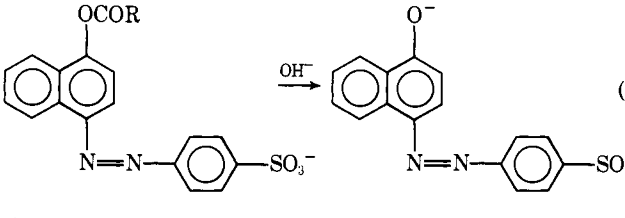
The Effect of Reacting and Competing Counterions on the Hydrolysis Kinetics of an Anionic Dye Ester in Mixed Micelles with CTAB

Richard L. Reeves

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York, 14650. *Received February 12, 1975*

Abstract: The kinetics of the base-catalyzed hydrolysis of Orange I acetate were studied by the stopped-flow method in mixed micelles with CTAB as a function of the concentration of hydroxide ion (0.01 to 1.5 *M*), fluoride ion, and chloride ion. In the absence of CTAB the rate shows a strict first-order dependence on [OH$^-$] and is independent of ionic strength. In the mixed micelles, the rate has a complex dependence on [OH$^-$] that varies with the stoichiometric surfactant–dye ratio (S/D). At low S/D ratios, the rate has a greater than first-order dependence on [OH$^-$] at low [OH$^-$] and becomes independent or approaches independence of [OH$^-$] at high concentrations. Increasing chloride concentration gives maxima in the second-order rate constants when [Cl$^-$] is varied at constant [OH$^-$] and when [Cl$^-$] and [OH$^-$] are both varied at constant concentration ratio. Fluoride ion competes poorly with OH$^-$ and increases the second-order rate constant, with maxima appearing only at high concentrations. All three counterions give changes in the absorption spectrum of bound ester when added to dispersions in water, with half-times of 2 to 12 msec. The changes are consistent with the formation of new micelles by addition of monomeric CTAB from solution. The salt effects are interpreted in terms of counterion selectivity and their effects on micellar structure and composition.

In previous papers[1,2] we have shown that aqueous solutions of anionic dyes and cationic surfactants give mixed micelles at concentrations far below the critical micelle concentration (cmc) for surfactant homomicelles. In the accompanying paper[2] we presented the results of our studies of the kinetics of the base-catalyzed hydrolysis of anionic dye esters (eq 1) in mixed micelles with dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) at constant ionic strength. The results were interpreted in terms of a continuous spectrum of mixed micelles containing increasing amounts of surfactant as the total concentration of surfactant was increased up to the cmc. In the present paper the effect of salts on the nature of the mixed micelles of the dye acetate (R = CH_3) and CTAB is examined.



(1)

It was anticipated that interesting counterion effects might be found, especially at low S/D ratios where surfactant-poor micelles predominate. In the absence of added salt, charge neutralization in the micelles by the oppositely charged head groups of dye and surfactant provides micellar stabilization without the need for a high degree of counterion binding. The reduced charge repulsion in the mixed micelles containing a small excess of surfactant permits the micelles to exist at much lower amphiphile concentrations than are possible for homomicelles. It is possible that these have larger sizes and different structures than the mixed micelles having a large excess of surfactant.[3] Binding of counterions to mixed micelles containing a small excess of surfactant should give rise to competition between the added counterions and the sulfonate head groups for the cationic head groups so that at a constant, low S/D ratio, it was anticipated that increasing counterion concentrations could change the structure of the micelles. The change should be detectable with the kinetic probe. It also seemed possible that hydroxide ion, acting as a counterion as well as a reacting ion, should be able to effect similar changes. To our knowledge, no such effect has been reported in the studies of micellar effects on base-catalyzed ester hydrolysis.

Experimental Section

The samples of the dye acetate and CTAB were the same as described previously.[2] The hydrolysis rates were measured at 25° by the stopped-flow method. Two methods of preparing the dispersions prior to introduction into the stopped-flow apparatus were investigated. In the first, aliquots of a 2–3 × 10^{-4} *M* ester stock solution were added by pipet with stirring to about 20 ml of the CTAB solution in 25-ml volumetric flasks and water was added to the mark. The resulting dispersions, containing 2.5 × 10^{-5} *M* ester, were mixed with the electrolyte–hydroxide solutions in the stopped-flow apparatus. In the second method, solutions of CTAB and the alkali halide salts were first allowed to equilibrate before adding aliquots of the ester stock solution, and these dispersions were mixed with alkali alone in the stopped-flow apparatus. Small but significant differences in the kinetic measurements were obtained by the two methods. Since the first gave better precision, it was used to obtain the results reported here.

