Selective Activation of Reactant Molecules by Reversed Micelles

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The oxidations by Ce(IV) ion of the cations of acridine orange (AOH⁺) and its N-alkyl derivatives (AO⁺–(CH₂)_nH) have been studied in water and in the reversed micellar system of cetylpyridinium chloride (CvPCl)/water/ chloroform. The length of a substituting alkyl chain (n) is varied from methyl to octadecyl groups. In both media, the oxidation is found to proceed via the two-step mechanism: (1) $AO^+(CH_2)_nH + Ce(IV) \rightarrow I + Ce(III)$ (k_1) and (2) I + Ce(IV) \rightarrow P + Ce(III) (k_2) , where I and P denote the one- and two-electron oxidized species, respectively. In water, the bimolecular rate constants, k_1 and k_2 , do not vary very much with the change of $n; k_1 = 7.0 \times 10^4 - 14 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \text{ and } k_2 = 2.1 \times 10^4 - 5.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \text{ for } n = 0.9 \text{ at } [\text{H}_2\text{SO}_4] = 6.0 \times 10^{-3}$ M, respectively. On the other hand, in the reversed micellar system, the first-order rate constant of step 1, k_1 , has a sharp maximum at n = 1; $k_1 = 1.9 \text{ s}^{-1}$ $(n = 0) \ll 58 \text{ s}^{-1}$ $(n = 1) > 18-3.8 \text{ s}^{-1}$ (n = 2-18). In contrast to this, the first-order rate constant of step 2, k_2 , is little dependent on n; $k_2 = 0.21-0.58$ s⁻¹ for n = 0-18 at $[CyPCl] = 8.8 \times 10^{-3}$ M and $[H_2O] = 5.6 \times 10^{-2}$ M. The remarkably high rate of the initial step for AO⁺-CH₃ is rationalized in terms of its favorable orientation at the boundary between the micellar water phase and the surfactant layer.

Introduction

The ternary system of surfactant/water/nonpolar solvent forms an aggregate called a W/O microemulsion.^{1,2}

When the system contains small amounts of water (e.g., [water]/[surfactant] < 10, the aggregate is termed a reversed micelle. In a reversed micelle, a water droplet of 10-50 Å in diameter is surrounded by the monolayer of surfactant molecules with their polar heads toward the water phase core.³⁻⁵ Stimulated by its similarity to the water pockets in bioaggregates like mitochondrial membranes, there have been several efforts to utilize the systems for mimicking enzymatic functions.⁶⁻⁸

We have studied the reactions of ion radicals and metal ions in the presence of reversed micelles.⁹⁻¹⁴ The enhancement of rates of the electron-transfer, ionization, and ligand replacement reactions has been observed to support the validity of the above approach. This paper describes an attempt to establish a model system in which the reversed micelle activates a particular species among a series of similar compounds by discerning the molecular sizes of the substrates.

The oxidation by Ce(IV) ion of acridine orange cation (AOH^+) and its *N*-alkyl derivatives $(AO^+-(CH_2)_nH)$ (Figure

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1) is compared between bulk water and the reversed micellar system of cetylpyridinium chloride (CyPCl)/ water/chloroform. It is hoped that the substrates are partitioned into various microphases of the reversed micellar system, depending on their hydrophobicity or the length of an attached alkyl group. As a result, a species solubilized close to the Ce(IV) ion is expected to acquire the highest reactivity.

Experimental Section

Acridine orange hydrochloride (AOH⁺Cl⁻), purchased from Wako Pure Chemical Industries, was recrystallized from methanol. N-Alkyl acridine orange derivatives $(AO^+-(CH_2)_nHX^-)$ were synthesized according to Miethke and Zanker.¹⁵ Acridine orange base was refluxed in benzene or toluene with either alkyl iodides (for n = 1-4) or alkyl bromides (for n = 5-7, 9, 12, 14, 16, and 18) for several hours. The resultant precipitates were recrystallized in an ethanol/ether mixture. The ethanol solution of the compound was further purified chromatographically over Al_2O_3 . The products were identified by NMR and elemental analysis; the assays were better than 93% even in the worst case (n = 18). CeSO₄·4H₂O (Merck) was used without further purification. Cetylpyridinium chloride (CyPCl) monohydrate (Wako Pure Chemical Industries) was recrystallized from water. Chloroform was freshly distilled over molecular sieves.

