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Polarographic Study of Catalytic Reduction of Tris(2,2′-bipyridine)-copper(II) in the Presence of Nitrite Ion

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The rigorously derived equation for a catalytic current was applied to the evaluation of the rate constant for the oxidation reaction of bis(2,2′-bipyridine)copper(I) by nitrite ion by use of a computer and subroutine program for the curve-fitting method. This method made it possible to calculate the rate constant from low limiting current in the presence of nitrite ion. The rate in acetate buffer solutions has first-order dependence on each reactant and hydrogen ion, and the apparent rate constant is 1×10^6 $\mathrm{M^{-2}\,s^{-1}}$ at 25 °C.

A polarographic catalytic process can be schematically represented by

$$\begin{tikzcd} \mathrm{O} + \mathrm{ne} \arrow[r] & \mathrm{R} & (1) \\ \mathrm{R} + \mathrm{Z} \arrow[r] & \mathrm{O} \arrow[ul] & (2) \end{tikzcd}$$

This refers to a post-electron transfer chemical reaction (2) which regenerates the original electrochemical species O. The reaction must be pseudo-unimolecular with respect to species R, when the oxidizing agent Z is present at a high and constant concentration at the electode surface. The theoretical equations describing a catalytic current have been developed by several workers[1–4] and derived on the assumption that a steady state at the dropping mercury surface set up by the combination of diffusion and chemical reaction, *i.e.*, a linear diffusion approximation concerning the concentration gradient at the electrode surface has been made. These equations should be used to evaluate a rate constant for a fast chemical reaction, such as the oxidation of titanium(III) by chlorate ion.[5] However, there are many slow reactions which cause a smaller catalytic current, such as the oxidation of titanium(III) by hydroxylamine,[6] and vanadium(II) by chlorate ion[7] and by vanadium(IV).[8]

Koutecky[9,10] has treated the diffusion problem using a more rigorous expanding sphere approximation and proposed a theoretical expression for the catalytic current. Since this equation is complicated and its application is very tedious to evaluate a rate constant, the graphical treatment of the equation has been carried out for some systems.[1,9] However, the curve-fitting method developed recently by use of a computer has been available for solving the equation, and, in the present work, this method was employed for determining the rate constant for the oxidation reaction of copper(I) by nitrite ion.

Experimental

Materials. Copper(II) stock solution was prepared by dissolving recrystallized $\mathrm{CuSO_4 \cdot 2H_2O}$ into the redistilled water and its concentration was determined by measuring the second diffusion current in ammonia-ammonium chloride solutions compared with that of standard copper(II) solution which was made from high purity copper metal(99.999%). The weighed amount of reagent grade 2,2′-bipyridine was dissolved into an acetic acid solution and then the buffer solution was made by adding sodium acetate, which was also used as a supporting electrolyte. Sodium nitrite solution was prepared by dissolving an appropriate amount of reagent grade chemicals in the water.

Apparatus and Procedure. A Yanagimoto polarograph Model P-8 was used to record the polarograms. Catalytic current appeared when sodium nitrite solution was injected into acetate buffered solution containing 2,2′-bipyridine with a micropipet. Ionic strength was kept 0.2 M throughout the present work. All the pH values were measured by a Toa Dempa pH meter Model HM-5A.

Results and Discussion

Evaluation of Rate Constant. Koutecký and Cizek[10] have proposed the theoretical equation for the catalytic current

$$\frac{i}{i_\mathrm{d}} = \Psi(\chi) + \xi[\Theta(\chi) - 0.78680\Psi(\chi)] = \Psi(\chi) - \xi\Phi(\chi) \quad (3)$$

and

$$\Psi(\chi) = \mathrm{e}^{-\chi}\sum_{i=0}^{\infty} a_i \chi^i \quad (4)$$

$$\Theta(\chi) = \mathrm{e}^{-\chi}\sum_{i=0}^{\infty} a_i r_i \chi^i \quad (5)$$

$$\xi = \sqrt{\frac{12D}{7r_1^2}}\, t^{1/6} \quad (6)$$

where i and i_d are the experimentally observed instantaneous currents for the reduction of species O in the presence and in the absence of Z, respectively. The parameter, ξ, corresponds to the function involving the diffusion coefficient, D, drop time, t, and mercury drop radius, r_1, at $t=1$ s, and in the present work the value of ξ was found to be 0.187. The parameter, a_i, is a complicated gamma function, whose values for $i=0$ to 15 are tabulated in the literature,[10] and the values of $\Phi(\chi)$ corresponding χ are also listed. The parameter, χ, in above equation is related to the apparent second-order rate constant, k_app, with respect to each reactant.

$$\chi = k_\mathrm{app} C_z t \quad (7)$$

where C_z denotes the concentration of oxidizing agent, Z, nitrite ion in the present work. The rate constant can be evaluated from this equation if the consumed amount of Z by the chemical reaction is negligibly small, and if an appreciable change of the concentration of Z takes place, another theoretical equation derived on the basis of the stoichiometric consideration[11] must be applied to obtain the rate constant.

