# Isomerizable N-Alkylmerocyanine Dyes as Probes of Micellar Solubilization Sites

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The thermal *cis* to *trans* isomerization of N-alkylmerocyanine dyes is catalyzed by both cationic and anionic micelles. The catalysis by cationic micelles of hexadecyltrimethylammonium bromide (CTABr) increases markedly with substrate N-alkyl group length and is exceptionally pronounced for N-alkyl groups larger than pentyl. Rate data fit the pseudophase model of micellar catalysis for CTABr concentrations between 0.005 and 0.1 M and binding constants ( $K_s$ ) and micellar rate constants ( $k_m$ ) were evaluated. Both  $K_s$  and  $k_m$  increased dramatically as the N-alkyl group was varied from N-methyl to N-pentyl so that the increase in catalysis with substrate hydrophobicity is due not only to increased substrate binding to the micelle but also to enhanced reactivity within the micelle. At CTABr concentrations greater than 0.1 M,  $k_m$  is not constant but increases, reflecting changes in micelle structure at high surfactant concentration. Eyring activation parameters were determined for the overall rate constant. The increase in reactivity as a function of N-alkyl group hydrophobicity was shown to be due primarily to an increase in  $\Delta S^*$ .

## Introduction

The association of surfactants in aqueous solution to form micelles has long been an area of active interest and research. One of the most interesting properties of micelles is their ability to catalyze certain chemical reactions. Review articles cite numerous examples of reaction rates accelerated in the presence of micelles<sup>1-4</sup> with rate increases of 5- to 100-fold over reactions in the absence of surfactants. Rate increases on the order on 100 000-fold have also been noted.<sup>5</sup>

For a reaction catalyzed by micelles, the observed rate constant  $(k_{obs})$  depends upon the surfactant concentration  $(C_D)$  in a manner that reveals the molecularity of the reaction.<sup>4</sup> For unimolecular reactions  $k_{obs}$  plotted against  $C_D$  rises as a sigmoidal curve culminating in a rate plateau.<sup>6,7</sup> At low  $C_D$ , below the critical micelle concentration (cmc), little or no catalysis is observed. At the cmc,  $k_{obs}$  increases dramatically as a result of micelle formation. An increase in  $C_D$  above the cmc effects a sigmoidal increase in  $k_{obs}$  up to a maximum level, at which point all of the substrate has been incorporated into the micelles. Additional surfactant causes little or no change in rate because the additional micelles do not contain substrate. Bimolecular reactions exhibit a similar behavior just above the cmc but  $k_{obs}$  is not constant at high  $C_D$  and typically decreases at high  $C_D$  because of the partitioning of the reactants into separate micelles.<sup>1,2,4</sup>

Two explanations have been proposed to account for micellar effects upon chemical reactions. The first, and most widely expressed, is catalysis by induced association. This is seen in bimolecular reactions when the effective concentrations of reactants in solution are increased within the micellar pseudophase causing an increase in reaction rate relative to that in the absence of surfactant.

The second mechanism is catalysis by substrate destabilization or transition-state stabilization. This arises when the substrate is forced into an environment which destabilizes the reactant ground state relative to the transition state. One example is the decarboxylation of 6-nitrobenzisoxazole-3-carboxylic acid (NBA) in micellized cetyltrimethylammonium bromide (CTABr).<sup>7</sup> Binding of NBA to CTABr micelles forces the molecule into a less polar environment that destabilizes the reactant ground state with its localized charge more than the transition state with its more delocalized negative charge. The result is a 95-fold increase in the rate of decarboxylation of NBA in the presence of micellized CTABr. The free energy changes are generally interpreted in terms of polar and electrostatic interactions between the micelle and reactant ground and transition states.

Catalysis by substrate destabilization is often accompanied by catalysis by induced association in second- and higher-order reactions. Study of the former process is complicated in these systems because one must consider the distribution of two or more reactants between micellar and aqueous environments. On the other hand, unimolecular processes are ideal for investigation of catalysis by substrate destabilization because one needs only to consider distribution of one reactant between the two environments. Despite this theoretical advantage relatively few firstorder reactions catalyzed in the presence of micelles have been studied in detail.

The primary purpose of this work was to examine the effects of micellar solutions upon the thermal *cis*- to *trans*-isomerization reactions of a series of *N*-alkylstilbazolium betaines (I). The *trans* members of this series of compounds are also known as Brooker or merocyanine dyes and have been studied by many because of their remarkable solvatochromism.<sup>8,9</sup> They have been traditionally considered resonance hybrids between uncharged quinone forms (Ia) and dipolar (Ib) forms. The *cis*  $\rightarrow$  *trans* 



reaction system, originally reported by Steiner and co-workers,<sup>10</sup> involves a one-way thermal isomerization of N-methylmerocyanine dye. The dye, originally in the *trans*-configuration, can be partially isomerized to the *cis*-conformation by UV-irradiation in acidic solution. The *cis*-dye, upon deprotonation, thermally isomerizes back to the original *trans*-conformation. NMR work has shown that the oxygen is protonated in the conjugate acid.<sup>10,11</sup>



This system confers the advantage that a homologous series of substrates can be compared. Differences in N-alkyl chain length confer differences in micelle binding affinity, yet these structural differences should have little direct effect (e.g. by induction) on the electronic structure of the ground and transition states in the absence of micelles. Another advantage is that the interaction of merocyanine dyes with micelles can also be studied spectroscopically. The visible spectra of merocyanine dyes are strongly dependent on solvent polarity.<sup>9</sup> The red shifts of several *trans*-*N*-alkylmerocyanine dyes in cetyltrimethylammonium bromide (CTABr) and in sodium dodecyl sulfate (SDS) solutions were investigated by Minch and Shah.<sup>12</sup> The series of *trans*-dyes were shown to bind to micelles with significant differences in binding affinity, and the average environment around the aromatic portion of the dye became less polar with increasing alkyl chain length.