The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer at 20 °C. The reaction rates were obtained with a Union Giken stopped-flow apparatus RA-1300.¹⁶ The infrared spectrum of the oxidized product of AOH⁺Cl⁻ was taken with a JEOL IR spectrophotometer, Model IR-G. The fluorescence spectra were recorded with a Hitachi fluorescence spectrophotometer, Model MPS-2.

Results

Reaction in Water. AOH⁺ Cl⁻ dimerizes in water.¹⁷ In the electronic spectrum, the monomer and dimer species

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TABLE I: Dimerization Equilibrium and Oxidation Rate Constants of $AO^+-(CH_2)_nHX^-$ (n = 0-18) in Water and CyPCl/H₂O/CHCl₃ Media

dye n	0	1	2	3	4	5	7	9	12	14	16	18
	Cl-	I-	I-	I⁻	I-	Br⁻	Br⁻	Br⁻	Br ⁻	Br⁻	Br ⁻	Br-
$\frac{K_{d}^{a}/10^{4} M^{-1}}{k_{1}^{c}/10^{4} M^{-1} s^{-1}} \\ \frac{k_{2}^{d}}{k_{2}^{d}/10^{4} M^{-1} s^{-1}} \\ \frac{k_{1}^{e}/s^{-1}}{k_{2}^{f}/s^{-1}}$	3.2 7.0 1.6 1.9 0.21	2.9 9.4 3.1 58 0.32	2.5 12 3.1 18 0.35	2.2 14 2.1 2.6 0.21	2.7 13 2.0 3.8 0.37	3.0 13 1.8 2.3 0.32	3.7 13 7.0 2.3 0.23	3.9 12 5.9 2.1 0.58	b b 2.1 0.46	b b 2.1 0.37	b b 2.3 0.46	b b 1.3 0.21

^a The dimerization equilibrium constant in water at 20 °C. No salt or buffer is added. ^b The compound is hardly dissolved in water. ^c The bimolecular rate constants of reaction 3 in water. $[H_2SO_4] = 6.0 \times 10^{-3}$ M. ^d The bimolecular rate constants of reaction 4 in water. $[H_2SO_4] = 6.0 \times 10^{-3}$ M. ^e The unimolecular rate constants of reaction 3 in the CyPCl/ $H_2O/CHCl_3$ system. $[CyPCl] = 8.8 \times 10^{-3}$ M. $[H_2O] = 0.056$ M. $[H_2SO_4] = 6.0 \times 10^{-3}$ M. ^f The unimolecular rate constants of reaction 4 in the CyPCl/ $H_2O/CHCl_3$ system. The conditions are the same as in e.



Figure 1. Acridine orange derivatives $(AO-(CH_2)_{n}H^+)$.

have absorption peaks at 490 and 468 nm, respectively. AO⁺-(CH₂)_nHX⁻ (n = 1-6 and 9) also has two peaks at about the same wavelengths when it is dissolved in water. Thus the dimerization equilibrium

$$2\mathrm{AO}^{+}(\mathrm{CH}_{2})_{n}\mathrm{H} \rightleftharpoons [\mathrm{AO}^{+}(\mathrm{CH}_{2})_{n}\mathrm{H}]_{2} \qquad K_{\mathrm{d}} \qquad (1)$$

is accrtained to exist, and the equilibrium constant is obtained in the same procedure as described in ref 17. The results are given in the first array of Table I.

The above dimerization equilibrium is little affected when 1×10^{-2} M CyPCl is added to the solution. Thus the present dye cations are concluded not to interact with the cationic micelle of CyPCl in water.