Pseudo-first-order rate constants for hydrolysis were obtained from the slopes of the initial linear segments of plots of ln (A_∞ − A) as a function of time, where A_∞ is the final absorbance at 518 nm (product band) after 10 or more half-lives, and A is the absorbance at the same wavelength at some time during the hydrolysis. The rates of the rapid micellar reequilibration accompanying the addition of salts to dispersions in water were measured by stopped flow near the ester absorption maximum (380 nm) by mixing CTAB-acetate dispersions in water from one syringe with electrolyte solutions from the second syringe. A relaxation of 2-msec duration due to a refractive index change was observed when water was mixed with 0.4 *M* sodium chloride. The absorbance change of 0.003 from this relaxation was negligibly small compared to the change accompanying micellar reequilibration.

Results and Discussion

Spectral Changes. The effect of increasing concentrations of potassium fluoride and sodium chloride on the absorption maximum of the acetate in micelles at low stoichiometric S/D ratios is shown in Figure 1. The red shifts of the absorption maximum are identical with the changes obtained by increasing the surfactant concentration at constant ionic strength.[2] There is also a progressive increase in absorptivity of the micelle-bound ester with increasing ionic strength. The relative effectiveness of the counterions in promoting

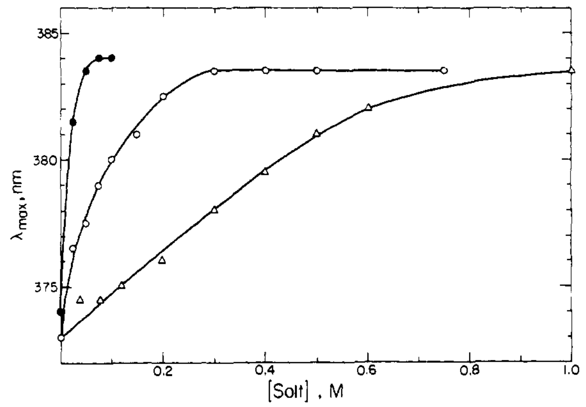


Figure 1. The effect of added salts on the position of the ester absorption maximum in CTAB micelles: (○) sodium chloride, S/D = 4; (△) potassium fluoride, S/D = 4; (●) sodium chloride, S/D = 8. $[\text{Ester}]_t = 1.25 \times 10^{-5}\ M$.

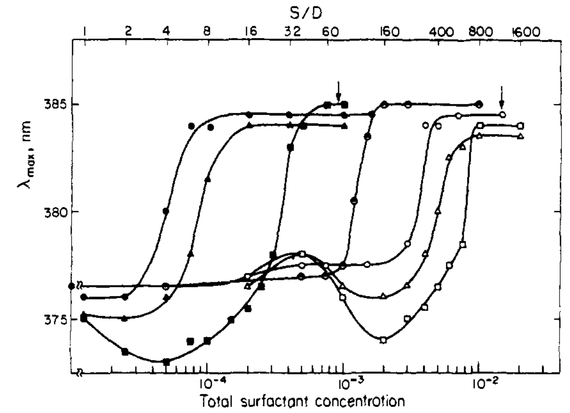


Figure 2. The position of the ester absorption maximum as a function of surfactant concentration in solutions of various anions. [Ester] = $1.25 \times 10^{-5}\ M$. Ionic strength = 0.1 except where noted. Open data points for dodecyltrimethylammonium bromide; filled data points for CTAB: (□ and ■) no added salt; (○ and ●) chloride; (△ and ▲) fluoride; (◒) 0.01 M thiocyanate.

the red shift parallels their tendency to bind to positively charged micelles and polyelectrolytes.[4,5]

Figure 2 shows the effect of CTAB and DTAB on the absorption maximum of the acetate in solutions of various anions at constant ionic strength. The vertical arrows indicate the cmc's for surfactant homomicelles in the absence of added electrolytes. The plots show that a given concentration of a particular electrolyte causes a larger lateral shift of the profile in the CTAB mixed micelles than in those from DTAB. The effectiveness of the counterions in shifting the plots follows their position in the lyotropic series. Thiocyanate ion caused precipitation of CTAB.

