Catalysis by Reversed Micelles in Nonpolar Solvents.
Trans–Cis Isomerization of Bis(oxalato)diaquochromate(III)

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Abstract: Rate constants for the trans–cis isomerization of bis(oxalato)diaquochromate(III) anion in the polar cavities of reversed alkylammonium carboxylate micelles in benzene are up to 63-fold faster than that in pure water. At constant water concentrations increasing concentration of the surfactants increases the rate to a maximum after which it remains constant. Similarly, at constant surfactant concentrations, at the plateau region, increasing water concentration increases the rate to a maximum after which it remains constant. The rate constant in the presence of 1.0×10^{-2} M D_2O solubilized in >0.1 M DAP-$(N)d_3$ in benzene at 24.5° ($k_\psi = 11.3 \times 10^{-3}$ sec^{-1}) is a factor of 2.99 greater than that in the presence of 1.1×10^{-2} M H_2O solubilized in >0.1 M DAP ($k_\psi = 3.85 \times 10^{-3}$ sec^{-1}). The observed isotope effect depends on the concentration of solubilized water. At high water concentration $k_\psi^{D_2O}/k_\psi^{H_2O}$ decreases to 1.16. These results are discussed in terms of solubilization of the substrate in the polar cavity of the reversed micelle where isomerization follows a mechanism which involves water in a rate-determining step. Linear dependencies have been observed between the logarithm of the rate constants for the trans–cis isomerization and the pK differences between the amines and carboxylic acids for two series of alkylammonium carboxylate surfactants.

Polar cavities of reversed micelles, formed in nonpolar solvents, provide a unique media for investigating reaction rates and interactions.[1-5] Rate constants for the mutarotation of 2,3,4,6-tetramethyl-α-D-glucose[2] and for the decomposition of Meisenheimer complexes, 1,1-dimethoxycyclohexadienylides,[4] in benzene in the presence of micellar alkylammonium carboxylates were found to be orders of magnitude greater than those observed for the corresponding reactions either in pure benzene or in pure water. These results have been rationalized in terms of favorable substrate orientation in the interior of the reversed micelle where bond breaking is assisted by proton transfer. An additional factor contributing to the overall rate enhancements is the increased effective activities in the micellar interior where considerable amounts of water can be solubilized. Since the concentration of this trapped water can easily be controlled, reversed micellar systems provide a novel means for investigating the mechanistic roles of water in a variety of reactions. We have rationalized the linear dependencies of aquation rates for [Cr(C$_2$O$_4$)$_3$]$^{3-}$ and [Co(C$_2$O$_4$)$_3$]$^{3-}$ on the concentration of dodecylammonium propionate solubilized water in benzene in terms of synchronous M–O bond breaking and nucleophilic water attack subsequent to the formation of the "one-ended dissociated" species.[5] Of equal significance, dramatic rate enhancements have been observed in these systems; the rate constant for the aquation of [Cr(C$_2$O$_4$)$_3$]$^{3-}$, for example, is 5×10^6 greater in the presence of octylammonium tetradecanoate than that in pure water. In order to examine further the utility of reversed micellar systems to localize reactive substrates and water, we have investi-