Preliminary reports from our laboratory have shown that the dye cis- to trans-isomerization reactions are dramatically increased in the presence of CTABr micelles.<sup>11</sup> Steiner and others have shown that the thermal isomerization reactions of N-methyl- and N-hexadecylmerocyanine dyes are profoundly sensitive to solvent polarity.<sup>13</sup> In general, solvents of decreasing polarity were found to lower the  $\Delta G^{*,13a}$  In this paper we call attention to several important aspects of this catalysis. Cationic micelles of CTABr and anionic micelles of sodium dodecyl sulfate both catalyze the isomerization. The magnitude of catalysis by CTABr can be exceptionally large. The result of added CTABr can be analyzed in terms of the pseudophase model for micellar catalysis in which the reaction rate in the micelle  $k_{\rm m}$  and the binding constant to the micelle  $K_s$  are measured.<sup>3</sup> The catalysis is exceptionally sensitive to subtle changes in micelle structure at high surfactant concentration. At [CTABr] > 0.1 M,  $k_{\rm m}$  is no longer constant and increases with added surfactant. By varying the nature of the N-alkyl group, from N-methyl to N-hexyl, we have found that increasing the hydrophobicity of these solubilized substrates increases both  $k_{\rm m}$  and  $K_{\rm s}$ . Usually the rate constants of completely bound substrates are independent of the length of a pendant chain on the substrate. The Arrhenius plots are linear,<sup>14</sup> and we are able to compare the Eyring activation parameters for solubilized substrates of different hydrophobicity.

## **Experimental Section**

**Materials.** The *trans*-merocyanine dyes used in this work were previously prepared by Minch and Shah.<sup>12</sup> CTABr (Aldrich) was purified according to the method already described.<sup>12</sup> All other reagents were of high commercial grade and were used without further purification. Distilled, deionized water was used in all aqueous preparations.

**Photoisomerization of Merocyanine Dyes.** Stock solutions containing  $2 \times 10^{-5}$  M *trans-N*-alkylmerocyanine dye and  $1 \times 10^{-3}$  M HCl in water were irradiated for 2 h in front of a 700-W medium pressure mercury vapor lamp or allowed to stand in sunlight until a minimum absorbance near 373 nm was reached. Photoisomerization was essentially complete within the first 10 min of irradiation in front of the mercury lamp. The decrease in absorbance corresponded to the photoisomerization to the *cis*-dye in acidic solution.<sup>10</sup> These solutions were stable for periods of 6 months or longer under normal laboratory conditions.

**Preparation of Surfactant-Dye Solutions.** Surfactant-dye solutions were prepared by dissolving weighed portions of purified CTABr in the photoisomerized *cis*-dye stock solutions. Gentle heating above 25 °C was necessary to fully dissolve the CTABr in some cases. Solutions were stored in airtight containers at room temperature. Solutions more than 1 month old were discarded.

**Kinetic Measurements.** All reactions were followed on a Varian Model 635 Techtron UV-vis spectrophotometer equipped with a water-jacketed cell compartment. Temperature was maintained within the cell to  $\pm 0.1$  °C using a Model 2095 Forma Scientific

water bath circulator. Temperature measurements were performed with a wire thermistor immersed in a cuvette within the light path of the spectrophotometer. The thermistor was thermocoupled to a Model BAT-12 digital readout thermometer (Bailey Instruments Inc.).

Reactions with and without surfactant were initiated with the addition of 20 µL of 0.3 N NaOH into 3.0 mL of cis-dye stock solution within a thermally equilibrated cuvette within the light path of the spectrophotometer. The thermistor was removed from the reaction mixture just prior to addition of base and placed into a cuvette of water thermally equilibrated within the same waterjacketed cell compartment as the sample cell. This was done to ensure that the temperature did not fluctuate more than  $\pm 0.1$  °C during the reaction. Rapid mixing, following addition of base, was assured with the use of a Teflon plunger designed to fit within the cuvette. All reactions were followed at 444 nm based upon maximum wavelengths of absorbance for the trans-isomer.<sup>12</sup> Reactions were followed for at least 10 half-lives until a maximum absorbance  $(A_{max})$  was reached. All reactions were followed by recording data by hand except for reactions with half-lives shorter than 5 s, which were followed on a chart recorder.

Protolytic equilibria between the acid and base forms of the dye are established within microseconds, but one cannot disregard such equilibria when observing the kinetics at a pH where significant levels of the acid form are present. Under such conditions the observed rate reflects the presence of both species.

$$k_{\rm eff} = \frac{[cis-I]}{[cis-I] + [cis-I-H^+]} k_{\rm cis \to trans}$$
(1)

To avoid this complication we initiated the reaction under conditions where the equilibrium is completely shifted to the basic form. The titration curves for  $5 \times 10^{-5}$  M trans-N-methyl dye with and without surfactant were determined by monitoring the absorbance at 450 nm as a function of pH. The pH was adjusted by adding various amounts of ammonium chloride solution to a sodium hydroxide solution of the dye. With either water or 0.05 M CTABr the titration curve inflection point corresponds to an approximate  $pK_a$  of 8.4. With 0.05 M SDS the titration curve is shifted to higher pH for an approximate  $pK_a$  of 11.6. Similar surfactant effects on phenol deprotonation have been observed before.<sup>3</sup> The profound suppression of substrate deprotonation by SDS ruled out a convenient study of catalysis by this anionic surfactant. With CTABr the addition of enough NaOH solution to bring the pH to 10 or higher gave essentially constant rates up to a pH of 12 for the methyl dye. Similar amounts of NaOH were added to examine effects of base upon N-ethyl- and N-npentylmerocyanine dye isomerization rates in 0.05 M CTABr solutions. Initiation of reaction was signaled, in all cases, by a sharp color change from a pale yellow to a dark yellow-orange. Because the reaction solutions had initial HCl concentrations of  $1 \times 10^{-3}$  M and were unbuffered, the addition of less than an equivalent of NaOH did not lead to an observable rate.