The spectral shifts are not consistent with the formation of counterion-stabilized CTAB homomicelles at the expense of the mixed micelles whereby free dye ester is released to solution. The results are consistent with the addition of surfactant from solution to form counterion-stabilized mixed micelles having a higher surfactant content than is possible at a given S/D ratio in the absence of added counterions. The red shift of the absorption maximum is the result of the changing microenvironment accompanying the addition of surfactant to the micelle.[2]

Kinetic Measurements. Our procedure for studying the effect of salts on the hydrolysis kinetics involved the mixing of CTAB-ester dispersions in water with the electrolyte solutions under the conditions of the rapid and efficient mixing of the stopped-flow method. Use of this method requires that the rates of reequilibration of the mixed micelles upon suddenly raising the ionic strength be much faster than the hydrolysis rates of ester in the reequilibrated micelles. To check this, we took advantage of the small spectral changes that accompany reequilibration (Figure 1) and measured the rates of change in absorbance of the ester band that occurred when a dispersion in water was mixed with alkali or salt solutions to give final ionic strengths of 0.05, 0.10, and 0.20. The rates of micellar reequilibration had half-times of 2 to 12 msec. The first-order rate constants were larger by factors of 40 or more than the fastest hydrolysis rates measured at the same S/D ratio. The hydrolysis rates reported here are those of the ester in reequilibrated micelles following introduction of electrolyte.

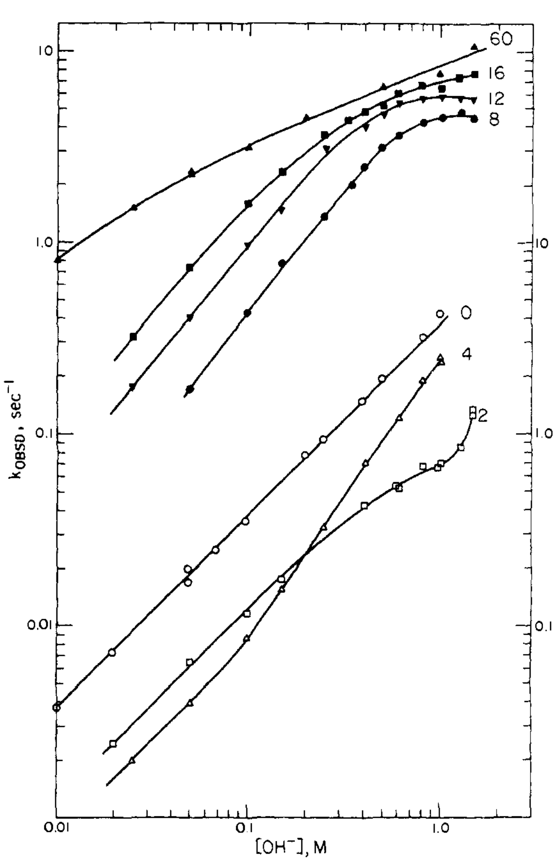


Figure 3. Log-log plot of the pseudo-first-order rate constant for hydrolysis of the acetate as a function of hydroxide concentration. Open data points refer to right-hand ordinate and filled points to left-hand ordinate. S/D ratios are shown at the right of the plots; $t = 25°$.

Effect of Hydroxide Ion. The rate expression for the base-catalyzed hydrolysis of the dye ester is given by eq 2.

$$\text{rate} = k_2[\text{ester}][\text{OH}^-] = k_{\text{obsd}}[\text{ester}] \qquad (2)$$

Under the conditions of our experiments, the hydroxide concentration remains constant throughout a given run. Accordingly, a plot of log k_{obsd} as a function of log $[\text{OH}^-]$ should be linear with a slope of unity. Curve 0 of Figure 3 shows such a plot for the hydrolysis of the acetate in the absence of CTAB for a 100-fold change of hydroxide concentration. The line through the data points is drawn with the theoretical slope of 1. In the range $[\text{OH}^-] \leq 0.1$ the ionic strength was maintained constant at 0.1 by addition of the necessary concentrations of potassium fluoride. In the range $0.05 < [\text{OH}] < 1.0$, the ionic strength varied with the hydroxide concentration. Since all values of k_{obsd} are fitted to a single line, the hydrolysis rate is independent of ionic strength. This conclusion was confirmed by showing that the rate at constant hydroxide concentration was independent of added sodium chloride at concentrations up to 0.5 M in the absence of CTAB.