The oxidations of the dyes are studied by mixing a solution of $Ce(SO_4)_2 \cdot 4H_2O$ (1 × 10⁻⁴–10 × 10⁻⁴ M) and 10⁻² M H₂SO₄ with a dye solution. The absorbance at 440–520 nm disappears instantly to give a rise to the shoulder beginning around 400 nm. In the case of AOH⁺Cl⁻, the resultant precipitate is collected and dried for the IR measurements. There are characteristic peaks at 1620 and 3250 cm⁻¹ being assigned to the C=O and N-H groups, respectively. Thus the overall change during the oxidation is concluded to be



As for the acridine orange derivatives, a similar type of reaction is assumed to occur.¹⁸

The rate of reaction 2 is determined by mixing a dye solution with a solution of $CeSO_4 \cdot 4H_2O$ and H_2SO_4 . The decrease of absorbance at the monomer peak (490 nm) is shown in Figure 2 for the case of AOH⁺Cl⁻. The final concentrations are 3.1×10^{-6} M AOH⁺Cl, 2.7×10^{-4} M $Ce(SO_4)_2$, and 6.0×10^{-3} M H_2SO_4 . At this concentration of the dye, more than 90% of the initial amount exists as a monomer. Besides the protonation on the methylated nitrogen atom is also neglected below $[H_2SO_4] = 0.1$ M. Evidently the decay of absorbance does not obey the





Figure 2. Plot of the logarithm of relative absorbance change, $A_{-}(t)/A(0)$ at 490 nm vs. time in the case of the oxidation of AOH⁺Cl⁻ in water. [AOH⁺Cl⁻] = 3.1 × 10⁻⁶ M, [Ce(SO₄)₂·4H₂O] = 2.7 × 10⁻⁴ M, and [H₂SO₄] = 6.0 × 10⁻³ M. Plot 1 represents log A(t)/A(0), plot 2 the asymptotic slope at the later stage of the reaction, and plot 3 the subtraction of plot 1 from plot 2.

first-order kinetics, although the oxidation is performed under the large excess of Ce(IV) over the dye. Since reaction 2 involves the two-electron oxidation of the dye, we assume the following two-step mechanism to interpret the kinetic results:

$$D + Ce(IV) \xrightarrow{\kappa_1} I + Ce(III)$$
(3)

$$I + Ce(IV) \xrightarrow{\kappa_2} P + Ce(III)$$
(4)

where I and P represent the one- and two-electron oxidized forms of the reactant dye, D, respectively. Two points should be mentioned as to the above scheme: (i) it is not certain what kind of reaction takes place until the final product in reaction 2 is obtained. However, it does not affect the following kinetic analysis, as long as solely D and I contribute to the observed absorbance change. (ii) Ce(IV) ion is complexed with SO_4^{2-} under the present conditions. According to the equilibrium constants given in ref 19, Ce(IV) is present as Ce(SO_4)²⁺ (1%), Ce(SO_4)₂ (24%), and Ce(SO_4)₃²⁻ (75%). Thus, the obtained k_1 and k_2 represent the average rate constants for these three kinds of complexes. Under the above scheme, the time course of the absorbance is expressed by eq 5,²⁰ where ϵ_1

$$A(t) = \epsilon_1 C_0 \exp(-k_1 [\operatorname{Ce}(\mathrm{IV})]t) + \epsilon_2 C_0 k_1 (k_2 - k_1)^{-1} [\exp(-k_1 [\operatorname{Ce}(\mathrm{IV})]t) - \exp(-k_2 [\operatorname{Ce}(\mathrm{IV})]t)]$$
(5)

and ϵ_2 are the extinction coefficients of D and I, respectively, C_0 is the initial concentration of D, and k_1 and k_2 are the bimolecular rate constants of reactions 3 and 4, respectively. According to the above expression, A(t) is

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Figure 3. Wavelength dependences of ϵ_1 and ϵ_2 .

dominated by the last term of $\exp(-k_2[\operatorname{Ce}(\mathrm{IV})]t)$ at the later stage of the reaction. Thus the asymptotic slope of the curve in Figure 2 gives the rate constant of k_2 . In addition, the extrapolated value of A(t) along the straight line to the initial time gives $\epsilon_2 C_0 k_1 (k_1 - k_2)^{-1}$. By plotting the subtraction of the contribution of the last term from A(t) against time, one obtains k_1 . In this way, all unknowns, k_1 , k_2 , and ϵ_2 , are determined. Both the rate constants k_1 and k_2 are found to be constant when [Ce(IV)] is varied from 2×10^{-4} to 10×10^{-4} M. The second and third arrays of Table give k_1 and k_2 values that are determined for other dyes in a similar way. Figure 3 shows the wavelength dependences of ϵ_1 and ϵ_2 , the latter of which gives the electronic spectrum of the one-electron oxidized intermediate, I.