Individual rate constants  $(k_{obs})$  were determined from the slopes of plots  $\ln(A_{max} - A)$  versus time. Lower weighting was given to values of  $\ln(A_{max} - A)$  near the end of reactions since they approached zero, thus lacking precision. In general, rates of reactions with half-lives greater than 5 s were defined by at least six points (and most by more than a dozen). Reactions with half-lives shorter than 2.5 s were considered too fast to yield accurate rate data by our methods. Reproducibility of rate constants was  $\pm 2\%$  for reactions using the same batch of stock solution. Between different batches of stock solutions, rate constants were reproducible to within  $\pm 4\%$ .

The reaction rate for the N-n-octylmerocyanine dye was too fast to measure by the conventional mixing methods described above, but rates in 0.028 M CTABr at  $25 \pm 1$  °C were followed by stopped flow addition of NaOH to an acidic solution of the *cis*-octyl dye. Results by this method were applicable only for

 TABLE I:
 Experimental Conditions and Estimated Uncertainties in the Measurement of Activation Parameters in 0.054 M

 CTABr for the Isomerization of N-Alkyl Dyes

| N-alkyl group | temp range, °C | no. of k-values <sup>a</sup> | correlation coeff <sup>b</sup> | slope $\pm ESD^c$ | intercept ± ESD <sup>c</sup> |
|---------------|----------------|------------------------------|--------------------------------|-------------------|------------------------------|
| methyl        | 25.0-48.2      | 16                           | 0.9984                         | -11 038 • 167     | $31.400 \pm 0.528$           |
| ethyl         | 25.0-37.4      | 7                            | 0.9984                         | $-10418 \pm 261$  | $29.892 \pm 0.850$           |
| n-propyl      | 25.0-37.4      | 12                           | 0.9952                         | -10 858 ± 336     | 31.729 ± 1.09                |
| n-butyl       | 25.1-35.0      | 5                            | 0.9980                         | -10 593 ± 390     | 32.094 ± 1.28                |
| n-pentyl      | 25.0-35.0      | 6                            | 0.9993                         | -11 925 ± 195     | $36.982 \pm 0.640$           |
| n-hexyl       | 25.8-29.3      | 3                            | 0.9999                         | -11 907 🏚 10      | $37.331 \pm 0.033$           |

<sup>a</sup> Number of rate constants used to determine the slope and intercept of the Arrhenius plot for data in Table V. <sup>b</sup> Least squares correlation coefficient for Arrhenius plot. <sup>c</sup> ESD, estimated standard deviation based on least squares fit analysis.



Figure 1. Effect of CTABr on the isomerization of various N-alkylmerocyanine dyes at 35.0 °C. The squares correspond to experimental rate constants for (increasing order) methyl-, ethyl-, n-propyl-, n-butyl-, and n-pentylmerocyanine dyes. The curves connect theoretical rate constants, as diamonds, calculated by the pseudophase model.

narrow temperature and CTABr concentration ranges and were not used to measure binding constants or kinetic parameters.

Changes in N-ethylmerocyanine dye concentrations, from 1.1  $\times$  10<sup>-5</sup> to 8.9  $\times$  10<sup>-5</sup> M, did not affect isomerization rates in 0.0545 M CTABr at 35 °C. On the basis of this result, it was assumed that all first-order rate constants, with or without surfactant, were independent of dye concentration.

**Thermodynamic and Activation Parameter Calculations.** Activation parameters were determined from Arrhenius plots of  $\ln(k)$  versus 1/T where T is the absolute temperature at which k was determined. Slopes and y-intercepts were evaluated from a linear least squares treatment of the rate data with equal weight given to each data point. Activation energies  $(E_a)$  were determined from values of the slopes, and frequency factors (A) were determined from values of the y-intercepts.<sup>14</sup> The temperature range, number of rate constants measured over this range, and the correlation coefficients of Arrhenius plots for all the dyes in 0.054 M CTABr are given in Table I. Free energies of activation  $(\Delta G^*)$ , enthalpies of activation  $(\Delta H^*)$ , and entropies of activation  $(\Delta S^*)$  were determined from values of  $E_a$  and calculated rate constants at 25 °C (from Arrhenius plots) according to transition-state theory.<sup>14</sup>

Determination of Binding and Micellar Rate Constants. Binding constants  $(K_s)$  and micellar rate constants  $(k_m)$  were evaluated according to the pseudophase model for micellar catalysis.<sup>1,3</sup> These parameters were calculated from the slopes and intercepts of plots of  $-1/(k_0 - k_{obs})$  versus  $N/(C_D - cmc)$ , where  $k_0$  is the rate constant in the absence of surfactant,  $k_{obs}$  is the observed rate constant,  $C_D$  is the detergent concentration, N is the micelle aggregation number, and cmc is the critical micelle concentration. Values for the cmc and the aggregation number for CTABr found in the literature<sup>3</sup> (9.4 × 10<sup>-4</sup> M at 25 °C and 61 at 25 °C, respectively). Least squares best fit lines were drawn through data points corresponding to  $C_D$  ranging from 0.005 M to above 0.1 M CTABr.