gated the rate of trans–cis isomerization of bis(oxalato)-diaquochromate(III) anion in the cavities of reversed micelles in benzene. Our choice was somewhat dictated by the availability of kinetic information on this reaction in water.[6-9] Studies on the trans–cis isomerization of bis(oxalato)diaquochromate(III) anion have shown that the rate of conversion is first order with respect to the concentration of [Cr(C$_2$O$_4$)$_2$-(H$_2$O)$_2$]$^-$ ion, independent of pH in the range 1.85–4.48, but catalyzed by >0.1 M HClO$_4$ as well as by divalent metal ions.[6-9] The three possible mechanisms by which the isomerization process for the acid-catalyzed path can take place are shown in Scheme I. Direct attack of a proton on the chelate oxalate forms A which, in agreement the generally accepted chemistry of the oxalate complexes of chromium,[10,11] goes to a "one-ended dissociated" species B or C. The equivalence of the two kinds of oxygen atom, "carbonyl" and "carboxyl," in [Cr(C$_2$O$_4$)$_3$]$^{3-}$ to oxygen exchange with H$_2$^{18}O negates the possibility of breaking the C–O bond instead of a Cr–O bond in these systems.[11] However, the fate of the octahedral site on the metal ion vacated by such a dissociation has not been unequivocally established. One school favors a rate-determining step (k_3) which involves the synchronous Cr–O bond breaking and nucleophilic attack by water to form the octahedral complex, C,[9,10] while there are arguments in support of an alternative mechanism in which the octahedral site remains vacant to form a five-coordinated intermediate with only one end of the oxalate bound to the chromium, B.[11] Subsequently,

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Scheme I

the released end of the oxalate becomes rebound to the chromium (k_1) with simultaneous release of the proton. Alternatively, B may undergo slow nucleophilic attack by water (k_2) to form C which then rapidly rearranges to form the cis isomer. There seems to be no unequivocal justification for the postulation that the site vacated by the dissociated end of the oxalato group is aquated. Indeed, the observation that the slow anation of bis-(oxalato)diaquochromate(III) anion by oxalate ion is independent of the concentration of oxalate ion,[12] and the lack of [18]O exchange of coordinated water of both the cis and trans isomers in both acid and neutral solutions,[13] indicate that the site remains vacant.

Kinetic investigations of the dependence of the isomerization rate on water concentration might provide sufficient evidence to allow distinctions between these alternate mechanistic pathways. We have investigated the trans–cis isomerization of bis(oxalato)diaquochromate(III) anion in the polar cavity of reversed micelles in benzene to elucidate the role of water in this reaction. We report, additionally, pronounced solvent deuterium isotope effects.

Experimental Section

trans-Sodium bis(oxalato)diaquochromate(III) pentahydrate was prepared by the method of Werner.[14] The sodium rather than the more common potassium salt was utilized because of its greater solubility in water.

Reagent grade benzene (<0.02% water) was distilled from sodium onto freshly activated Linde Type 5A molecular sieve and stored under nitrogen.

Octylammonium propionate (OAP), butanoate (BAP), nonanoate (OAN), dodecanoate (OAD), tetradecanoate (OAT), and butyl (BAP), hexyl (HAP), decyl (DeAP), and dodecylammonium propionate (DAP) were prepared by the method of Kitahara[15] as described previously.[16–18] The purity of these surfactants was established by the observation of sharp melting or boiling points and by their infrared and proton magnetic resonance spectra.[15–18]

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Deuterated dodecylammonium propionate, DAP-$(N)d_3$, was prepared by dissolving 15.0 g (0.058 mol) of five-times recrystallized DAP in 30 ml (1.658 mol) of D_2O (Diaprep, 99.8% D), allowing the gel to stand for 24 hr, and removing the solvent by careful, due to foaming, vacuum rotary evaporation. The partially deuterated DAP so obtained was exchanged two more times with D_2O (45 and 30 ml) and treated analogously each time with the exception that the solution was allowed to stand for *ca.* 1 hr before evaporation. After the second exchange, <9% undeuterated material could be present in the product as determined from its ^{1}H nmr integrated spectrum. After the third exchange, the product was dried *in vacuo* over P_2O_5 for 24 hr, removed, pulverized, and dried for an additional 72 hr. Its purity was established by its melting point of 55.5–56.5° (DAP mp 55.5–56.5°) and by the absence of undeuterated DAP or other impurities in its ^{1}H nmr spectrum.

Some of these surfactants are very hygroscopic and appropriate care was taken to exclude atmospheric moisture in making up the stock solutions.