Reactions in $CyPCl/H_2O/CHCl_3$. Both AOH⁺Cl⁻ and AO⁺-(CH₂)_nHX⁻ dissolve readily in chloroform to display a single peak around 500 nm. Since the extinction coefficients do not depend on the dye concentrations, it is concluded that the dyes are present as monomer.

A chloroform solution of CyPCl is capable of cosolubilizing water up to ca. $[H_2O]/[CyPCl] = 10$. The resultant solution is considered to contain reversed micelles, as stated in the Introduction.³⁻⁵ On the basis of a simple model, it was determined that the size of the micelle is dependent solely on the ratio of [CyPCl] to $[H_2O]$ (ref 14)

$$m = 3.8[H_2O]^2/[CyPCl]^2$$
 (6)

where \mathbf{m} denotes the aggregation number of CyPCl per one micelle.

The interaction of the dye with a reversed micelle is studied by adding various amounts of CyPCl and H_2O at a constant ratio of [CyPCl] to [H_2O].

On addition of 0.019 M CyPCl and 0.13 M H₂O to a solution of 5.2×10^{-6} M AO⁺-CH₃I⁻, an increase in absorbance of ~4% is observed at $\lambda_{max} = 495$ nm (Figure 4). The absorbance stays constant with the further addition of CyPCl and water (insert in Figure 4). A remarkable increase of fluorescence is also observed on the introduction of the reversed micelle, as shown in Figure 5. We ascribe these spectral changes to the solubilization of the dye in the reversed micelle (eq 7). The I⁻ or Br⁻ ions

$$AO^{+}-(CH_2)_nHX^{-} + CyPCl/H_2O \rightleftharpoons$$
$$AO^{+}-(CH_2)_nH\cdot CyPCl/H_2O \quad (7)$$

paired with the cationic dye originally may be either dissociated or replaced with Cl^- ion during the above process. The constancy of absorbance with the further increase of reversed micelle implies that the solubilization of the dye is already complete at the lowest possible concentration of the reversed micelle ($\sim 2 \times 10^{-3}$ M). Below this value of the concentration, the cosolubilized water separates from the solution.



Figure 4. Change of electronic spectrum of $AO^+-CH_3I^-$ on addition of CyPCi and water to chloroform: (---) [dye] = 5.2 × 10⁻⁶ M; (--) [dye] = 5.2 × 10⁻⁶ M, [CyPCi] = 0.019 M, and [H₂O] = 0.13 M.



Figure 5. Increase of fluorescence due to $AO^+-CH_3I^-$ in chloroform on addition of CyPCI and water: (---) [dye] = 5.0×10^{-6} M; (--) [dye] = 5.0×10^{-6} M, [CyPCI] = 0.019 M, and [H₂O] = 0.13 M. Excitation light = 470 nm.

In contrast to the bulk water system, the dye does not dimerize in the reversed micellar system even in the presence of cosolubilized water. All of the above facts are similarly observed for the other dyes with n = 0-18.

The rate of the solubilization process (eq 7) in the case of n = 1 is measured by mixing a solution of 5.10×10^{-6} M AO⁺-CH₃I⁻ with a solution of 4.0×10^{-3} M CyPCl and 0.028 M H₂O with a stopped-flow apparatus. Although the net absorbance increases after mixing, any transient change is not observed at 495 nm. This means that the solubilization process is complete within the dead time of the apparatus (ca. 2 ms). According to eq 6, the concentration of the reversed micelle is estimated to be 2.2×10^{-5} M under the above experimental conditions. Thus if reaction 7 is expressed by the second-order kinetics between the dye and the reversed micelle, the lower limit of the biomolecular rate constant of reaction 7 is estimated to be 2.3×10^7 M⁻¹ s⁻¹.