Dipole Moment and Structure Calculations. Molecular mechanics MM2 and extended Hückel calculations were run with Tektronix Personal CAChe Molecular Modeling Software (Innovator+ version 3.0, CAChe Scientific) on a MacIntosh Quadra 950 computer. The dihedral angle search program of this software permits the systematic variation of one locked bond to yield a series of structures otherwise geometry optimized by the MM2 method. The dipole moment as a function of "ethylene" H-C-C-H dihedral angle was calculated by the following method. The geometry for the 180° trans-isomer was optimized by the MM2 method, to a convergence of 0.001 kcal/mol, before extended Hückel calculation of the dipole moment, using a STO-3G contraction set and a Wolfsberg-Helmholtz constant of 1.75. The dipole moment for all subsequent forms related by rotation about the H-C-C-H dihedral angle were calculated by the extended Hückel method after MM2 geometry optimization of each structure, with a locked dihedral angle, to within 0.001 kcal/mol. The structures for the cis- and trans-forms given in Figure 7 were optimized by this method. Calculations of dipole moments for all non trans dihedral forms without MM2 optimization are also discussed below.

#### Results

Effect of Surfactants on Dye Isomerization Rates. Figure 1 shows the effect of increasing CTABr concentration on the isomerization rates of the various N-alkylmerocyanine dyes. Below the cmc for CTABr (approximately  $1 \times 10^{-3}$  M at 25 °C),<sup>3</sup> little or no catalysis of dye isomerization rates was observed. Increasing CTABr concentration above the cmc caused marked increases in isomerization rates for all dyes studied. Isomerization rates approached maximum values at high surfactant concentrations. The effect of CTABr on reaction rate becomes more pronounced as the N-alkyl chain length is increased from methyl to n-octyl. The rate enhancements  $(k_{obs}/k_0)$  observed in 0.054 M CTABr at 35 °C are 38-fold for methyl, 83-fold for ethyl, 144-fold for propyl, 332-fold for butyl, 514-fold for pentyl, and 933-fold for hexyl. The octyl dye gives 1100-fold catalysis in only 0.028 M CTABr. Isomerization rates for the N-decylmerocyanine dye in CTABr solution (above the cmc) were too fast to follow even with our stopped flow apparatus. Anionic micelles of SDS were also catalytic. The rate enhancement for the methyl dye in 0.069 M SDS is 15-fold. Studies at higher SDS concentrations or with more hydrophobic substrates are complicated by the deprotonation equilibrium.

 TABLE II:
 Binding Constants for N-Alkylmerocyanine Dyes

 in Micellized CTAB and Rate Constants for Dye
 Isomerization Rates in Aqueous and Micellar Pseudophases

 at 25 °C
 °C

| N-alkyl group | $10^4 k_0,^a s^{-1}$ | $10^2 k_{\rm m},^{b} {\rm s}^{-1}$ | $K_{s},^{b} M^{-1}$ |
|---------------|----------------------|------------------------------------|---------------------|
| methyl        | 2.90                 | 3.27                               | 31.1                |
| ethyl         | 2.72                 | 6.35                               | 626.4               |
| n-propyl      | 2.9                  | 9.02                               | 614                 |
| n-butyl       | 3.04                 | 21.8                               | 1052                |
| n-pentyl      | 3.06                 | 30.5                               | 1819                |

<sup>a</sup> Rate constants determined in the absence of surfactant. <sup>b</sup> Binding constants  $(K_s)$  and micellar rate constants  $(k_m)$  determined from rate data, such as those illustrated in Figure 2, and the pseudophase model for micellar catalysis.

The results in Figure 1 were treated according to the pseudophase model for micellar catalysis.<sup>2</sup> In this model the observed rate constant is related to the concentration of micelles [M] by eq 2 which in turn is related to the surfactant concentration of eq 3. Results of this treatment are shown in Table II. Binding

$$k_{\rm obs} = \frac{k_0 + k_{\rm m} K_{\rm s}[M]}{1 + K_{\rm s}[M]} \tag{2}$$

$$[M] = \frac{C_{\rm D} - \rm cmc}{N} \tag{3}$$

constants  $(K_s)$  and micellar rate constants for dye isomerizations  $(k_m)$  were calculated by fitting data to the model (eq 4) while rate constants in the absence of surfactant  $(k_0)$  were determined experimentally. The data fit the model well, giving linear double

$$\frac{1}{k_0 - k_{obs}} = \frac{1}{[k_0 - k_m]} + \frac{1}{[k_0 - k_m]} \frac{1}{[C_D - cmc]} \frac{N}{K_s}$$
(4)

reciprocal plots of  $-1/(k_0 - k_{obs})$  versus  $N/(C_D - cmc)$  for CTABr concentrations between 0.005 and 0.1 M. Above this CTABr concentration, the rate constants are larger than predicted and the points for these concentrations fall below the line in double reciprocal plots. The more hydrophobic substrates do not show rate plateaus even at CTABr concentrations high enough to incorporate virtually all the substrate. The increase in rate constant above 0.1 M CTABr reflects the sensitivity of this isomerization to the changes in aggregation number and head-group packing that occur at high surfactant concentrations. The values of  $K_s$  and  $k_m$  are based on least squares lines, fit to all points including the high CTABr ones. Correlation coefficients were better than 0.995. Typical plots are shown in Figure 2 for the *N*-ethyl-, *N*-propyl-, and *N*-butylmerocyanine dyes in CTABr at 35 °C.

 $K_s$  values increase with increasing N-alkyl chain length or hydrophobicity of the dyes. Data in Table II also show increased  $k_m$  within the micellar pseudophase as the N-alkyl chain length is increased, while  $k_0$  values are essentially constant for the series of dyes.