The evaluation of χ from the observed value of i/i_d

was made as follow: equation (3) was simplified by the first assumption that the term $\xi\Phi(\chi)$ could be neglected. This is verified by our experimental results as mentioned below. In the course of the calculation an approximate value of χ, which is given in Koutecký's Table,[9)] is necessary to solve the function $\Phi(\chi)$ by use of a subroutine programs for the curve-fitting method. Thus, a more accurate value of χ can be obtained and used to evaluate the term $\Phi(\chi)$ by using the value in the table on the assumption that a linearity of $\Phi(\chi)$ with χ holds in the narrow range. Using this trial $\Phi(\chi)$ and the observed value of ξ, the value of χ is recalculated by use of Eq. (3) until the consistent value can be obtained. In the present work, one or two cycles were sufficient to define the value of χ within experimental error. This method is very convenient to evaluate the rate constant from the low value of i/i_d.

Kinetic Results. The typical polarograms are shown in Fig. 1. The two reduction waves with a polarographic maximum in the absence of nitrite ion appeared and it is concluded from their half-wave potentials that the first wave corresponds to the one-electron reduction of $Cu(bipy)_3^{2+}$ to $Cu(bipy)_2^{1+}$ and the second wave to that of $Cu(bipy)_2^{1+}$ to copper metal. The polarographic behavior of these species has been studied systematically by Onstott and Laitinen.[12)] The first wave was increased by adding nitrite ion, indicating the catalytic current. When nitrite ion was in sufficiently high concentration compared with that of copper(II) ion, the first wave became larger than the second one, showing that the catalytic nature is specific to the first wave. The maximum at rising portion of the second wave increased with increasing concentration of copper(II) ion. The maximum suppressor was not used in this experiment, because the substance adsorbed on the mercury electrode would disturb the reaction layer at the electrode surface and make the experimental data inaccurate. However, the presence of this maximum and the large catalytic wave caused a narrow plateau of the first wave and made it difficult to measure the limiting current. Thus, it is necessary in the present system to evaluate the rate constant from the comparably small limiting current, *i.e.*, the low value of i/i_d.

Values of the catalytic current obtained at various concentrations of nitrite ion are presented in Table 1.

Table 1. Apparent rate constants of the oxidation of copper(I) by nitrite ion in acetate buffer solution of 1.94×10^{-4} M Cu(II)+ 1×10^{-2} M bipy, at 25 °C

pH	$[NO_2^-]$ mM	$-E$ V *vs.* SCE	i μA	i/i_d	k_{app} $M^{-1}s^{-1}$
4.1	—	0.160	0.510	—	—
	21.8	0.150	2.070	4.059	(141)[a)]
4.8	21.8	0.175	0.984	1.853	23.9
	43.7	0.170	1.440	2.812	30.2
	84.9	0.175	2.046	3.853	(31.3)[a)]
5.0	21.8	0.187	0.760	1.407	12.8
	43.7	0.182	0.965	1.770	10.6
	84.9	0.180	1.254	2.322	10.7
5.3	21.8	0.184	0.608	1.160	3.64
	43.7	0.190	0.724	1.382	4.40
	84.9	0.190	0.852	1.626	4.15
	163.5	0.190	1.050	2.004	3.86

a) Parenthesized values of k were calculated by using the simplified equation as described in this article.

The value of secondly difined χ' is about 10% larger than that of the first one and little differences can be observed between χ' and χ'', or χ'' and χ''' for a given condition, where χ'' and χ''' are thirdly and fourthly defined values of χ. In the case of $\chi>10$, Eq. (4) diversed and a finite value of χ could not be given by the present method. This was caused by using only the sixteen values of a_i involved in the function $\Phi(\chi)$. In this case, the value of k_{app} shown in the parenthesis was calculated from the simplified equation proposed by Koutecký[9)] and corrected by employing the value of $\xi\Phi(\chi)$ in order to obtain a more accurate value. As shown in Table 1, though the half-wave potentials obtained in the presence of nitrite ion is thought to shift slightly to a more negative potential compared

