.07 M; pH 3.9 (acetate buffer); 25 °C, and in solutions containing dissolved air. b) In the presence of 1×10^{-6} M in copper(II) sulfate and of 5×10^{-3} M in disodium dihydrogen ethylenediaminetetraacetate (EDTA); the other conditions are the same as those in a). c) In the presence of 1×10^{-6} M in copper(II) sulfate; air or nitrogen gas was bubbled through the reacting solution; the other conditions are the same as those in a). d) In the presence of 1×10^{-6} M in copper(II) sulfate, 0.5 or 1% acrylonitrile (AN); the other conditions are the same as those in a). The white sediments of polyacrylonitrile were found in the reacting solution; thus, the concentrations of peroxodisulfate were determined after the removal of the sediments.

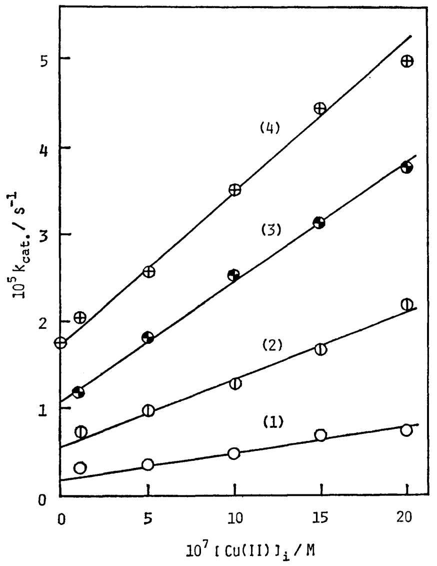


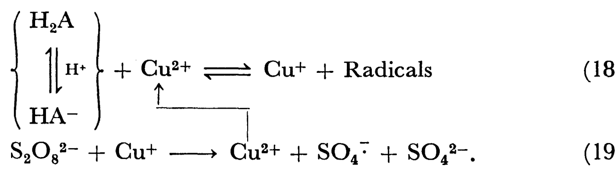
Fig. 5. Examples of plots of $k_{cat.}$ *vs.* $[Cu(I)]_i$ (Eq. 17).
All lines——indicate the calculated ones by using the rate constants k_a, k_b, and k_c obtained from the data at 0.01 M perchloric acid (pH 2.1) in Table 5. Initial concentrations of L-ascorbic acid are 0.002, 0.01, 0.02, and 0.03 M for lines (1), (2), (3), and (4), respectively.

TABLE 5. RATE CONSTANTS, $k_{cat.}$, IN Eq. 16 AT VARYING CONCENTRATIONS OF L-ASCORBIC ACID AND COPPER(II)[a]

$10^7[Cu(II)]_i$/M	$10^5 k_{cat.}/s^{-1}$ $10^3[AA]_i$/M								
	1	2		3	4	10	20		30
0	7[b]	—	10[b]	14[b]	24[b]	—	—		1.67[b]
1	18[b]	0.30	31[b]	40[b]	62[b]	0.71	1.14		2.06
5	50[b]	0.37	98[b]	130[b]	169[b]	0.95	1.77		2.55
8	77[b]	—	147[b]	180[b]	241[b]	—	—		—
10	91[b]	0.47	180[b]	255[b]	444[b]	1.25	2.54		3.47
15	—	0.66	—	—	—	1.63	3.15	3.13[c]	4.44
20	—	0.73	—	—	—	2.17	3.75		4.95

a) The conditions are $[S_2O_8^{2-}]_i=2.0\times10^{-3}$ M, $[HClO_4]=0.01$ M (pH 2.1), and in solutions containing dissolved air at 25 °C (in the dark). b) The conditions are the same as those in a), but the pH value in 4.31 in the 0.05 M sodium acetate—0.1 M acetic acid solution, with no perchloric acid ($HClO_4$) added. The values of $k_{cat.}$ in this case were evaluated by using the initial slope of the plots of $[S_2O_8^{2-}]$ *vs.* t with a relationship of $-\Delta[S_2O_8^{2-}]_i/\Delta t=k_{cat.}[S_2O_8^{2-}]_i$. c) The conditions are the same as those in a), but in a solution saturated with pure nitrogen gas.