Activation Parameters for Dye Isomerization. All dye isomerization rates typically showed strong temperature dependences. This result is illustrated in Figure 3 for N-butylmerocyanine dye isomerization rates in CTABr solution. An approximate doubling of rate constants was observed for each 5-day increase in temperature for all dye isomerization rates either in the presence or absence of surfactant. Temperature ranges studied were from approximately 25 to 40 °C and from 25 to 35 °C for the N-methyl through N-propyl dyes and for the N-butyl and N-hexyl dyes, respectively. At temperatures below 25 °C, CTABr tended to crystallize, while at the high-temperature limits, reaction rates were either too fast to follow or temperatures could not be accurately regulated. Figure 4 shows an Arrhenius plot for the isomerization of N-pentylmerocyanine dye in 0.054 M CTABr.



Figure 2. Double reciprocal plots for the isomerization rates in water  $k_0$  and in CTABr micelles  $k_{obs}$  as a function of reciprocal micelle concentration for  $(\Box)$  N-ethyl-,  $(\blacklozenge)$  N-propyl-, and  $(\Box)$  N-butylmerocyanine dyes at 35 °C. The lines correspond to the pseudophase model.



Figure 3. Temperature dependence of N-butylmerocyanine dye isomerization in 0.0531 M CTABr: 30.1 °C (□); 32.7 °C (△); 35.0 °C (○).

Data for all dyes fit the Arrhenius relationship quite well. Linear least squares analyses of  $\ln(k_{obs})$  versus 1/T gave correlation coefficients of at least 0.995 with most better than 0.998.

Activation parameters for N-methyl and N-pentyl dye isomerization rates in the absence of surfactant are given in Table III. Values of  $E_a$  and A were reinterpreted according to transitionstate theory<sup>14</sup> to yield more meaningful Eyring activation parameters. Data of Steiner and co-workers<sup>10</sup> for *N*-methylmerocyanine dye is included in Table III for comparison. Our results show essentially no differences in activation parameters for the *N*-methyl and *N*-pentyl dyes. These results are consistent with the fact that dye isomerization rates in the absence of surfactant ( $k_0$ , Table II) were essentially independent of *N*-alkyl chain length.

Table IV reveals the effect of increasing CTABr concentration upon activation parameters for N-methylmerocyanine dye isomerizations, but caution in interpretation is warranted since micellar effects on the energetics of substrate binding and reactivity cannot be separated using the available data. All CTABr concentrations studied were above the cmc. The increasing rate over the range of 0.054–0.2 M surfactant can only be analyzed in terms of overall activation parameters that reflect effects on both  $K_s$  and  $k_m$ . From eq 2 it can be shown that, at CTABr concentrations well above the cmc, the slope of the Arrhenius plot depends on both  $\Delta H^*_m$ and  $\Delta H^\circ_{s}$ .

slope = 
$$-\left(\frac{\Delta H^*_m + \Delta H^\circ_s}{R}\right) - \frac{\Delta H^\circ_s}{R}\left(\frac{[M]K_s}{1 + [M]K_s}\right) - T$$
 (5)

At higher surfactant concentration and with more hydrophobic dyes (larger  $K_s$ ) the second term reduces the contribution of  $\Delta H^{o_s}$ but under none of the conditions examined by us was the enthalpy due entirely to the  $\Delta H^*_m$ . The most obvious effect of micellized CTABr is a dramatic lowering (with respect to the reaction in the absence of CTABr) of the  $\Delta G^*$  by more than 2 kcal/mol. For the N-methyl dye, the decrease in  $\Delta G^*$  can be accounted for by a decrease in  $\Delta H^*$  of 4.6 kcal/mol which is partially offset by a decrease in  $\Delta S^*$  of 5 eu/mol relative to the activation parameters observed in absence of surfactant. Increases in CTABr concentrations from 0.054 to 0.199 M give an additional decrease in  $\Delta G^*$  due either to increases in  $\Delta S^*$  or decreases in  $\Delta H^*$ . The data do not reveal a smooth trend for either parameter over this CTABr concentration range.

Effect of Dye Hydrophobicity upon Activation Parameters. Activation parameters for various N-alkylmerocyanine dye isomerization reactions in 0.0545 M CTABr are presented in Table V. At constant micelle concentration  $\Delta G^*$  decreases as N-alkyl chain length is increased from a methyl to an *n*-pentyl group. In going from N-methyl to N-ethyl dye the increased reaction rates result mainly from a lowering of  $\Delta H^*$  for the N-ethyl dye relative to that of the N-methyl dye. The  $\Delta S^*$  for the N-ethyl dye. For the other dyes, the decrease in  $\Delta G^*$  results from large increases in  $\Delta S^*$  as the N-alkyl chain length is increased.

### Discussion

There is little question that these isomerization reactions are catalyzed by micelles since reaction rates were dramatically increased above the cmc for CTABr micelles. The behavior of N-alkyl dye isomerization rates in CTABr (Figure 1) is typical of first-order reactions catalyzed by micellar solutions.<sup>2,7</sup> Small rate enhancements below the cmc were observed, with this effect more pronounced in the presence of the more hydrophobic dyes. This effect may be due to the formation of catalytically-active premicellar aggregates or to a lowering of the cmc. It has been suggested that the more hydrophobic dyes can induce micellization of CTABr on the basis of shifts in absorption spectra of various N-alkylmerocyanine dyes.<sup>11</sup> Others have noted, in general, that increasingly hydrophobic solutes lower surfactant cmcs.<sup>15,16</sup>

The pseudophase model for micellar catalysis fits the data reasonably well for all dyes in CTABr solutions between 0.005 and 0.1 M. Deviations from the equation at low CTABr concentration result from the sensitivity of the model to the choice of cmc value.<sup>1,2</sup> As expected,  $K_s$  values increase with increasing



Figure 4. Arrhenius plot for the isomerization of N-pentylmerocyanine dye in 0.0544 M CTABr.