Rates of isomerization were measured spectrophotometrically by following the increase in absorbance at 416 nm (ϵ_{trans} 34.4 $M^{-1}cm^{-1}$ and ϵ_{cis} = 68.5 M^{-1} cm^{-1})[11] on a Beckman Kintrac VII recording spectrophotometer. The temperature in the cell compartment was maintained within ±0.05°, as monitored by NBS thermometers.

Reactions were initiated by injecting known volumes (1–100 µl) of aqueous solutions of trans-Na[Cr(C_2O_4)$_2$(H_2O)$_2$]·5H$_2$O to thermostated solutions (5 ml) of the surfactant in sodium dried benzene. The substrate was dissolved in D_2O before injecting into solutions of deuterated DAP. Good first-order plots were obtained in all cases up to 90% reaction. The product of the reaction was identified as cis-[Cr(C_2O_4)$_2$(H_2O)$_2$]$^-$ from its known spectrum.[2] The concentration of complex was (2–30) × 10^{-4} *M*.

Results

Rate constants for the isomerization of trans-bis-(oxalato)diaquochromate(III) anion in the presence of dodecylammonium propionate solubilized water in benzene at 24.5° are given in Table I. Increasing concentrations of DAP at a constant water concentration causes an initial increase in rate followed by a plateau. The magnitude of the rate enhancement depends also on the concentration of added water. Rate constants at a constant DAP concentration, in the plateau region, increase linearly with increasing concentrations of added water up to a maximum followed by a plateau. Figure 1 illustrates dependencies of the isomerization rate constants in benzene, k_ψ, on the concentrations of DAP and water. In the plateau regions rate constants for the isomerization in reversed micellar systems in benzene are factors of 15 times greater than that in water.

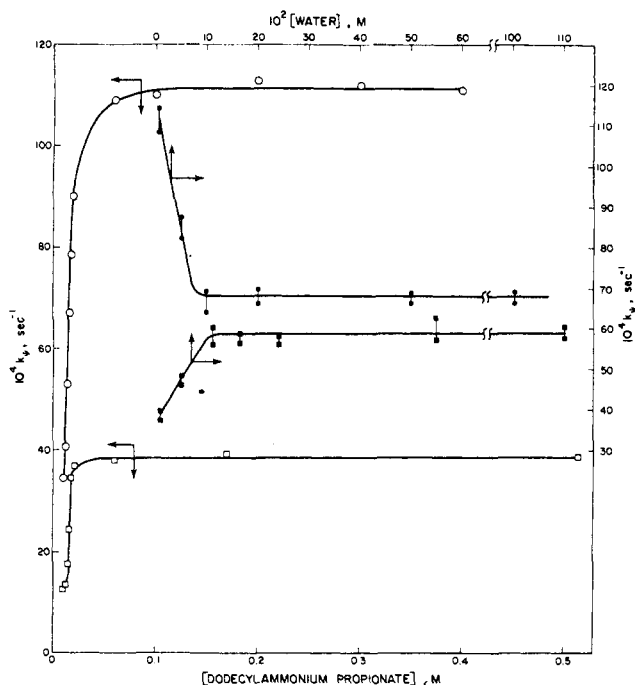Trans–cis isomerization of bis(oxalato)diaquochro-

Figure 1. Rate constants for trans–cis isomerization of (2-30) × 10^{-4} M Na[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·5H$_2$O by DAP solubilized H$_2$O (1.1 × 10^{-1} M) (□) and by DAP-$(N)d_3$ solubilized D$_2$O 1.0 × 10^{-1} M) (○) in benzene at 24.5°. Insert: maximum rate constants for isomerization as a function of the concentration of added H$_2$O (■) and D$_2$O (●).