The electronic spectrum of $AO^+-CH_3I^-$ is not affected when 0.017 M H₂SO₄ is dissolved under the condition of Figure 4. At this value of $[H_2SO_4]$ the micellar concentration of the proton $[H^+]_m$ attains a value as high as 1.9 M according to the relation $[H^+]_m = 55.5 \times 2[H_2SO_4]/$ $[H_2O]^{.21}$ On the other hand, the protonation on the methylated nitrogen in the dye occurs already above $[H^+]$ = 0.10 M in bulk water. In this respect, the solubilization of the dye in the reversed micelle makes the dye inert against the attack of proton.

 $Ce(SO_4)_2$ ·4H₂O is soluble in the present reversed micellar solution. Since the water phase contains a large amount

⁽²¹⁾ The density of the micellar water phase is assumed to be 1 g mL⁻¹.



Figure 6. Plot of the logarithm of relative absorbance change, $A_{-}(t)/A(0)$ vs. time in the case of the oxidation of AOH⁺Cl⁻ in the CyPCl/H₂O/chloroform system. [AOH⁺Cl⁻] = 5.0×10^{-8} M, [CyPCl] = 8.8×10^{-3} M, [H₂O] = 0.056 M, [Ce(SO₄)₂·4H₂O] = 1.4×10^{-4} M, and [H₂SO₄] = 6.0×10^{-3} M. Plots 1–3 are the same as mentioned in Figure 2.



Figure 7. The plot of log k_1 in the CyPCI/H₂O/chloroform system vs. the length of the substituting alkyl chain (*n*).

of Cl^- ions which are dissociated from CyPCl, Ce(IV) ion is considered to be complexed with Cl^- ions.

When a AOH⁺Cl⁻ solution is mixed with a solution containing 18×10^{-3} M CyPCl, 0.11 M H₂O, 2.8×10^{-4} M Ce(SO₄)₂·4H₂O, and 12×10^{-3} M H₂SO₄, the rapid decrease of absorbance is observed at 480 nm (Figure 6). As is also seen in the reaction in bulk water, the logarithm of A(t)does not decrease linearly with time. If one assumes the same reaction mechanism as reactions 3 and 4, the absorbance change is interpreted according to eq 8. The

$$A(t) = \epsilon_1 C_0 \exp(-k_1 t) + \epsilon_2 C_0 k_1 (k_2 - k_1)^{-1} [\exp(-k_1 t) - \exp(-k_2 t)]$$
(8)

expression is identical with eq 5, except that k_1 and k_2 are unimolecular rate constants. This modification reflects the fact that in the present measurements the concentration of Ce(IV) ion is varied by keeping constant the ratio of [Ce(IV)] to the concentration of the reversed micelle. Thus, the micellar concentration of Ce(IV) ion as given by 55.5 [Ce(IV)]/[H₂O] stays constant, as long as each micelle acts as an independent reacting system. Accordingly the apparent rate of the decrease of the whole dye amount does not change in spite of the increase of the bulk concentration of Ce(IV) ion.

If one follows the similar procedure described in the bulk water system, k_1 , k_2 , and ϵ_2 are obtained. k_1 and k_2 are found to be independent of [Ce(IV)], confirming the above assumption for the independence among each micelle.²² The dependence of ϵ_2 on wavelength gives a spectrum similar to the one which is shown in Figure 3. The fourth and fifth arrays in Table I give k_1 and k_2 obtained for other dye derivatives, being based on the same scheme, reactions 3 and 4. In order to emphasize the variation of k_1 with the length of an alkyl chain, we have plotted $\log k_1$ against n in Figure 7.

Discussion

The results in Figure 7 show that the selective activation occurs at n = 1 among the group of acridine orange and its N-alkyl derivatives. In other words, the reversed micelle has demonstrated its potentiality to discern the length of the alkyl groups attached to the substrates. In the following we try to rationalize the present results.