TABLE III: Kinetic Parameters for the *cis*- to *trans*-Isomerization of *N*-Alkyl Dyes in the Absence of Surfactant at 25  $^{\circ}C^{4}$ 

| N-alkyl<br>group    | 10 <sup>5</sup> k <sub>obs</sub> ,<br>s <sup>-1</sup> | $E_{\rm s},$ kcal/mol | ln(A)   | $\Delta G^*$ , kcal/mol | $\Delta H^{\bullet}$ , kcal/mol | $\Delta S^*,$<br>eu/mol |
|---------------------|---|-----------------------|---------|-------------------------|---------------------------------|-------------------------|
| methyl <sup>b</sup> |   | 28.6                  |         | 23.1                    | 28.0                            | 16.5                    |
| methyl              | 8.57  | 26.6 ± 0.5            | 35.4324 | 23.0                    | $26.1 \pm 0.5$                  | $9.9 \pm 1.6$           |
| n-pentyl            | 8.6   | $25.8\pm0.6$          | 34.114  | 23.0                    | $25.2\pm0.6$                    | 7.3 ± 1.8               |

<sup>a</sup> At least six or more values of k determined over a temperature range from 25 to 55 °C were used to determine values of  $E_a$  and A from Arrhenius plots. <sup>b</sup> Values reported by Steiner and co-workers<sup>10</sup> at 298 K.

dye hydrophobicity. This increase implies an increase in equilibrium distribution of the more hydrophobic dye molecules into the micellar pseudophase as hydrophobicity is increased. This behavior is commonly observed with increasingly hydrophobic solutes in micellar solution.<sup>2,17,18</sup>

Differences in  $K_s$  can be better understood using the treatment of Bunton and Sepulveda.<sup>19</sup> In their treatment, the free energy of transfer from water to micelle  $(\mu_M - \mu_W)$  is assumed to be the sum of free energies of transfer of the alkyl group  $(\Delta \mu_R)$  and the remainder of the molecule  $(\Delta \mu_A)$ . The  $\Delta \mu_R$  was further considered to be a sum of equal and independent contributions from each methylene (or methyl) group  $(\Delta \mu_C)$ . The above values may be determined from the following equation:

$$\mu_{\rm M} - \mu_{\rm W} = \Delta \mu_{\rm A} + n \Delta \mu_{\rm C} = -RT \ln(55.5) - RT \ln(K_{\rm s}) \quad (6)$$

where *n* is the total number of methyl and methylene carbons in the *N*-alkyl chain. A plot of *n* versus  $\mu_M - \mu_W$  is given in Figure 5. A line through the points for the three most hydrophobic substrates corresponds to values of  $\Delta\mu_C$  and  $\Delta\mu_A$  of -330 and -5400 cal/mol at 35 °C, respectively. For comparison purposes, the values recalculated at 25 °C (at constant  $K_s$ ) are -320 and -5200 cal/mol for  $\Delta\mu_C$  and  $\Delta\mu_A$ , respectively. Free energies of

TABLE IV: Effect of CTAB upon the Kinetic Parameters for the *cis*- to *trans*-Isomerization Reactions of N-Methylmerocyanine Dye at 25 °C<sup>4</sup>

| [CTABr], M | $10^3 k_{\rm obs},  {\rm s}^{-1}$ | $E_{a} \pm \text{ESD}, \text{kcal/mol}$ | ln(A)   | $\Delta G^*$ , kcal/mol | $\Delta H^* \pm \text{ESD}, \text{kcal/mol}$ | $\Delta S^* \pm ESD$ , eu/mol |
|------------|-----------------------------------|---|---------|-------------------------|--|-------------------------------|
| 0.00       | 0.0857                            | $26.6 \pm 0.5$                          | 35.4324 | 23.0                    | $26.1 \pm 0.5$                               | 9.9 ± 1.6                     |
| 0.054      | 3.62                              | 21.9 🛳 0.3                              | 31.3998 | 20.8                    | $21.3 \pm 0.3$                               | $1.9 \pm 1.1$                 |
| 0.099      | 5.2                               | $22.3 \pm 0.2$                          | 31.4484 | 20.6                    | $21.7 \pm 0.2$                               | $3.9 \pm 0.7$                 |
| 0.149      | 7.4                               | $21.5 \pm 0.4$                          | 31.3749 | 20.4                    | $20.9 \pm 0.4$                               | $1.8 \pm 1.3$                 |
| 0.199      | 8.7                               | $22.9 \pm 0.5$                          | 33.9509 | 20.3                    | $22.3 \pm 0.5$                               | $6.9 \pm 1.6$                 |

<sup>a</sup> Values of  $E_{t}$  and A determined from Arrhenius plots of 7, 16, 26, 8, and 14 individual rate constants, respectively, over a temperature range of 25-45 °C.

