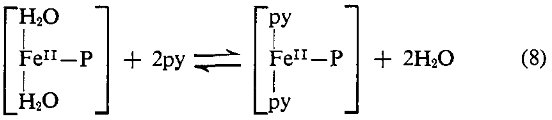
It is to be noted by comparing eq 3 and 6 that the product resulting from the reduction of the hydroxoaquo complex depends on the solution composition, *i.e.*, the reduction product in pyridine solution, is the pyridine hemochrome whereas, in the absence of pyridine, the *trans*-diaquoprotoporphyrinferrate(II) ion is formed. Cyclic voltammetry indicates that the ligand-exchange reaction

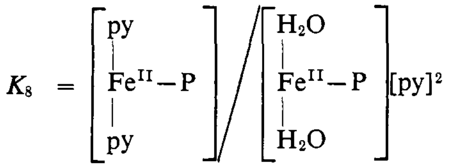


$$\begin{bmatrix} \mathrm{H_2O} \\ | \\ \mathrm{Fe^{II}-P} \\ | \\ \mathrm{H_2O} \end{bmatrix} + 2\mathrm{py} \rightleftharpoons \begin{bmatrix} \mathrm{py} \\ | \\ \mathrm{Fe^{II}-P} \\ | \\ \mathrm{py} \end{bmatrix} + 2\mathrm{H_2O} \qquad (8)$$

is very fast. Under these circumstances, it is possible to develop, by conventional means, a thermodynamic equation relating the change in $E_{1/2}$ due to the different electrode reactions to K_8, the equilibrium constant for reaction 8. Equation 9 defines this relationship where the $E_{1/2}$ values refer to potentials obtained for reactions 3 and 6 at the same pH.

$$(E_{1/2})_6 - (E_{1/2})_3 = 0.0591 \log K_8 \qquad (9)$$

where



$$K_8 = \begin{bmatrix} \mathrm{py} \\ | \\ \mathrm{Fe^{II}-P} \\ | \\ \mathrm{py} \end{bmatrix} \Bigg/ \begin{bmatrix} \mathrm{H_2O} \\ | \\ \mathrm{Fe^{II}-P} \\ | \\ \mathrm{H_2O} \end{bmatrix} [\mathrm{py}]^2$$

Log K_8 was evaluated as 2.87 ± 0.05 from data taken at five different pH values. A value of log $K = 5.0$ for reaction 8 in 2.5% cetyltrimethylammonium bromide aqueous solution has been reported.[3]

A study of some of the rates of displacement of one ligand by another with complexes of this type is now underway in this laboratory.

Acknowledgment. This investigation was supported by Public Health Service Grant AM-08248 from the National Institutes of Arthritis and Metabolic Diseases.

Polarographic Kinetic Currents in Mixtures of Persulfate and Copper(II) in Chloride Medium[1]

I. M. Kolthoff and R. Woods

Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, and the Chemistry Department, University of Melbourne, Parkville N.2, Victoria, Australia. Received November 4, 1965

Abstract: The polarographic reduction of mixtures of copper and persulfate in 0.1 or 1 *M* chloride medium yields two waves. The second diffusion current is the sum of the Cu(II) → Cu(0) and persulfate reductions. The first wave is interpreted as the sum of the Cu(II) → Cu(I) wave and a kinetic current due to reaction of the copper(I) formed at the electrode with persulfate. The rate constant for the reaction was determined to be 1.4×10^3 l. mole^{-1} sec^{-1} at 25°. Reduction of persulfate at the electrode at potentials corresponding to the first wave is postulated to be completely suppressed by the adsorption of copper(I) chloride complex. Cuprous thiocyanate, adsorbed in a monomolecular layer, completely suppresses persulfate reduction at the dme.