Table I. Isomerization of *trans*-Bis(oxalato)diaquochromate(III) in Dodecylammonium Propionate Solubilized Water in Benzene at 24.5° [a-c]

10[H$_2$O], M	[DAP], M	10^4k_ψ, sec^{-1}	10[D$_2$O], M	[DAP-$(N)d_3$], M	10^4k_ψ, sec^{-1}
0.11	0.0100	12.8	0.10	0.010	34.5
	0.0121	13.3		0.012	40.7
	0.0141	17.6		0.014	52.9
	0.0161	24.5		0.016	67.1
	0.0181	34.7		0.018	78.6
	0.0201	36.9		0.020	90.3
	0.0604	38.0		0.060	109
	0.171	39.3		0.100	110
	0.512	38.4		0.200	113
0.55	0.171	47.6		0.300	112
	0.512	47.6		0.400	111
	0.853	46.4	0.50	0.100	86.1
1.10	0.0603	59.5		0.200	82.5
	0.171	56.6		0.300	87.5
	0.341	56.5	0.100	0.100	64.7
	0.512	57.3		0.174	66.5
	0.682	61.1		0.200	68.2
	0.854	59.2		0.300	67.7
1.65	0.171	58.0		0.100	69.6
	0.341	57.4		0.200	69.3
	0.512	57.0		0.300	66.5
2.20	0.171	57.4	5.00	0.100	68.0
	0.341	56.3		0.200	67.3
	0.512	57.7		0.300	67.2
5.50	0.309	59.8	10.0	0.100	69.0
	0.412	58.0		0.200	66.5
	0.515	62.4		0.300	67.7
11.0	0.309	58.5			
	0.412	59.8			
	0.515	59.2			

[a] Initial concentration of sodium bis(oxalato)diaquochromate(III) = 2–30 × 10^{-4} M. [b] $10^4k_{\psi(H_2O)}$ = 4.14 sec^{-1}; $10^4k_{\psi(D_2O)}$ = 3.80 sec^{-1}. [c] $10^4k_{\psi(2.90\,M\,H_2SO_4)}$ = 249 sec^{-1}; $10^4k_{\psi(2.90\,M\,D_2SO_4)}$ = 419 sec^{-1}.

mate(III) anion has also been examined in the presence of deuterated dodecylammonium propionate, DAP-$(N)d_3$, and D$_2$O (Table I). The rate constant in the presence of 1.0 × 10^{-2} M D$_2$O solubilized in >0.1 M DAP-$(N)d_3$ in benzene at 24.5° (k_ψ = 11.3 × 10^{-3} sec^{-1}) is a factor of 2.99 greater than that in the presence of 1.1 × 10^{-2} M H$_2$O solubilized in >0.1 M DAP (k_ψ = 3.85 × 10^{-3} sec^{-1}). Dependencies of k_ψ values on DAP-$(N)d_3$ concentration at constant concentrations of D$_2$O ($\geq$1.0 × 10^{-2} M) are analogous to that observed for DAP (Figure 1). Increasing concentrations of DAP-$(N)d_3$ increases the rate to a maximum, which is then followed by a plateau. Dependency of k_ψ on D$_2$O concentration at constant DAP-$(N)d_3$ concentration is different from that observed in the case of H$_2$O (Figure 1). When k_ψ at constant DAP-$(N)d_3$ concentration (in the plateau region) is plotted against the concentration of added D$_2$O, there is an initial linear decrease in rate, followed by a plateau (Figure 1). In this plateau region the ratio of the rate constants, k_ψ in DAP-$(N)d_3$–D$_2$O to that in DAP–H$_2$O, has fallen to 1.16 from the initial $k_\psi^{D_2O}/k_\psi^{H_2O}$ of 2.99 (see inserts in Figure 1). For the purpose of comparison we have measured solvent deuterium isotope effects for the isomerization of *trans*-bis(oxalato)diaquochromate anion in water at 24.5°. At pH = 5, $k_\psi^{H_2O}/k_\psi^{D_2O}$ = 1.09 and in 2.90 M acid $k_\psi^{D_2SO_4}/k_\psi^{H_2SO_4}$ = 1.69.