| N-alkyl group | $10^{3}k_{\rm obs}{}^{b}{\rm s}^{-1}$ | $E_a \pm \text{ESD},^c \text{kcal/mol}$ | $\ln(A)$ | $\Delta G^*$ , kcal/mol | $\Delta H^* \pm \text{ESD}, \text{kcal/mol}$ | $\Delta S^* \pm \text{ESD}, eu/mol$ |
|---------------|---------------------------------------|---|----------|-------------------------|--|-------------------------------------|
| methyl        | 3.62                                  | $21.9 \pm 0.3$                          | 31.3998  | 20.8                    | $21.3 \pm 0.3$                               | 1.9 ± 1.1                           |
| ethyl         | 6.41                                  | $20.7 \pm 0.5$                          | 29.8920  | 20.4                    | 20.1 • 0.5                                   | $-1.1 \pm 1.9$                      |
| n-propyl      | 9.21                                  | $21.6 \pm 0.7$                          | 31.7290  | 20.2                    | 21.0 🛳 0.7                                   | $2.5 \pm 2.2$                       |
| n-butyl       | 32.2                                  | 21.1 ± 0.8                              | 32.0940  | 19.5                    | $20.4 \pm 0.8$                               | $3.3 \pm 2.5$                       |
| n-pentyl      | 47                                    | $23.7 \pm 0.5$                          | 36.9827  | 19.2                    | $23.1 \pm 0.3$                               | $12.9 \pm 1.3$                      |
| n-hexyl       | 74                                    | 23.6 🛳 0.1                              | 37.3312  | 19.0                    | $23.1 \pm 0.1$                               | $13.6 \pm 0.1$                      |

<sup>a</sup> Values of  $E_a$  and A determined from Arrhenius plots determined by 16, 7, 12, 5, 6, and 3 individual rate constants ( $k_{obs}$ ), respectively. <sup>b</sup> Values of  $k_{obs}$  at 25.0 °C by interpolation of Arrhenius line defined by at least six rate constants with at least one rate constant measured within 1 degree of 25.0 °C. <sup>c</sup> ESD, estimated standard deviation based on least squares fit analysis.



Figure 5. Change in free energy of transfer  $(\mu_M - \mu_W)$  of merocyanine dyes from water to CTAB micelles with increasing number (n) of N-alkyl carbon atoms.

transfer per CH<sub>2</sub> group from water to CTAB micelles have been reported to be -310 cal/mol for alkyl phenoxide ions and alkylphenols (in 0.02 M electrolyte at 25 °C)<sup>19</sup> and near -300cal/mol for benzoic acids and anilines.<sup>19</sup> The same compounds showed free energies of transfer per CH<sub>2</sub> group from water to *n*-heptane near -900 cal/mol.<sup>20</sup> These results were taken to imply that the compounds were solubilized within an aqueous environment such as near the micellar interface region.<sup>20</sup> Our results indicate similar solubilization sites for the *N*-alkylmerocyanine dyes in CTAB micelles.

In addition to increased binding of the more hydrophobic dyes, the micellar rate constants  $(k_m)$  also increased with increased dye hydrophobicity (Table II). This is an unusual observation and must reflect differences in the interactions between ground and transition states with surfactant that depend upon the N-alkyl pendant group. The mechanism for the thermal *cis*- to *trans*isomerism in these compounds is undoubtedly a rotation about



Figure 6. Dipole moment (D) as a function of central dihedral angle. Calculated by extended Hückel methods with (b, right) and without (a, left) MM2 optimization and rotation about the Ar-C bonds for intermediate angles.

the central C(6)-C(7) bond. The electronic structures of these dyes are extremely sensitive to solvent polarity,9-11 and the solvatochromism has often been rationalized in terms of increased importance of quinoid resonance forms in nonpolar solvents, with a lessened  $\pi$ -bond character of the C(6)–C(7) bond in the ground state, although the proton donor character of the solvent is also significant.<sup>21</sup> Increases in the cis- to trans-isomerization rate of the N-methyl dye in solvents with decreasing solvent polarity are explained in terms of the strong coupling of molecular conformation, electronic charge distribution, and solvent polarization.<sup>22</sup> Steiner asserts that the solvent dependence of the free energy of activation for the isomerization is due largely to the free energy of solvation of the cis-species. Asano and Okada<sup>23</sup> found a positive activation volume  $\Delta V_0^*$  for the *cis*- to *trans*-isomerization of the methyl dye in water and an increase in  $\Delta V_0^*$  upon going to aqueous methanol. This is consistent with less charge separation and less solvent electrostriction in the transition state. An earlier MNDOC calculation by Tavan and Schulten<sup>25</sup> showed that O-protonation lowers the energy of the cis-form and increases the barriar between the cis- and trans-forms. Presumably hydrogen bonding with water would have an analogous effect. They found that a nearly planar (12°) unprotonated cis-form of methyl dye was even higher in energy than the perpendicular conformation, and they concluded there should be a negligible activation barriar in a solvent incapable of forming hydrogen bonds to the dye oxygen. Steiner and co-



Figure 7. MM2 optimized conformations for (a, left) cis- and (b, right) trans-N-methylmerocyanine dye.

workers took this as evidence of the importance of solvation in determining the rate of the *cis*- and *trans*-isomerization. In protic solvents, the higher energy of the transition state relative to the *cis*-form was explained in terms of lost solvation in the perpendicular transition state.