Figure 3 shows that quite different results are obtained when hydrolysis rates are measured as a function of hydroxide concentration in the presence of CTAB. Values of k_{obsd} are only proportional to hydroxide concentration at low hydroxide concentrations and low S/D ratios. The deviations from a first-order dependence for hydrolysis in the micelles must arise from changes in structure or composition of the mixed micelles with counterion concentration where, here, hydroxide serves as a counterion and a reacting ion. If the nature of the micelle and the hydroxide partition coefficient were independent of concentration at a given S/D ratio, the rate should be proportional to the total hydroxide concentration. If, however, an increased hydroxide concentration can stabilize micelles having a higher CTAB content at constant S/D, the fraction of the total concentration that is partitioned into the micelle domains will increase. In this case the hydrolysis rate in the micelles will increase more rapidly than expected from the increase in the total hydroxide concentration. This is the observed result at an S/D ratio of 4 at high hydroxide concentration and at S/D ratios of 8 to 16 at low concentrations. The values of $k_{\mathrm{obsd}}/[\mathrm{OH}^-]$ could also increase with hydroxide concentration if the micellar structure were modified to make the reaction sites more accessible (see below).

Figure 3 shows that at S/D = 2, values of $k_{\mathrm{obsd}}/[\mathrm{OH}^-]$ decrease in the range $0.1 < [\mathrm{OH}^-] < 1.0$ M and then increase at $[\mathrm{OH}^-] > 1.0$ M. This behavior is also consistent with the proposal that increasing counterion concentration increases the CTAB content in the micelles at a given S/D. Figure 3 of ref 2 shows that at a constant hydroxide concentration of 0.1 M, increasing the S/D ratio from 2 gives a rate decrease initially which is followed by an increase. At this low S/D ratio, increasing the hydroxide concentration from 0.1 to 1.5 M at constant S/D is about equivalent to increasing the S/D ratio from 2 to 5 at a constant hydroxide concentration of 0.1 M.

Further evidence for micellar restructuring by hydroxide counterion is indicated by the very rapid change in absorbance of the acetate band following the mixing of a dispersion in water with 0.2 and 0.4 M potassium hydroxide in the stopped-flow apparatus. This change occurred at rates similar to those obtained with nonreacting electrolytes and was essentially complete before the onset of the slower absorbance change due to hydrolysis.

The saturation of rates at high hydroxide concentrations indicates that micellar alteration and counterion partitioning become saturated. The dependence of k_{obsd} on hydroxide concentration at S/D = 60 is anomalous in that a low apparent kinetic order with respect to hydroxide concentration is found over a 150-fold range of concentrations. The CTAB concentration at S/D = 60 is near the cmc for homomicelles in the absence of added electrolyte (9.20×10^{-4} M), so the mixed micelles present at this S/D ratio should closely resemble normal CTAB micelles. By analogy with other alkyltrimethylammonium micelles, it is expected that CTAB micelles should undergo considerable change in micellar molecular weight and shape within the concentration range of electrolyte covered here.[3,6] The kinetic effects of such transitions are unknown. It is also likely that the increase in ionic strength increases the number of micelles, and that some of these will contain no ester. The homomicelles will compete for hydroxide ion with the mixed micelles, resulting in a smaller increase in rate than would occur if each micelle contained ester.[7]

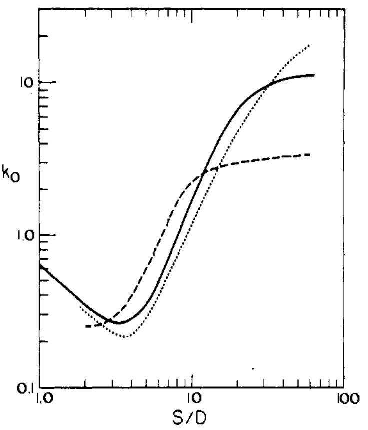


Figure 4. Relative rate constants for hydrolysis of the acetate as a function of S/D ratio at hydroxide concentrations of 0.02 M (···), 0.10 M (—), and 0.50 M (- - -); t = 25°.