Persulfate yields a reduction wave at the dropping mercury electrode (dme) which starts at the potential of anodic dissolution of mercury. The persulfate current–potential curve exhibits certain anomalous characteristics under various conditions, this being a common feature of the electroreduction of multivalent anions.[2] Krjukova[3] found a minimum on the persulfate wave, the decrease commencing at potentials more negative than the electrocapillary maximum. The decrease is dependent on the nature and concentration of supporting electrolyte and is due to electrostatic repulsion of the persulfate ion by the negatively charged electrode surface. This repulsion can be eliminated by the adsorption of capillary active cations of the type NR_4^+.[4]

The reduction of persulfate at a positively charged electrode surface can be inhibited by the adsorption of anions, the inhibiting action increasing with increase in the adsorbability of the anion.[5,6] This inhibiting action increases greatly in the presence of surface-active cations of the type NR_4^+, resulting in minima on the current–potential curve.[4] Kolthoff and Okinaka[7] found that the formation of an insoluble film of mercurous iodide depresses the persulfate diffusion current considerably, concentrations of iodide as low as 10^{-4} *M* being effective; the film behaves like a negatively charged surface-active substance. A similar decrease was observed in the presence of mercurous bromide.

The polarographic reduction of copper(II) in chloride medium occurs in two steps, Cu(II) → Cu(I) and Cu(I) → Cu(0), producing a double wave.[8] The present

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[1] This investigation was carried out under a grant from the National Science Foundation in Minnesota and a Research Fellowship in Melbourne.

[2] A. N. Frunkin and N. Nikolaeva-Fedorovich, *Progr. Polaro.*, **1**, 223 (1962).

[3] T. A. Krjukova, *Dokl. Akad. Nauk SSSR*, **65**, 517 (1949).

[4] A. N. Frumkin, "Proceedings of the 2nd International Congress on Surface Activity, Electrical Phenomena." Butterworths, London, 1957, p 58.

[5] T. Kalish and A. Frumkin, *Zh. Fiz. Khim.*, **28**, 473 (1954).

[6] A. Frumkin, N. Nikolaeva-Fedorovich, and R. Ivanova, *Can. J. Chem.*, **37**, 253 (1959).

[7] I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **83**, 47 (1961).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers Inc., New York, N. Y., 1952, p 493.

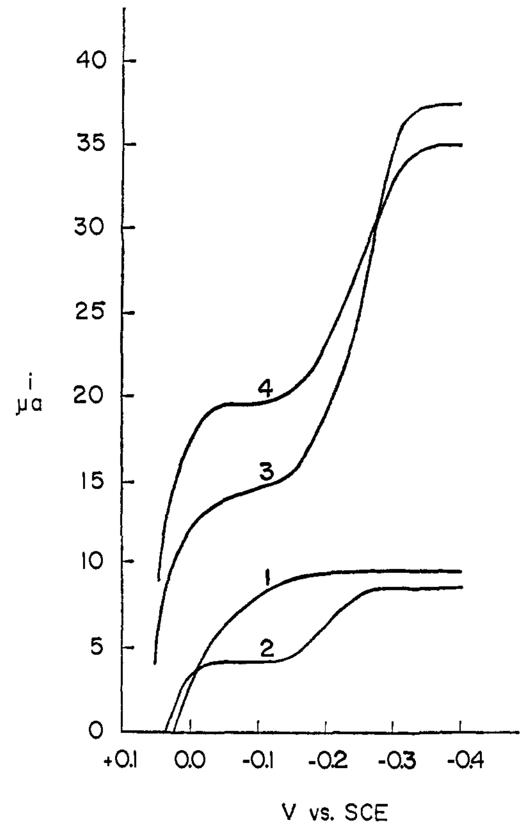

Figure 1. Polarograms in 1 *M* KCl–0.01% PAM of (1) 1 m*M* $S_2O_8^{2-}$, (2) 1 m*M* Cu(II), (3) 1 m*M* Cu(II) + 3 m*M* $S_2O_8^{2-}$, and (4) 3 m*M* Cu(II) + 1 m*M* $S_2O_8^{2-}$.