Rate constants for the trans–cis isomerization of bis-(oxalato)diaquochromate(III) anion have also been measured in water solubilized by a series of alkylammonium carboxylates in benzene. Rate constants in octylammonium propionate (OAP), butanoate (OAB), nonanoate (OAN), dodecanoate (OAD), and tetra-decanoate (OAT) are given in Table II. Table III presents rate constants in the presence of butylammo-

nium (BAP), hexylammonium (HAP), and decylammo-nium (DeAP) propionates. In all of these surfactants the rate constant–surfactant concentration profile is identical. At a given water concentration, increasing concentrations of the alkylammonium carboxylate cause an initial increase in the rate which is followed by a plateau. Maximum rate enhancement is observed for solutions of OAD > 0.1 M where the rate constant (k_ψ = 2.60 × 10^{-2} sec^{-1}) is factors of 63 and 10.5 greater than that in aqueous solution (k_ψ = 4.14 × 10^{-4} sec^{-1}) and in 0.9 M HClO$_4$ (k_ψ = 2.47 × 10^{-3} sec^{-1} at 25.0° [9]), respectively.

Discussion

Localization of *trans*-sodium bis(oxalato)diaquo-chromate(III) pentahydrate and water in the hydrophilic cavity of reversed micellar alkylammonium carboxylates in benzene results in the formation of *cis*-sodium bis(oxalato)diaquochromate(III) anion. The rate of this trans–cis isomerization depends on the temperature, on the nature and concentration of the alkylammonium carboxylates, as well as on the concentration of added water. In all cases rate constants in benzene in the presence of alkylammonium carboxylates are greater than that in pure water (Tables I–III). The magnitude of this rate enhancement, factors of up to 63-fold, is, however, considerably smaller than that observed for the aquation of tris-(oxalato)chromate(III) anion.[5] This difference in the efficiency of catalysis by reversed micelles may originate,

Table II. Isomerization of *trans*-Sodium Bis(oxalato)diaquochromate(III) in Octylammonium Carboxylate Surfactant Solubilized Water in Benzene at 24.5° [a]

10[H$_2$O], M	[OAP], M	10^{4}k$_\psi$, sec^{-1}	[OAB], M	10^{4}k$_\psi$, sec^{-1}	[OAN], M	10^{4}k$_\psi$, sec^{-1}	[OAD], M	10^{4}k$_\psi$, sec^{-1}	[OAT], M	10^{4}k$_\psi$, sec^{-1}
0.55							0.0898	58.1		
0.55							0.359	61.4		
1.10	0.100	39.5	0.101	26.6	0.108	34.6	0.112	262	0.193	187
1.10	0.201	40.7	0.202	26.6	0.287	34.8	0.201	256	0.399	192
1.10	0.309	39.9	0.303	28.0			0.298	258		
1.65	0.100	40.1			0.287	36.5	0.201	252	0.300	195
1.65	0.201	41.0			0.367	36.7	0.298	263	0.399	188
1.65	0.309	40.3								
2.20			0.202	28.6						
2.20			0.303	28.2						

[a] Initial concentration of sodium bis(oxalato)diaquochromate(III) = 4–20 × 10^{-4} M.

Table III. Isomerization of *trans*-Sodium Bis(oxalato)diaquochromate(III) in Alkylammonium Propionate Surfactant Solubilized Water in Benzene at 24.5° [a]

10[H$_2$O], M	[BAP], M	10^{4}k$_\psi$, sec^{-1}	[HAP], M	10^{4}k$_\psi$, sec^{-1}	[DeAP]	10^{4}k$_\psi$, sec^{-1}
1.10	0.317	22.0	0.105	24.7	0.104	29.2
1.10	0.375	21.2	0.210	25.7	0.208	29.2
1.10	0.562	21.5	0.350	25.4		
1.10	0.750	21.9				
1.65	0.562	21.5	0.210	24.1	0.104	26.2
1.65	0.750	21.5	0.350	24.5	0.208	28.0
1.65	0.937	21.0				

[a] Initial concentration of sodium bis(oxalato)diaquochromate-(III) ≈ 10^{-3} M. For DAP and OAP see Tables I and II, respectively.