Since the rates at constant S/D ratios show a complex dependence on hydroxide concentration, profiles of rate constant as a function of surfactant concentration or of S/D will be different for various hydroxide concentrations. Several such profiles were constructed from the data of Figure 3 and are shown in Figure 4. The reference rates are the rates at the same hydroxide concentration in the absence of CTAB. It is seen that increasing the hydroxide concentration shifts the profiles to lower CTAB concentrations, in accord with the hypothesis that the increased counterion concentration produces micelles of higher surfactant content at a given S/D ratio. In addition, the rate accelerations at high S/D ratios are diminished at the higher hydroxide concentrations. This is due in part to the saturation effects shown in Figure 3.

Effect of Competing Counterions. The kinetic effect of added alkali halides on the hydrolysis in mixed micelles formed at low S/D ratios depended on the method of preparing the dispersions. Dispersions prepared by adding a stock solution of dye ester into a stirred solution of CTAB that had been equilibrated with salt gave poorly reproducible rates. Curved first-order rate plots indicated considerable polydispersity. Dispersions prepared by adding the ester stock solution to a solution of CTAB alone (below the cmc) followed by mixing with the halide-hydroxide mixture in the flow apparatus gave more reproducible and slightly lower initial rates. The first-order rate plots obtained by the second method indicated less polydispersity than those obtained by the first method. At low S/D ratios and low ionic strengths the second method gave standard deviations for replicate determinations that were 10% of the average or less, which is poorer precision than that obtained by the same mixing method in the absence of added halides. The precision improved with increasing ionic strength. Whereas the second method was adopted as an expedient, it is realized that either method gives kinetically controlled, nonequilibrium micellar states, so the results must be interpreted with this in mind.

Figure 5 shows the effect of added counterions and of hydroxide on the second-order rate constants for hydrolysis at several S/D ratios. The effects of varying the halide ion concentration at constant hydroxide concentration and of varying both concentrations at constant ratio are shown. The maxima in the plots become progressively smaller and move to lower ionic strengths as the S/D ratio is increased, disappearing at S/D > 16. To our knowledge, there has been no report of such rate maxima in bimolecular reactions involving nucleophilic anions in cationic micelles. The inhibition of such reactions by anionic counterions has been studied.[4,7,8] Most kinetic studies have been made at surfactant concentrations near and above the cmc for surfactant homomicelles, where we find no maximum.