In the perpendicular transition state there should be minimal conjugation between the two aromatic rings to afford a zwitterionic structure akin to Ib. We used extended Hückel methods to calculate the dipole moment as a function of the central dihedral angle to estimate changes in substrate polarity along the reaction coordinate from cis-reactant to trans-product. Two approaches were used. In one approach, one ring and C-H bond were moved as a rigid unit relative to the other so that each aromatic ring was constrained to be nearly coplanar with its nearby ethylene C-H bond without Ar-C rotation. In other words we compared the dipole moments of a series of substrate structures differing only by dihedral angle. These substrate structures were not MM2 optimized. The calculated dipole moment  $\mu$  varied with the central H-C(6)-C(7)-H dihedral angle with minima at  $0^{\circ}$  (the nearly planar cis-conformation) and at 90°. The latter result indicates little charge separation in this most twisted conformation. A second approach allowed for more extensive conformational changes along with a change in dihedral angle. Extended Hückel dipole moment calculations as a function of dihedral angle were made for structures where the rings are no longer nearly coplanar and in which the geometry is reoptimized by MM2 methods at each choice of dihedral angle (see Figure 6b). The calculated minimum in this case corresponds to a nonplanar  $140 \pm 5^{\circ}$  form in which each ring is coplanar with its nearby C-H bond. Also the Hückel energy and MM2 potential energy (not shown) are at maxima at  $130 \pm 15^{\circ}$ , not at 90°. Even though such calculational methods only imprecisely determine the conformation of a transition state, we feel that ring twisting and the possibility of a nonperpendicular transition state should not be ignored. MM2 optimization for the cis- and trans-forms (in vacuo) show significant out-of-plane tilting of the two aromatic rings. In the cis-form the pyridinium and phenoxide rings are rotated 30° and 39° out of the plane defined by the eclipsed C-H bonds. These conformations are not unlike those calculated and observed for the related stilbenes<sup>24</sup> and are shown in Figure 7. Our extended Hückel energy for the planar cis form is also much higher than that for the perpendicular orientation, as Tavan and Schulten<sup>25</sup> claimed, but this energy is reduced by out-of-plane tilting of the aromatic rings. This ring tilting reduces the energy of the *cis*-form and may be as important a factor as loss of solvation upon going from ground to the transition state in micelles.

Activation parameters in the absence of surfactant (in Table III) are insensitive to the nature of the N-alkyl group. Any differences in Eyring activation parameters for different N-alkyl dyes in CTABr solution reflect differences in substrate microenvironments within the micelle. These can be interpreted in terms of increased micelle penetration and a less polar microenvironment for the more hydrophobic cis-dye molecules. However, because of the importance of out-of-plane twisting of the substrate, constraints on dye conformation caused by interactions with adjacent surfactant chains cannot be ruled out. Several studies have shown that the solubilization sites of most aromatic molecules are near the headgroup or interface region of CTABr micelles.<sup>7a,17,26-29</sup> This should especially be the case for a phenoxide ring.<sup>7a</sup> Trans-N-alkylmerocyanine dye molecules have been reported to reside near the headgroup region of CTABr micelles based on spectrophotometric shifts.<sup>11</sup> Extensive hydration of dyes within this region has also been noted.<sup>11</sup> The N-alkyl chain of the cis-substrate anchors the pyridinium ring into the micelle, and the phenoxide ring is associated with the surfactant headgroups but with the oxygen largely buried, reducing the solvation of the oxygen relative to that of the more extended trans-dye which can protrude outward. If the oxygen is hydrated, it is by buried waters. A relatively nonplanar >90°-twist conformation about the "ethylenic" bond axis is proposed for the transition state. In this conformation the interactions of the phenoxide moiety with the ammonium headgroup and with buried waters are disrupted. Results given in Table IV for the N-methylmerocyanine dye show a dramatic reduction in  $\Delta H^*$ and in  $\Delta S^*$  for the reaction in micellar solution relative to that in the absence of surfactant. A decrease in  $\Delta H^*$  implies that the transition-state enthalpy is reduced upon solubilization more than is that of the ground state. We cannot say whether this stems from the change in polarity of the environment or whether there are also contributions from beneficial hydrophobic interactions with surfactants that favor the transition state over the solubilized ground state. Reduction in the  $\Delta S^*$  may result from a reduced number of ordered water molecules about the phenoxide oxygen as it is incorporated into the micelle. Steiner and co-workers<sup>10</sup> originally suggested that the high  $\Delta S^*$  value for the *N*-methyl dye isomerization reaction in water was due to a free reorganization of water molecules in the relatively nonplanar excited state. This contribution to  $\Delta S^*$  would be reduced in the micelle.

Changes observed in  $\Delta H^*$  and  $\Delta S^*$  with increasing dye hydrophobicity are consistent with the location of a solubilization site near the interface region but with deeper penetration for the more hydrophobic substrates. From the results of the pseudophase model, we know that the more hydrophobic dyes exhibit an increased binding to CTABr micelles. This increased binding accounts for much of the reduction in  $\Delta G^*$  with increased dye hydrophobicity in Table V. Spectroscopic data of Minch and Shah<sup>12</sup> suggest that even the most hydrophobic *trans*-dyes were oriented near the micellar surface where they could be partially hydrated. The chromophore of trans-N-hexadecylmerocyanine dye has also been reported to reside within the headgroup region of CTABr micelles.<sup>30</sup> The activation parameters for the isomerization reactions given in Table V are dependent upon the hydrophobicity of the dyes in an interesting way.  $\Delta H^*$  is independent of dye hydrophobicity, within experimental error, whereas  $\Delta S^*$  increases with the more hydrophobic dyes. In other words it parallels the effect of increasing surfactant concentration. We suspect that the increase in  $\Delta S^*$  sets in at a lower CTABr concentration with the more hydrophobic substrates because of their greater capacity to perturb the packing of surfactant chains and to pull waters more deeply into the micelle to be released upon transition-state desolvation. This interpretation is consistent with a decrease in  $\Delta G^*$  due mainly to increases in  $\Delta S^*$ . That some probes used in micellar studies may drag water molecules into the micellar environment and perturb the micellar structure has been of some concern.<sup>31,32</sup> Further studies using the reaction system described here, including the effect of added salts and micelle modifiers, may provide additional information which can help us to better describe the structures of micelles and the interactions which are important in effecting catalysis of reactions in micellar solutions.

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