at least in part, from differences between the neutral and acid-catalyzed rates of these compounds in water. Thus, while aquation of tris(oxalato)chromate(III) anion proceeds at least three orders of magnitude faster in acids than in water,[11] trans–cis isomerization of bis(oxalato)diaquochromate(III) anion is only modestly catalyzed by acids.[9] A further difference is the behavior of the observed rate constants as functions of surfactant and water concentrations. At constant water concentrations increasing concentrations of surfactants decrease logarithmically with the rate of aquation of the tris(oxalato)chromate(III) anion.[5] This behavior has been rationalized by assuming that subsequent to an optimum saturation of the polar cavity of the reversed micelle by water, increasing surfactant concentration results in a decrease in the effective water concentration per micelle and hence a decrease in the rate. Conversely, at constant water concentration, increasing surfactant concentration increases the rate constant for the trans–cis isomerization of bis-(oxalato)diaquochromate(III) anion to a maximum after which the rate remains constant (Figure 1). This latter type of saturation kinetic behavior has often been observed in aqueous micellar systems[19] and it is quite reasonable for the trans–cis isomerization since this process does not involve the net consumption of water molecules (Scheme I). At constant surfactant concentrations in the plateau region of the catalysis, dependence of the isomerization rate on the concentration of solubilized water (Figure 1) can be rationalized analogously. The initial linear rate increase with increasing water concentration implies the involvement

(19) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, 2, 329 (1969); E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, 8, 271 (1970).

of water in the rate-determining step. The subsequent invariance of the rate with water concentration at the plateau is simply the consequence of saturating the micelles with water in excess of the solvation requirements of the substrate.

The observed initial dependence of the rate constant on the concentration of added water is compatible either with synchronous breaking of the Cr–O bond and nucleophilic attack by water (k_3 in Scheme I) or with a mechanism which involves nucleophilic attack by water on the one-ended dissociated intermediate (k_2 in Scheme I). The path which does not involve water in the rate-determining step (k_1 in Scheme I) can be unequivocally rejected for the trans–cis isomerization of bis(oxalato)diaquochromate(III) anion in benzene in the presence of alkylammonium carboxylate micelles.

The mechanism of the trans–cis isomerization in the reversed micellar environment was probed further by determining solvent deuterium isotope effects. At surfactant concentrations in the plateau region the extent of the deuterium isotope effect depends, however, on the concentration of solubilized water (or D$_2$O) (Table I and Figure 1). Such behavior indicates a composite behavior of the solubilized water and the surfactant. At low water concentration the rate is 2.99-fold greater in DAP-(N)d_3–D$_2$O than in DAP–H$_2$O. This result is compatible with a preequilibrium proton transfer since in D$_2$O the effective concentration of the conjugate acid (A in Scheme I) is increased with respect to that in H$_2$O due to the greater proton donating ability, *i.e.*, acidity, of DAP-(N)d_3 relative to that of DAP. As the concentration of added water is increased, the micelles become saturated with water in excess of the reaction and solvation requirements of the conjugate acid. Consequently, the isotope effect on the rate-determining step (k_2 and/or k_3 in Scheme I) increasingly competes with that on the preequilibrium proton transfer. Rates of bimolecular reactions which involve water in the rate-determining step are faster, of course, in H$_2$O than in D$_2$O. The observed isotope effect in the reversed micellar system ($k_\psi^{DAP-d_3-D_2O}/k_\psi^{DAP-H_2O} = 2.99$) is greater than that found in aqueous 2.90 M acid ($k_\psi^{D_2SO_4}/k_\psi^{H_2SO_4} = 1.69$), and at high concentrations of solubilized water in the presence of reversed micelles there is a small inverse isotope effect ($k_\psi^{DAP-d_3-D_2O}/k_\psi^{DAP-H_2O} = 1.16$), whereas in water at pH 5 a positive solvent deuterium isotope effect has been observed ($k_\psi^{H_2O}/k_\psi^{D_2O} = 1.09$). These data suggest that the activity of water in the cavity of reversed micelles is considerably increased with respect to that

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Scheme II

trans ⇌ (C₂O₄)Cr →ₖ₄ slow cis

Figure 2. Plots of the logarithm of the maximum observed rate constant at 24.5° against the ΔpK (amine — carboxylic acid) for alkylammonium propionates and octylammonium carboxylates.

water activity are factors contributing to the catalysis in the micellar environment.