paper is concerned with the polarography of a mixture of persulfate and copper(II) in the presence of chloride. When the chloride concentration is large enough, two waves are observed, the first limiting current corresponding to the reduction of Cu(II) to Cu(I) plus reduction of a fraction of the persulfate. The total diffusion current at a more negative potential is equal to the sum of the diffusion currents of the persulfate and the Cu(II) to Cu(0) reductions. Evidence is presented that persulfate is not electroreduced on the first wave but that the exaltation of the first copper wave, denoted as i_k in this paper, is kinetic in nature and caused by a chain reaction according to the mechanism

$$\mathrm{Cu(II)} + e \longrightarrow \mathrm{Cu(I)}$$

$$\mathrm{Cu(I)} + S_2O_8^{2-} \longrightarrow \mathrm{Cu(II)} + SO_4^{2-} + SO_4\cdot^{-} \tag{1}$$

$$\mathrm{Cu(I)} + SO_4\cdot^{-} \longrightarrow \mathrm{Cu(II)} + SO_4^{2-} \tag{2}$$

$$SO_4\cdot^{-} + e \longrightarrow SO_4^{2-} \tag{2a}$$

Reaction 1 is the rate-determining step.

The polarography of a mixture of persulfate and copper(II) has also been investigated in the presence of thiocyanate instead of chloride. The polarograms in such a mixture are quite different from those in chloride.

Experimental Section

All chemicals were AR grade and used without further purification. Polyacrylamide (PAM) 75, used as a maximum suppressor, was a product of Cyanamid Australia Ltd., Melbourne.

Polarography was carried out in solutions deaerated with "oxygen-free" nitrogen and thermostated at 25 ± 0.1°. The characteristics of the dropping mercury electrode in 1 *M* potassium chloride at −0.1 v *vs.* saturated calomel electrode (sce) were m = 3.06 mg/sec, t = 2.55 sec, and h = 36.0 cm. All potentials in this paper refer to the sce.

Polarograms were recorded with a Cambridge recording polarograph. Time-average currents during the lifetime of the mercury drops are reported.

Results

1 *M* Chloride. Curve 2 in Figure 1 is a polarogram of copper(II) in 1 *M* potassium chloride; the two waves are well defined. The persulfate wave (curve 1) in the same medium is drawn out as a result of the decrease of the rate of reduction by adsorbed chloride. Examples of the appearance of the waves in solutions in which persulfate is in excess over copper(II) (curve 3) and in which copper is in excess over persulfate (curve 4) are also given in Figure 1. The exaltation of the first limiting current, i_k, is for Cu(II) → Cu(I)

$$i_k = i_{\text{exptl}} - i_d$$

Values of i_k in solutions with a constant concentration of copper(II) and varying concentrations of persulfate are reported in Table I, while Table II refers to constant persulfate and varying copper concentrations.

Table I. Effect of Persulfate Concentration[a]

$[S_2O_8^{2-}]$, m*M*	Current, μa: Assuming no interaction, −0.1 v	−0.4 v	Experimental, −0.1 v	−0.4 v	i_k, μa
0.0	4.2	8.5	4.2	8.5	...
0.125	5.25	9.7	4.75	9.6	0.55
0.25	6.3	10.95	5.25	10.9	1.05
0.50	8.35	13.4	6.5	13.1	2.3
1.00	12.5	18.3	8.5	18.1	4.3
1.50	16.65	23.2	10.0	22.5	5.8
2.00	20.8	28.3	11.75	27.5	7.55
3.00	29.1	37.9	14.5	37.2	10.3
5.00	45.7	57.5	18.7	57.2	14.5
10.00	87.2	106.5	25.7	106	21.3
20.00	170.2	204.5	36.2		32.0

[a] 1 *M* KCl, 1 m*M* Cu(II), 0.01% PAM.

Table II. Effect of Copper(II) Concentration[a]

[Cu(II)], m*M*	Current, μa: Assuming no interaction, −0.1 v	−0.4 v	Experimental, −0.1 v	−0.4 v	i_k, μa
0.0	8.3	9.8	8.3	9.8	...
0.25	9.35	11.9	4.75	12.0	(3.7)
0.50	10.4	12.75	5.0	13.0	2.9
1.00	12.5	18.3	8.5	18.0	4.3
1.50	14.6	22.55	11.85	22.2	5.55
2.00	16.7	26.8	14.5	26.4	6.1
3.00	20.9	35.3	19.5	35.0	6.9
5.00	29.3	52.3	29.2	52.0	8.2

[a] 1 *M* KCl, 1 m*M* $S_2O_8^{2-}$, 0.01% PAM.