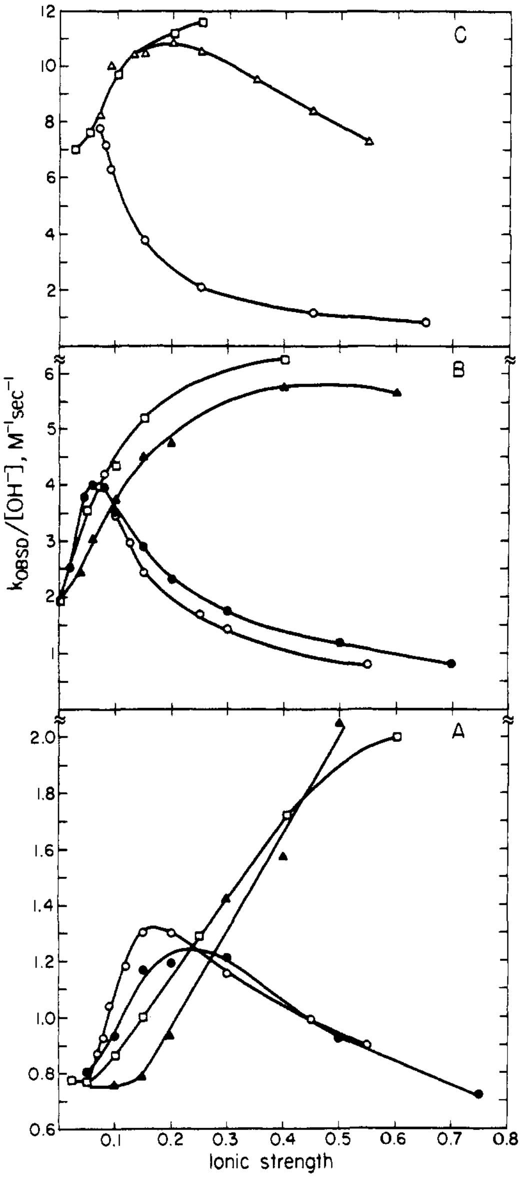


Figure 5. The effect of added salts on the second-order rate constants for hydrolysis of the acetate. Open data points: salt concentration varied at a constant $[OH^-] = 0.05$ M. Filled data points: salt and hydroxide concentration both varied at a constant concentration ratio of one. (□) hydroxide; (○ and ●) sodium chloride; (△ and ▲) potassium fluoride; $t = 25°$. A, S/D = 4; B, S/D = 8; C, S/D = 12.

Binding selectivity alone does not explain the maximum in the second-order rate constants. Such considerations would require a reversal in selectivity at the maximum, whereby hydroxide would be more strongly bound at low ionic strength. In the closely related process of ion exchange on polyelectrolytes, a given selectivity is not reversed but is reinforced at low electrolyte concentration.[9] A more plausible explanation for the increase in rate constant may lie in structural changes in the micelles. Charge shielding by added electrolyte permits the incorporation of more CTAB into the micelle than can be tolerated in the absence of the electrolyte. The resulting repulsion of cationic head groups should give a looser structure than exists in the absence of added electrolyte and should make the reaction sites more accessible to hydroxide ion. The increase in CTAB content will also increase the surface potential and the counterion binding. When the added electrolyte contains only hydroxide as the anion, or contains the weakly bound fluoride, the increases in the second-order rate constant continue to high ionic strengths. When the added electrolyte contains a more strongly bound, competing anion, the rate maximum results. Apparently, the structures of the surfactant-poor micelles are extremely sensitive to small changes in ionic strength. As long as the surface potential is low, competitive counterion binding is less important than micellar reorganization at low ionic strengths. It is only after sufficient CTAB has been incorporated into the micelle to raise the potential that competitive binding becomes important enough to cause the rate constant to pass through a maximum. Since the suggested loosening of the micellar structure results from a competition between counterions and anionic head groups for the cationic head groups, its effect should be more important at low S/D ratios; it is not expected to be very important in micelles consisting predominantly of CTAB. On the contrary, increased charge shielding in cationic homomicelles should give a tighter structure, by analogy with polyelectrolyte solutions.

Comparison of the effect of sodium chloride on the spectral shifts of the bound ester (Figure 1) and on the hydrolysis rates (Figure 5) shows that the rate increases and the spectral shifts occur in the same range of ionic strengths. This confirms that the rate increases result from significant structural changes in the micelles that produce new microenvironments for the substrate.

Bunton and his coworkers have observed similar rate accelerations by added salts in unimolecular reactions catalyzed by cationic micelles.[10,11] In these cases counterion competition is not a factor and the total effect can be ascribed to changes in micellar structure.

Addition of sodium chloride to dispersions prepared at low S/D ratio suppresses the aging effects observed in the absence of salt. Figure 3E of ref 2 shows that dispersions prepared at S/D = 8 in water undergo structural changes over a 4.5 hr period prior to crystallization that are detected by changes in the hydrolysis rate of incorporated ester. At the same S/D ratio but in the presence of 0.1 M sodium chloride, no change in rate was observed over the same period. This result is consistent with the other evidence that the added salt stabilizes micelles with a higher CTAB content than exists in water at the same S/D ratio. We have shown that aging effects are diminished with increasing S/D ratios in the absence of added salt.[2]

Nonequilibrium Micellar States. There is abundant kinetic evidence that the monomer-micelle equilibrium is rapidly established. Relaxation times in the millisecond time scale have been determined by perturbing the micellar equilibrium with a temperature jump,[12,13] dilution from above to below the cmc,[14] mixing oppositely charged amphiphiles,[1] and by changing ionic strength (present paper). The systems studied include cationic and anionic micelles with and without ionic indicator dyes. Evidence from line widths in NMR spectra indicates still faster relaxation times.[15] There is also abundant evidence that some micellar solutions formed by the rapid aggregation of monomeric amphiphiles consist of micelles in kinetically controlled, nonequilibrium states or distributions, and that long periods are required to achieve final micellar equilibrium.[16-19] Nash has offered a plausible explanation for the apparent rate paradox by pointing out that once a solution consists almost entirely of micelles in a nonequilibrium distribution, the rate of reaching the equilibrium distribution may be slow if, on the average, about as many monomers enter a given micelle as leave it. This could result in a slow formation of new micelles from old ones.