The surfactant concentration–rate profile for the catalysis is quite similar for all the alkylammonium carboxylate surfactants investigated. Increasing surfactant concentrations and increasing water concentrations both increase the rate. Maximum rate enhancement has been obtained for solutions of OAD (Table II). It is apparent that an increase in the alkyl chain length of both the ammonium and carboxylate ions of the surfactant causes an increase in the rate; however, it is more sensitive to changes in the hydrocarbon chain length of the acid than to that of the ammonium ion. This behavior is undoubtedly a composite result of changes in the structure of the micelle and of the interactions, and hence orientation, of the substrate and water in the interior of these reversed micelles. · Plots of the ΔpK's (amine — carboxylic acid) for the surfactants vs. log k_ψ(max) are essentially linear as illustrated in Figure 2. It is apparent here also that the rate depends to a greater extent on the carboxylate ion than on the ammonium ion. Since the rate depends on the ΔpK for both and the pK's of the amines are essentially invariant with chain length[20] while those of the acids increase with increasing chain length,[22] both hydrophobic and hydrophilic interactions are important. For the octylammonium series, the weaker the acid the greater the catalysis, and for both series, of course, the smaller the difference in the pK's the greater the rate. Since the $\Delta pK'$s reflect the tightness of the ion pairs and consequently the electron density, and therefore acidity, of the ammonium ion, these results also indicate that proton transfer from the ammonium ion of the surfactant to the chromate anion is a primary contributing factor in the observed catalysis. Other factors are also apparent from these results. The anomalies in Figure 2 are for those surfactants (OAP and OAD) with significantly higher aggregation numbers. (Those for OAP and OAB are 5 ± 1 and 7 ± 1, respectively, while they are ca. 3 ± 1[16,17] for the other alkylammonium carboxylates in benzene.) Since k_ψ(max) is independent of the stoichiometric surfactant concentration and the concentration of added water, the greater catalysis in higher aggregation number surfactants, i.e., larger micelles, may well be the consequence of the fact that the larger micelles are more compact, the methylene groups having less mobility near the interior cavity, and the substrate and water are thereby held more rigidly in the orientation required for reaction. It is clear that in addition

of bulk water. This fact alone may account for the possible mechanistic differences of the trans–cis isomerization of bis(oxalato)diaquochromate(III) anion in bulk and surfactant solubilized water. In the former water molecules only act as solvates and the available evidence (lack of ^{18}O exchange of "bound" water in neutral solution[13]) indicates that water is not involved in the rate-determining step (k_4 in Scheme II). Conversely, water trapped in the cavity of reversed micelles acts primarily as a nucleophile capable of forming covalent bonds in the transition state.

The origin of the catalysis of the trans–cis isomerization is quite analogous to that postulated for the aquation of chromium(III) and cobalt(III) complexes.[3] Hydrogen bonding between the oxygen atoms of the substrate and the ammonium ion of the surfactant facilitates the preequilibrium proton transfer thereby increasing the concentration of the one-ended dissociated species (B and C in Scheme I). The apparent proton donating power of the dodecylammonium propionate is twice as great as that of 1.0 M acid. In addition to proton transfer, favorable orientation and enhanced

(20) The pK's of n-butyl, n-hexyl, octyl, n-decyl, and n-dodecylamine at 20–25° in water are 10.77, 10.56, 10.65, 10.64, and 10.63,[21] respectively.

(21) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1972.