The kinetic current, i_k, in the presence of 1 m*M* copper(II) and 20 m*M* persulfate was determined as 32.2, 32.0, and 30.4 μa at values of the height of the mercury column of 62.0, 36.0, and 22.5 cm, respectively.

Allyl acetate in a concentration of 1% has no effect on either the persulfate or copper currents in 1 *M* chloride. It does, however, reduce the height of the

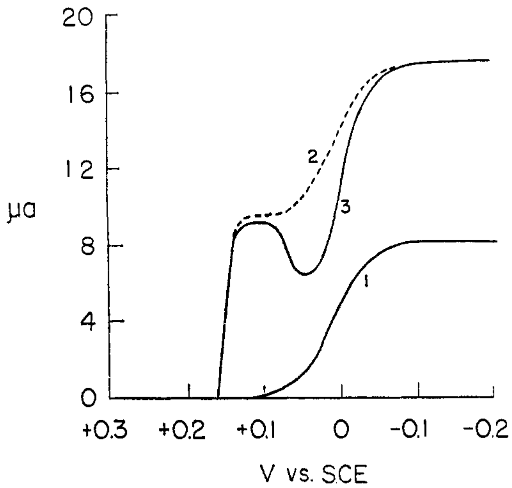

Figure 2. Polarograms in 0.1 *M* $NaClO_4$–0.01 *M* NaCl–0.01% PAM of (1) 1 m*M* Cu(II), (2) summation of individual currents of 1 m*M* Cu(II) and 1 m*M* $S_2O_8^{2-}$, and (3) experimental curve of 1 m*M* Cu(II) + 1 m*M* $S_2O_8^{2-}$.

first wave in a mixture of persulfate and copper(II), but does not effect the second wave.

Table III. Effect of Allyl Acetate (AA)[a]

$[S_2O_8^{2-}]$, m*M*	[Cu(II)], m*M*	i_k, µa	
		0% AA	1% AA
1.00	1.00	4.3	3.7
5.00	1.00	14.5	12.9
1.00	5.00	8.2	7.2

[a] 1 *M* KCl, 0.01% PAM.

The first limiting current in a mixture of 0.1 m*M* copper(II) and 0.1 m*M* persulfate is approximately 20% lower than the sum of the individual currents at −0.1 v, the limiting current at potentials greater than −0.3 v being equal to the sum of the individual diffusion currents. The current at −0.1 v is much greater than anticipated for $i_k + i_d$ (Cu(II) → Cu(I)), and therefore in this case some persulfate is reduced electrochemically at the electrode. The results given in Table II suggest that 0.5 m*M* copper(II) is necessary to suppress the 1m*M* persulfate current completely.

0.1 *M* Chloride. The general characteristics of the copper and persulfate waves in 0.1 *M* chloride medium are similar to those in 1 *M* chloride, but the separation of the copper waves is not as good as in 1 *M* chloride. Polarograms of mixtures of persulfate and copper(II) in 0.1 *M* sodium chloride and 0.9 *M* sodium perchlorate show the same characteristics as in 1 *M* chloride, the first limiting current being much less than, and the second equal to, the sum of the individual diffusion currents. The kinetic current is approximately equal to that in 1 *M* chloride at the same ionic strength (Table IV).

0.01 *M* Chloride. In the presence of 0.01 *M* chloride, copper(II) yields only one reduction wave to Cu(0) (Figure 2). However, the current at the beginning of the wave is greater than in the absence of chloride, indicating that some reduction of copper(II) to copper(I) is taking place, insufficient chloride being present to completely stabilize copper(I) to give two waves.