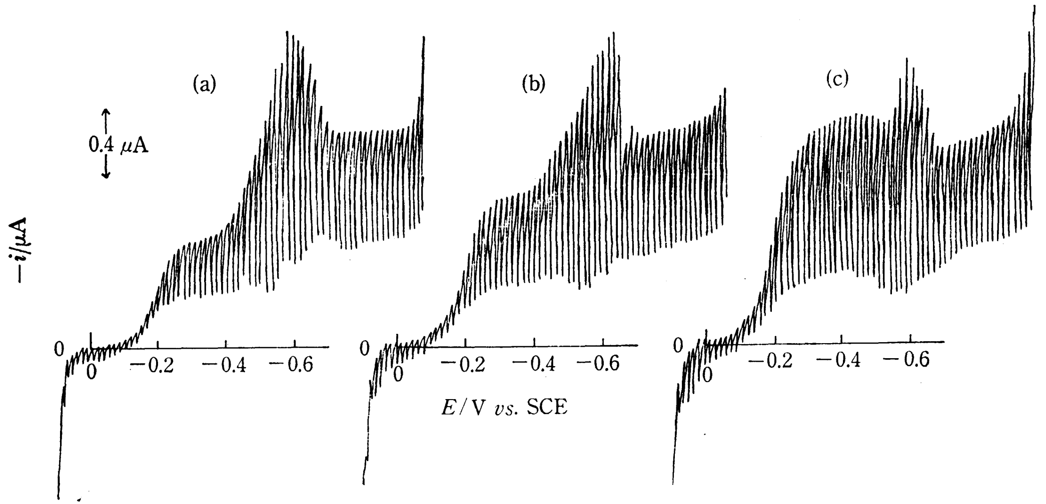

Fig. 1. Typical catalytic waves in acetate buffer solution of 1.94×10^{-4} M Cu(II)+1×10^{-2} M bipy, pH 5.3. The concentrations of nitrite ion are (a) 0, (b) 4.37×10^{-2}, (c) 1.63×10^{-1} M.

with that of the wave in the absence of oxidizing agent, no significant effect was observed.

Taking into account relative inaccuracy of the experimental data, it was concluded that almost consistent values of rate constants at the same pH value could be obtained. This supports the validity that the present method is useful to evaluate the rate constant from the small catalytic current, *i.e.*, $i/i_d<3$. The rate constants obtained under the condition of low nitrite ion concentration from 7.95 to 21.8 mM were 22.9 ± 1.6 $M^{-1}s^{-1}$ at pH 4.90. In this calculation, Eq. (3) was used provided that the change in nitrite ion concentration consumed by the chemical reaction could be practically neglected. This condition was comfirmed by the presence of at least twenty times larger amount of nitrite ion than that of copper(II), though the consistent value could not be obtained in the presence of 3.99 mM nitrite ion. The rate constants are much smaller than those of the oxidation reaction of bis(2,2′-bipyridine)copper(I) by oxygen and hydrogen peroxide.[13)]

Effects of Drop-time and Bipyridine. The effect of the corrected height of mercury reservoir, h_{corr}, or the effect of drop time, on the limiting currents is seen in Fig. 2. Since the limiting current in the absence of nitrite ion is linearly proportional to the square root of h_{corr}, it is diffusion-controlled. On the other hand, the limiting current in the presence of 0.163 M nitrite ion was independent of h_{corr}, indicating the dominant contribution of catalytic nature to total current. The apparent rate constant was found to be 4.06 ± 0.19 $M^{-1}s^{-1}$ at pH 5.28. Though the wave is essentially of catalytic nature, the small variation of the limiting currents observed in the presence of 0.0849 M nitrite ion is likely to result from the adsorption of depolarizer or bipyridine on mercury electrode.

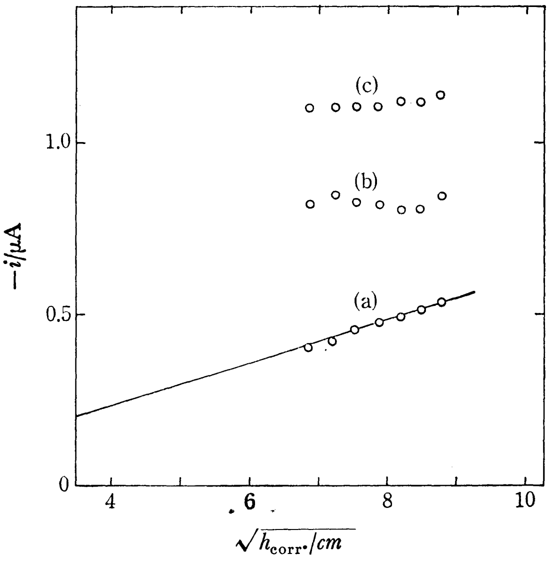

Fig. 2. Dependence of limiting currents on the corrected height of mercury reservoir in the acetate buffer solution of 1.94×10^{-4} M Cu(II) $+1\times10^{-2}$ M bipy, pH 5.3. The concentrations of nitrite ion are (a) 0, (b) 8.49×10^{-2}, (c) 1.65×10^{-1} M.