(22) The pK's of propionic, butyric, nonanoic, dodecanoic, and tetradecanoic acid at 20–25° in water are 4.87,[21] 4.81,[21] 4.96,[21] 5.31,[23] and ≤ 6.3,[23] respectively.

(23) V. Nyren and E. Back, Acta Chem. Scand., 12, 1305 (1958).

to water activity, the structure of the micellar aggregate and the interactions therein influence the catalytic efficiency of these systems.

Stereochemistry of the Photoaquation of Chloropentaamminechromium(III)

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Abstract: The $Cr(NH_3)_4(^{15}NH_3)Cl^{2+}$ complex ion has been prepared, isotopically labeled either trans or cis relative to chloride, and has been photolyzed at two different excitation wavelengths. The $^{15}N/^{14}N$ ratio of photoaquated ammonia was determined by means of proton magnetic resonance spectra. At 503 nm ($^4A_{2g} \rightarrow {}^4T_{2g}$ transition) at least 75% of NH_3 is photoreleased from the position trans to chloride, *i.e.*, on the weak average-field axis, while only 40 to 50% of NH_3 labilized at 254 nm (CT transition) was originally trans to Cl^-. The configuration of the photoproduct, *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, shows that the photoreaction, upon d–d band irradiation, involves stereochemical change, a feature which now appears to be general for chromium(III) complexes.

Several $Cr(NH_3)_5X^{2+}$ type complex ions, with X = Cl,[2] NCS,[3] Br,[4] N_3,[5] and $RCOO$,[6] have been investigated photochemically. The main photoreaction mode upon ligand-field band irradiation is known to be ammonia release while in the dark only the aquation of the acido group, X, is observed.[7] This photochemical behavior is typically "antithermal" and is predictable by a set of semiempirical rules.[8] These state that in mixed-ligand chromium(III) complexes (i) labilization occurs along the axis of the octahedron having the smallest average crystal field and (ii) if the labilized axis contains two different ligands, the one of greater field strength is preferentially aquated. The type of labilization is consistent with the population of the lower lying σ antibonding orbital in the lowest excited quartet state.[9] The principal photoproduct, $Cr(NH_3)_4(H_2O)X^{2+}$, was found to have a cis configuration.[2a,4,6,10] The latter result has given rise to some discussion about the usefulness of the rules.[10,11] At least three views may be (and have been) taken: (a) the rules imply no more than the data upon which they were constructed, namely that one thereby is able to predict the type of ligand which is predominantly labilized toward substitution, for example, ammonia in the case of $Cr(NH_3)_5Cl^{2+}$; (b) the rules specify which actual ligand (if two or more are the same) is labilized, for example, the trans ammonia in the above case; (c) the rules imply not only b but also that the substitution process is stereoretentive, for example, that the product will be *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. This last view turns out to be an unwarranted mechanistic interpretation. Not only is the cis product obtained in the case of $Cr(NH_3)_5Cl^{2+}$ but also with $Cr(NH_3)_5(NCS)^{2+}$.[12] An important further observation is that *trans*-$Cr(en)_2Cl_2^+$ photolyzes primarily to *cis*-$Cr(en)_2(H_2O)Cl^{2+}$[13] and that the corresponding pattern of behavior applies to the *trans*-$Cr(en)_2XY$ family generally[13,14] and to *trans*-$Cr(NH_3)_4XY$ complexes,[15] that is that the X and/or Y acido group is labilized and that the product is cis. The last group of results does suggest, however, that interpretation b of the rules is valid.

In view of the isomerization that is observed, it was suggested[11] that for Cr(III) ammine complexes change in configuration might be a common photochemical feature, in contrast to the stereorigidity of the thermal substitution process.[7,16] Certainly, the importance of mechanism in the excited-state reaction is indicated by the photoinertness of *trans*-$Cr(cyclam)Cl_2^+$.[17] It appears that the implicated ligand field excited state (probably the first quartet excited state) is reactive only if stereomobility is possible.

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