pH 4.31. The k_b corresponds to the rate constant for the uncatalyzed-reaction path, while the rate constants k_a and k_c are those for the catalyzed-reaction paths. The ratios of $k_b:k_a:k_c$ were $1:3600:1\times10^6$ at pH 2.1 and $1:3000:1.4\times10^7$ at pH 4.31. These values indicate that the copper(II) ion is very strong catalyst for the reaction between L-ascorbic acid and peroxodisulfate. It is obvious that the copper(II)-catalyzed reaction is complosed of a chain reaction of the redox cycle of Cu(I) and Cu(II), and that the origin of the reaction mechanism can be written as follows:



$$\left\{\begin{matrix} H_2A \\ \Big\downarrow\!\!\uparrow H^+ \\ HA^- \end{matrix}\right\} + Cu^{2+} \rightleftharpoons Cu^+ + \text{Radicals} \quad (18)$$

$$S_2O_8^{2-} + Cu^+ \longrightarrow Cu^{2+} + SO_4^{\cdot -} + SO_4^{2-}. \quad (19)$$

The rate constant for Reaction 19 has been reported as $1.4\times10^3\ M^{-1}\ s^{-1}$ in 1 M potassium chloride at 25 °C,[15] about 100-fold that for Reaction 20:

$$O_2 + Cu^+ \longrightarrow Cu^{2+} + O_2^-. \quad (20)$$

Recently, Ito *et al.*[16] reported that the rate of Reaction 18 was 5×10^5-fold faster than that of Reaction 20. Therefore, it can be said that Reaction 20 hardly ever occurs in a catalyzed reaction, even in an air-saturated solution. This is consistent with the fact that the catalyzed-reaction rate is utterly indifferent to the presence or absence of oxygen (see Table 4). The strong inhibition effect of EDTA on the catalyzed reaction is attributable to the retardation of Reaction 18 by the complex formation of EDTA with the copper (II) ion. Separate, preliminary experiments showed that Reaction 18 was retarded by either nitrilotriacetate (NTA) or oxalate as well as by EDTA. The acrylonitrile effect may be accounted for by the following reactions:

$$X + Cu^{2+} \rightleftharpoons Cu^+ + X^{\cdot +} \quad (18)$$

$$S_2O_8^{2-} + Cu^+ \longrightarrow Cu^{2+} + SO_4^{\cdot -} + SO_4^{2-} \quad (19)$$

$$Cu^+ + SO_4^{\cdot -} \longrightarrow Cu^{2+} + SO_4^{2-} \quad (21)$$

$$Cu^{2+} + X^{\cdot +} \longrightarrow Cu^+ + \text{Products} \quad (22)$$

$$X^{\cdot +} + SO_4^{\cdot -} \longrightarrow SO_4^{2-} + \text{Products}, \quad (23)$$

where $X=H_2A+HA^-$ and Products$=A+H^+$. The backward reaction of (18) and Reaction 19 are competing with Reactions 20 and 21. Thus, when the acrylonitrile scavenged the radicals of $SO_4^{\cdot -}$ and/or $X^{\cdot +}$, the rate of the forward reactions of (18) and (19) might be accelerated. Actually, polyacrylonitrile was found in the reacting solutions upon the addition of acrylonitrile of the monomer, indicating the removal of the radicals, and the copper(II)-catalyzed reaction was a little accelerated by the presence of acrylonitrile (see Table 4). On the other hand, no clearly rational explanations could be made for the fact that the rate in the presence of 1% acrylonitrile is slightly slower than that in the 0.5% acrylonitrile; the propagating radical of an acrylonitrilepolymer may react with the copper(I) ion, competing with Reaction 19 or other competing reactions may occur.

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