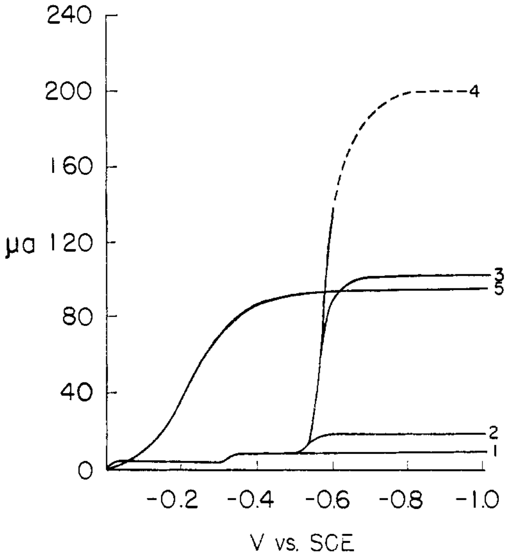

Figure 3. Polarograms in 0.1 *M* KCNS–0.01% PAM of (1) 1 m*M* Cu(II), (2) 1 m*M* Cu(II) + 1 m*M* $S_2O_8^{2-}$, (3) 1 m*M* Cu(II) + 10 m*M* $S_2O_8^{2-}$, (4) 1 m*M* Cu(II) + 20 m*M* $S_2O_8^{2-}$, and (5) 1 m*M* $S_2O_8^{2-}$ on current scale × 0.1.

The persulfate wave in the presence of 0.01 *M* chloride starts at +0.16 v and is fully developed at +0.12 v. The current potential curve of a mixture of persulfate and copper(II) shows a minimum at −0.05 v (curve 3), the decrease in persulfate current commencing at the potential where copper(II) reduction begins.

Table IV. Effect of Chloride Concentration[a]

[Cu(II)], m*M*	$[S_2O_8^{2-}]$, m*M*	i_k, µa	
		1 *M* KCl	0.1 *M* NaCl + 0.9 *M* $NaClO_4$
1.00	1.00	4.3	4.7
1.00	2.00	7.55	8.0
1.00	5.00	14.5	14.9
2.00	1.00	6.1	6.5
5.00	1.00	8.2	8.4

[a] 0.01% PAM.

0.1 *M* Thiocyanate. Copper(II) yields three waves at the dme in 0.1 *M* thiocyanate.[9] Persulfate in 0.1 *M* thiocyanate is reduced at potentials more negative than 0 v. The wave is drawn out, probably owing to adsorption of thiocyanate ions at the dme, but is fully developed at −0.4 v (curve 5, Figure 3). In a mixture of 1 m*M* copper(II) and persulfate, only the copper is reduced at potentials more positive than −0.5 v even in the presence of 20 m*M* persulfate (curve 4). The onset of the persulfate wave coincides with the beginning of the third copper wave.

Discussion

Although adsorbed chloride causes the persulfate wave to be drawn out (curve 1, Figure 1), the diffusion current is attained at −0.05 v in 1 *M* chloride, whereas in the presence of copper(II) no electroreduction of persulfate occurs at −0.1 v. This must be attributed to

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(9) I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **82**, 3528 (1960).

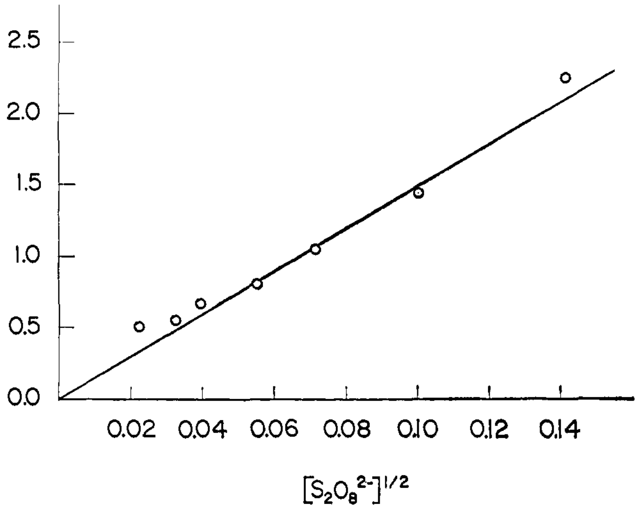

Figure 4. Plot of $i/\mu k$ against $(S_2O_8^{2-}]^{1/2}$ for kinetic currents of 1 mM Cu(II) in 1 M KCl-0.01% PAM and varying persulfate concentrations.