The effect of 2,2′-bipyridine concentration on the rate constans is shown in Table 2. This shows that the value of rate constant increased somewhat with increasing bipyridine concentration and approached the consistent value obtained at 1×10^{-2} M bipyridine. Since the wave in 1.28×10^{-3} M bipyridine was poorly defined and the limiting current became inaccurate, it was not clear from the present data that bipyridine participated in the chemical reaction. Futhermore, the considerably low rate constant could not be explained. However, the shift of the half-wave potentials in the absence of nitrite ion corresponded to the dissociation of one bipyridine molecule in the electrode reaction, which could be substantiated by the reported value of the half-wave potential for the system of copper(II) and bipyridine.[12)]

TABLE 2. APPARENT RATE CONSTANTS AT VARIOUS CONCENTRATIONS OF 2,2′-BIPYRIDINE IN ACETATE BUFFER SOLUTION OF 1.94×10^{-4} M Cu(II) AT pH 5.2

bipy mM	$[NO_2^-]$ mM	$-E_{1/2}$ V *vs.* SCE	i μA	i/i_d	k_{app} $M^{-1}s^{-1}$
1.28	—	0.142	0.486	—	—
	21.8	0.144	0.550	1.132	2.93
	43.7	0.145	0.640	1.317	3.69
2.18	—	0.166	0.490	—	—
	21.8	0.160	0.596	1.216	4.91
	43.7	0.160	0.670	1.367	4.35
	84.9	0.156	0.846	1.727	4.89
5.13	—	0.175	0.490	—	—
	21.8	0.165	0.600	1.224	5.21
	43.7	0.170	0.722	1.473	5.78
	84.9	0.174	0.910	1.857	5.97
	163.5	0.172	1.142	2.331	5.47

Catalytic Reaction Mechanism. In view of the above results the electrode reaction scheme can be written as

$$\begin{tikzcd} \mathrm{Cu(bipy)_3^{2+}} \arrow[r, "+1e", "-bipy"'] & \mathrm{Cu(bipy)_2^{1+}} \arrow[r, "+1e", "-2bipy"'] \arrow[l, bend left=60, "+NO_2^-"] & \mathrm{Cu(0)} \end{tikzcd} \qquad (8)$$

This shows that the catalytic current due to nitrite ion is concerned only with the first wave and is quite indifferent to the second wave which corresponds to the reduction current of copper(I) to amalgamated copper metal. The value of rate constant decreased about 15% with a two-hold increase of copper(II) concentration. Further reaction between copper(I) and products of nitrite ion must be considered, and if the reaction product is bis(2,2′-bipyridine)copper(II), this species would undergo the electroreduction and cause the increase of catalytic current. Though the oxidation product of copper(I) is not clear from the present data, the rate law for the chemical reaction can be represented as

$$-\frac{d[\mathrm{Cu(bipy)_2^{1+}}]}{dt} = k_{app}[\mathrm{Cu(bipy)_2^{1+}}][\mathrm{NO_2^-}]. \qquad (9)$$

Neverthless, it is not necessary that the rate corresponds to the increment of tris(2,2′-bipyridine)copper(II). A plot of $\log k_{app}$ against $\log [H^+]$ was approximately linear and yields a best straight line of slope 1.19 ± 0.04, from which it can be deduced that the rate has also first-order dependence with respect to hydrogen ion, *i.e.*, $k_{app}=k'_{app}[H^+]$, and the value of k'_{app} is *ca.* $1\times10^6\ M^{-2}\,s^{-1}$ at 25 °C. This suggests that the equilibrium between nitrite ion and nitrous acid exists and nitrous acid should participate in the chemical oxidation. Nitrous acid is, in general, a more powerful oxidizing agent than nitrite ion.[14] Though the reaction is thought to be non-complementary, there is insufficient information about the reaction stoichiometry and the possibility that nitrite ion acts as a two-equivalent oxidizing agent to copper(I).

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