In our systems of aggregates of oppositely charged amphiphiles, the final state at low S/D ratios consists of insoluble crystalline salts in equilibrium with solutions of monomeric and/or aggregated amphiphiles. Since it usually takes days for final equilibrium to be reached, we have been interested in studying the nonequilibrium micellar state, because many studies involving the interactions of oppositely charged dyes and surfactants may have been made on nonequilibrium states. As we show in the present papers, the properties of the aggregates may depend on their past history, including the method of preparation and the time of aging, so the diversity of opinion regarding the nature of the aggregates should not be surprising (references cited in ref 2). Our results are reproducible when we use the specified methods, but we are dealing with metastable states on the time scale of most of our observations. We have shown that the properties of the metastable state can be governed by the route to the state.

When our dispersions are prepared at a dye concentration of 2.5×10^{-5} M and at low S/D ratios, the solubility product of the dye-CTAB salt is exceeded and the formation of crystallites (thermodynamic state) can compete to a small extent with micelle formation (kinetic state).[2] Once the micelles are formed, equilibration is very slow. The light-scattering intensity from the micellar solutions at low S/D ratios is greater than that from solutions containing CTAB at concentrations near the cmc, so the number of micelles or the micellar molecular weights in the very dilute solutions must be appreciable and must account for most of the ester present. Under these conditions the concentrations of monomeric ester must be less than the solubility product for the salts so that growth of new crystal nuclei probably does not occur from the bulk solution but by reorientation within the mixed micelles.

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Luminescence of Heterobischelated Complexes of Iridium(III). I. Resolution of the Multiple Emissions of *cis*-Dichloro-1,10-phenanthroline-5,6-dimethyl-1,10-phenanthrolineiridium(III) Chloride

Richard J. Watts,* Marty J. Brown,[1] B. G. Griffith,[1] and J. S. Harrington

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received January 6, 1975*

Abstract: Luminescence decay curves of *cis*-dichloro-1,10-phenanthroline-5,6-dimethyl-1,10-phenanthrolineiridium(III) chloride have been determined as a function of emission wavelength. A two-level model has been used to decompose each decay curve into a sum of two exponentials with lifetimes of 9.5 and 65 μsec. From this analysis, the total emission spectrum has been decomposed into two component spectra. The levels giving rise to these spectra are split by 200–300 cm^{-1}, and appear to arise from $d\pi^*$ and $\pi\pi^*$ orbital parentage. Analysis of luminescence decay curves as a function of excitation wavelength indicates that upper states of $d\pi^*$ parentage tend to feed the $d\pi^*$ emission and states of $\pi\pi^*$ parentage feed the $\pi\pi^*$ emission. On the basis of these results we suggest the following selection rules for radiationless transitions in heavy-metal complexes: $d\pi^* \leftrightarrow d\pi^*$; $\pi\pi^* \leftrightarrow \pi\pi^*$; $d\pi^* \nleftrightarrow \pi\pi^*$.

Numerous studies of energy transfer processes among the electronic excited states of highly symmetrical complexes of d^6 metal ions at 77 K suggest that radiationless transitions from upper electronic excited states to the lowest excited state occur with nearly 100% efficiency.[2a] Experimental evidence now indicates that this "lowest excited state" is often a manifold of thermally equilibrated levels which are split by energies of less than kT.[2b] Studies of photochemical processes in highly symmetrical complexes of d^6 metal ions also indicate that the lowest excited state is often responsible for the photochemical activity regardless of which state is initially excited.[3] There is, however, mounting evidence that the lowest excited state of some d^6 heavy-metal complexes is not always populated with 100% efficiency.[3] Studies of both photochemical[4] and photophysical[5] energy transfer processes in certain Rh(III) complexes suggest that the lowest excited states may not be efficiently coupled to higher states by radiationless processes. Preliminary studies of photophysical energy transfer processes in complexes of Ir(III) with low symmetry also suggest that electronic excited states may not be coupled to one another via radiationless pathways in these systems.[6]

Although the occurrence of light emission from several nonequilibrated states of heavy-metal complexes is a rather

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