the effect of adsorption of a copper(I) chloride complex at the surface of the electrode.[5-7]

The three waves observed in the presence of thiocyanate[9] are due to the reduction of copper(II) to cuprous thiocyanate, cuprous thiocyanate to copper amalgam, and an adsorbed monomolecular layer of cuprous thiocyanate, respectively. The current potential curves of mixtures of persulfate and copper(II) in 0.1 M thiocyanate medium clearly demonstrate that even a monomolecular layer of cuprous thiocyanate adsorbed on the electrode completely suppresses the reduction of persulfate at the dme. No persulfate is reduced at the electrode in the presence of copper(II) in 0.1 M thiocyanate until the onset of the third copper wave, that is, until less than a monomolecular layer of cuprous thiocyanate is present at the electrode surface. This is the case even when the persulfate concentration is 20 times that of copper(II) (curve 4, Figure 3).

The effect of 0.01 M chloride on the persulfate wave in the presence of copper demonstrates the inhibiting effect of cuprous chloride on the persulfate wave. The persulfate wave is completely developed before any copper(II) is reduced at the electrode. However, the persulfate current is substantially reduced at potentials corresponding to the onset of the copper wave, where some copper(I) is produced, the current potential curve displaying a minimum. No minimum occurs at this potential in perchlorate medium in the absence of chloride, that is, when no copper(I) is produced at the electrode.

In 1 M chloride, where the Cu(II) → Cu(I) and Cu(I) → Cu(0) waves are completely separated, the presence of 0.1 mM copper(II) inhibits the reduction of 0.1 mM persulfate but does not completely suppress it. In the presence of 1 mM copper(II) and 20 mM persulfate, the difference between the observed current at -0.1 v and the first copper wave is practically independent of mercury height, showing that it is kinetically and not diffusion controlled. Assuming complete inhibition on the first copper wave of the electrochemical reduction of persulfate by an adsorbed copper(I) chloride complex, the rate constant of reaction 1 can be calculated at copper(II) concentrations greater than 0.5 mM.

Brdička and Wiesner[10] derived an expression for the kinetic current of a system where the reduced species of a depolarizer is reoxidized at the electrode surface by an oxidizing agent in solution. For the over-all reaction, the sum of reactions 1 and 2, the kinetic current is given by

$$i_k = \frac{2Fq\mu ka[S_2O_8^{2-}][Cu(II)]}{a \times 10^{-3} + 2Fq\mu k[Cu(II)]} \qquad (3)$$

where F is the Faraday, q the average surface area of the drop in cm^2, μ the thickness of the reaction layer in cm, k the rate constant of the rate-determining step (reaction 1) in l. mole^{-1} sec^{-1}, and a the Ilkovič coefficient for persulfate (*i.e.*, i_d(persulfate) = $a[S_2O_8^{2-}]$) in μa M^{-1}; i_k is expressed in μa.

It can be seen from eq 3 that if the second term in the denominator is much greater than the first, the kinetic current will approach the value $a[S_2O_8^{2-}]$, that is, the diffusion current of persulfate. In this case the first limiting current will approach the sum of the diffusion currents of copper(II) to copper(I) and persulfate. It can be seen from Table II that as the copper(II) concentration is increased, the kinetic current approaches the diffusion current of persulfate as anticipated by this relationship. If the difference between the Cu(II) → Cu(I) current and the experimental current were due to incomplete inhibition of the persulfate wave, rather than a kinetic wave, it would be anticipated that the difference would decrease with increase in copper(II) concentration.

The thickness of the diffusion layer, μ, as originally considered by Wiesner, is the distance moved by the copper(I) species in its mean lifetime τ, which according to the Einstein and Smoluchowski equation will be $(2D\tau)^{1/2}$. Correlation of the approximate treatment of Brdička and Wiesner with more rigorous derivations has shown that practically the same results are obtained if μ equals $(D\tau)^{1/2}$.[11,12] This essentially redefines μ as the distance from the surface of the electrode at which the concentration of copper(I) decreases to $1/e$ times the value at the electrode surface,[13] e being the base of the natural logarithm.