First, it should be noted that the chemical reactivities of the dyes are substantially modified when the medium is changed from bulk water to the reversed micelle system. The dimerization, as well as the protonation, of the dyes does not occur in the latter system. As for the properties of the micellar water phase, the NMR studies by Wong, Thomas, and Nowak 23 showed that the molecular motion in the water droplet approaches that in the bulk water when the ratio of cosolubilized water to surfactant exceeds some critical value. In the case of the sodium diisooctyl sulfosuccinate (AOT)/H₂O/heptane system, this occurs above $[H_2O]/[AOT] \simeq 8.^{22}$ Our previous study of the aquation of CoCl₄²⁻ ion in the dodecylpyridinium chloride $(DPCl)/H_2O/chloroform$ also showed that the solubilized water can be treated as a homogeneous phase when $[DPCl]/[H_2O]$ exceeds 1.¹⁴ Since the present experiments have been done at $[CyPCl]/[H_2O] = 6.8$, the water phase similar to bulk water is already formed. The only difference between the bulk water and the present micellar water is that the latter contains a great number of chloride ions. If the degree of dissociation of Cl⁻ from CyPCl is around 25%, as deduced previously in the case of DPCl,¹⁴ the concentration of Cl⁻ is estimated to be 2.0 M. In water, however, the Cl⁻ ion is reported to enhance the dimerization of AOH⁺ rather than to depress it.¹⁷ There is no positive reason to assume that Cl⁻ ion reduces the protonation of the dyes, either. Thus the absence of dimerization and protonation of the solubilized dyes seems to be difficult to explain, if the dyes are present inside the water phase. In other words, it is suspected that the dyes are either located in the surface region of the water droplet or embedded in the surfactant layer. This seems reasonable if the dyes are pulled into the surfactant layer because of the hydrophobic interaction between alkyl groups and surfactant molecules. This picture is consistent with the recent findings by Fendler and his co-workers concerning the interaction of pyrene derivatives with the reversed micelle of dodecylammonium propionate/water/cyclohexane.²⁴ They report that pyrene does not interact with the reversed micelle, being present exclusively in external solvent. On the other hand, pyrenebutyric acid is located in the surfactant layer with its carboxylate group close to the micellar interior. Pyrenesulfonic acid is inside the micellar water phase because of its highly ionic character.

On the basis of the above picture, it is expected that the encounter between the dye molecules and Ce(IV) ion becomes less frequent as the alkyl group becomes longer. Here Ce(IV) ion is assumed to be present in the water phase by being complexed with Cl⁻ ion like $[CeCl_n(SO_4)_m]^{4-2m-n}$ with n + m < 6. This may be the main cause for the low value of k_1 for n > 3. If the hydrophobicity is the only factor to determine the reactivity of dye with Ce(IV) ion, AOH⁺ would take the highest value of k_1 among the used dye series. Since this is not the case, as

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seen in Figure 7, the presence of another factor is suggested to affect the reaction rates of the present oxidation. It is speculated that the most favorable steric conditions are met in the case of n = 1 for the attack of Ce(V). For example, the methyl group in AO⁺-CH₃ may be directed toward the inside of surfactant layer. As a result, the carbon atom C₉, which is considered to be the site attacked by Ce(IV) ion, is exposed toward the water phase. On the other hand, the interaction of AOH⁺ with surfactant molecules is mostly due to the dispersive force between

 π -electron groups. Thus the benzene ring in AOH⁺ is faced with the surfactant layer to result in the blocking of the C₉ atom by the bulky surfactant molecules. These steric factors may cause the higher reactivity of AO⁺-CH₃ as well as the lower reactivity of AOH⁺ than expected from their hydrophobicity scale.

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Reverse Pulse Voltammetry. Application to Second-Order Following Reactions

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Reverse pulse voltammetry is applied to the quantitative treatment of second-order chemical reactions following reversible electron transfer. Simple algebraic and graphical procedures based on the results of simulations are employed to estimate the backward rate constant of the chemical reaction from an approximation to the equilibrium constant (K) which is obtained experimentally. One iteration produces accurate values of the forward and backward rate constants and the true equilibrium constant as shown by detailed fitting of experimental results to simulated results. For the following dimerization of N-methyl-2-carbomethoxypyridinyl radical the technique yields values of $K = 10^{4.68} \text{ M}^{-1}$, $k_f = 10^{4.03} \text{ M}^{-1} \text{ s}^{-1}$. The treatment is applicable for $-1.3 \leq \log (K'C) \leq 4$.