If persulfate is in excess, then

$$\tau = {}^1/_2k[S_2O_8^{2-}]$$

and

$$\mu = (D/2k[S_2O_8^{2-}])^{1/2}$$

therefore

$$1/\mu k = (2/Dk)^{1/2}[S_2O_8^{2-}]^{1/2} \qquad (4)$$

The value of μk at different persulfate concentrations can be determined from eq 3, all other quantities being known. A plot of $1/\mu k$ against $[S_2O_8^{2-}]^{1/2}$ for kinetic currents at 1 mM copper(II) is shown in Figure 4. The plot is linear in accordance with eq 4, the slope giving the value $Dk = 8.9 \times 10^{-3}$. Taking D for the copper(I) species to be equal to the value for Cu^{2+} of 7.2×10^{-6},[14] $k = 1.2 \times 10^3$ l. mole^{-1} sec^{-1}.

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(10) R. Brdička and K. Wiesner, *Collection Czech. Chem. Commun.*, **12**, 39 (1947).

(11) J. Koutecky, *ibid.*, **18**, 311 (1953).

(12) J. Koutecky, *ibid.*, **18**, 597 (1953).

(13) J. Koutecky, R. Brdička, and V. Hanus, *ibid.*, **18**, 611 (1953).

(14) I. M. Kolthoff and J. J. Lingane, ref 8, Vol. 1, p 52.

Koutecky[15] derived a relationship for a bimolecular reaction by a more rigorous treatment of the electrode process

$$\frac{i}{i_d} = 0.812(\alpha kt[S_2O_8^{2-}])^{1/2}\gamma H(u_1) \qquad (5)$$

where i_d is the first diffusion current of copper(II), i is the experimental current, $i_k + i_d$, α is the stoichiometry factor which is 2 in this case, t is the drop time, and

$$\gamma = \left(1 + \frac{2D_1[Cu(II)]}{3\alpha D_2[S_2O_8^{2-}]}\right)^{1/2}$$

$$u_1 = \frac{\left(\frac{kTD_1[Cu(II)]^2}{\alpha D_2[S_2O_8^{2-}]}\right)^{1/2}}{\gamma}$$

D_1 and D_2 are the diffusion coefficients of copper(II) and persulfate, respectively. The function $H(u_1)$ has been tabulated by Koutecky.[15] Using this equation Matyska[16] obtained good agreement between the k value calculated from the kinetic current and the chemically determined value in the reaction of iron(III) EDTA and hydrogen peroxide.

The product $\gamma H(u_1)$ becomes one for a pseudo-first-order reaction, and it is then possible to evaluate k. However, in our system it is not possible to obtain pseudo-first-order conditions as it would necessitate the measuring of kinetic currents in the presence of much less than 1 mM copper(II) concentration where the persulfate current is not completely suppressed. With 1 mM copper(II) pseudo-first-order conditions are not obtained even with 20-fold excess of persulfate, as shown by the fact that the second term in the denominator of the Brdička–Wiesner equation cannot be neglected compared with $a \times 10^{-3}$.

However, $\gamma H(u_1)$ can be calculated for each value of the kinetic current using $k = 1.2 \times 10^3$ l. mole^{-1} sec^{-1}, obtained from the Brdička–Wiesner equation. A plot of $i/i_d\gamma H(u_1)$ against $[S_2O_8^{2-}]^{1/2}$ is shown in Figure 5 for kinetic currents obtained with 1 mM copper(II). A linear plot, in agreement with eq 5, is obtained and from the slope, $k = 1.4 \times 10^3$ l. mole^{-1} sec^{-1}, in good agreement with the value of 1.2×10^3 from the approximate treatment of Brdička and Wiesner.

The effect of changing copper(II) concentration at constant persulfate concentration is accounted for by the change in $\gamma H(u_1)$. Values of i/i_d at 1 mM persulfate in the presence of increasing concentrations of copper(II) were calculated from the value at 1 mM copper(II)

$$i/i_d = (i/i_d)_1[\gamma H(u_1)]_1/\gamma H(u_1)$$

where the subscript 1 refers to 1 mM copper(II), and are presented in Table V. Good correlation exists between the experimental and calculated values of i/i_d.

The addition of allyl acetate to the solution decreases the kinetic current (Table III). The effect is small and can be attributed to some reaction between allyl acetate and the intermediate sulfate free radical

$$RCH{=}CH_2 + SO_4\cdot^- \longrightarrow R\dot{C}H{-}CH_2SO_4^- \qquad (6)$$

$$R\dot{C}H{-}CH_2SO_4 + nRCH{=}CH_2 \longrightarrow \text{polymer}$$

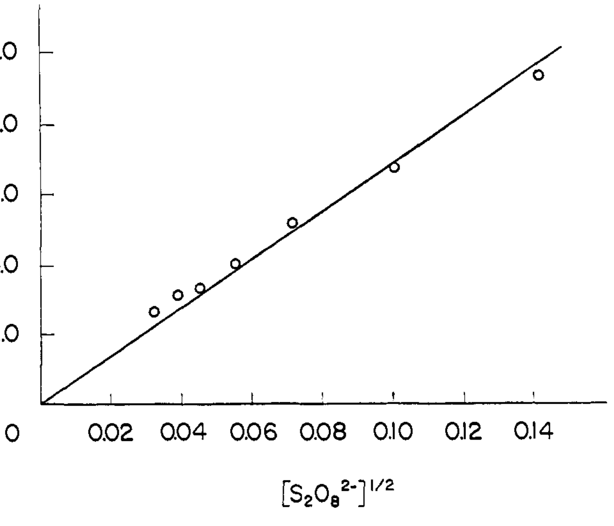

Figure 5. Plot of $i/i_d\gamma H(u_1)$ against $[S_2O_8^{2-}]^{1/2}$ for kinetic currents of 1 mM Cu(II) in 1 M KCl–0.01% PAM and varying persulfate concentrations.

If reaction 6 is very much faster than reaction 2, the stoichiometry factor, α, in the Koutecky equation will be 1. The ratio i/i_d in this case will be related to the ratio in the absence of allyl acetate by the expression

$$(i/i_d)_{\alpha=1} = \frac{(i/i_d)_{\alpha=2}}{2}\frac{[\gamma H(u_1)]_{\alpha=1}}{[\gamma H(u_1)]_{\alpha=2}}$$

Values of i_k for $\alpha = 1$ calculated from this equation are 1.8 in 1 mM copper(II)–1 mM persulfate and 9.0 in 1 mM copper(II)–5 mM persulfate, compared with the experimental values in the presence of allyl acetate of 3.7 and 12.9, respectively. Apparently there is incomplete scavenging of sulfate free radicals by allyl acetate, the stoichiometry factor being between 1 and 2.

Table V. Comparison of Experimental and Calculated Values of i/i_d[a]

Cu(II), mM	i/i_d Exptl	Calcd
1.00	2.02	. . .
1.50	1.88	1.86
2.00	1.75	1.69
3.00	1.55	1.50

[a] 1 M KCl, 1 mM $S_2O_8^{2-}$, 0.01% PAM.

The kinetic current in the presence of 0.1 M chloride is approximately the same as in 1 M chloride. The copper(I) species reacting with persulfate in this case, therefore, is a copper(I) chloride complex, possibly $CuCl_3^{2-}$.

The good correlation between the experimental currents at potentials corresponding to the first copper wave and the theoretical expressions for kinetic currents, combined with the fact that the current is hardly affected by the height of the mercury, substantiate the postulation that this current is the sum of the Cu(II) → Cu(I) current and a kinetic current with no contribution from electrochemical reduction of persulfate at the electrode.

In the presence of thiocyanate, no kinetic current is observed, and therefore oxidation of the insoluble cuprous thiocyanate to copper(II) by persulfate must be a comparatively slow process.

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(16) B. Matyska, *ibid.*, **22**, 1758 (1957).