Introduction

Previous work has described the technique of reverse pulse polarography (RPP) (or reverse pulse voltammetry)¹ and its application to the study of homogeneous reactions coupled with electron-transfer processes.²⁻⁴ The purpose of this paper is to describe the quantitative treatment of RP data for second-order following reactions. To our knowledge the case of reversible following dimerization reactions has not been treated before.⁵

Consider the reaction sequence

$$0 \stackrel{e^{-}}{\underset{e^{-}}{\longleftarrow}} \mathbf{R} \cdot \qquad 2\mathbf{R} \cdot \stackrel{k_{t}}{\underset{k_{b}}{\longleftarrow}} \mathbf{D}$$
(1)

An approximate equation for the equilibrium constant for dimer formation can be derived by using the RP currents to estimate the concentrations of radical (R) and dimer (D) in the diffusion layer. The experiment is the following. The potential is held for a time $(\tau - t_p)$ at a value for which the material initially present, O, is reduced at the diffusion-limited rate. During that period radical and dimer are formed near the electrode. Then a pulse of duration t_p is applied in the positive direction. The experiment is repeated with successively more positive values of the pulse

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potential until the waves for oxidation of the radical and dimer are obtained. If $(\tau - t_p)$ is sufficiently long in comparison with t_p then the concentration profiles for both radical and dimer should be very flat on the time scale t_p , and therefore the RP limiting currents, $i_{RP,R}$ and $i_{RP,D}$, for the radical and dimer, respectively, can be said to arise from average concentrations in the diffusion layer, \bar{C}_R and \bar{C}_D , respectively, which are nearly equal to the surface concentrations of these species. Thus we may write eq 2 and 3, where $i_{RP,R}$ is the RP diffusion-limited current for

$$i_{\rm RP,R} = FA\bar{C}_{\rm R}[D_{\rm R}/(\pi t_{\rm p})]^{1/2}$$
 (2)

$$i_{\rm RP,D} = 2FA\bar{C}_{\rm D}[D_{\rm D}/(\pi t_{\rm p})]^{1/2}$$
 (3)

the radical, R (R of eq 1); $i_{\text{RP,D}}$ is the RP diffusion-limited current for the dimer, D (eq 1); F is the Faraday constant; A is the electrode area; and D_{R} and D_{D} are the diffusion coefficients of R and D, respectively. The factor of 2 in the equation for $i_{\text{RP,D}}$ arises because we assume that the oxidation of dimer requires two electrons per mole. The equilibrium constant for dimer formation (eq 1) is then given by

$$K' = \bar{C}_{\rm D} / (\bar{C}_{\rm R})^2 = i_{\rm RP,D} FAD_{\rm R} / [2i_{\rm RP,R}^2 (\pi D_{\rm D} t_{\rm p})^{1/2}]$$
(4)

The normal pulse (NP) current for the reduction of O is just

$$i_{\rm NP} = FAC^{\rm b} [D_0 / (\pi t_{\rm p})]^{1/2}$$
 (5)

where C^{b} is the bulk concentration of O, and D_{O} the diffusion coefficient of O. If $D_{O} = D_{R} = D_{D}$, then we can combine eq 4 and 5 to obtain

⁽¹⁾ Osteryoung, Janet; Kirowa-Eisner, Emilia, Anal. Chem. 1980, 52, 62-6.

⁽²⁾ Kashti-Kaplan, S.; Hermolin, J.; Kirowa-Eisner, E., submitted to J. Electrochem. Soc.

⁽³⁾ Osteryoung, Janet; Hermolin, Joshua; Kashti-Kaplan, S.; Kirowa-Eisner, Emilia, submitted to J. Electroanal, Chem.

⁽⁴⁾ Hermolin, Joshua; Kashti-Kaplan, S.; Kirowa-Eisner, Emilia, submitted to J. Electroanal. Chem.