Catalysis by Reversed Micelles in Non-polar Solvents: Aquation and Electron-transfer Reactions of Chromium(III) and Cobalt(III) Complexes in Benzene[1]

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Rate constants for aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ by octylammonium tetradecanoate-solubilized water in benzene and for aquations of $[Cr(C_2O_4)_3]^{3-}$, $[Co(C_2O_4)_3]^{3-}$, and *cis*-$[Co(en)_2(N_3)_2]^+$ (en = ethylenediamine) by dodecylammonium propionate-solubilized water in benzene are factors of up to 5×10^6, 1×10^6, *ca.* 1 500, and 11, respectively, greater than those for the same reactions in water. At constant surfactant concentration there is a linear dependence of the aquation rate on the concentration of solubilized water, while at constant water concentration increasing surfactant concentration results in an exponential rate decrease. These results are discussed in terms of favourable substrate orientation in polar cavities of alkylammonium carboxylate aggregates, formed from these surfactants in benzene, where hydrogen bonding facilitates proton transfer and enhanced water activity accelerates synchronous M–O bond-breaking and nucleophilic attack by water. An implication of these results is that, in the hydrophilic environment of the reversed micelle, aquations of Co^{III} and Cr^{III} complexes follow rate-determining bimolecular mechanisms subsequent to formation of 'one-ended dissociated' species. No micellar effects have been observed for the electron-transfer process in the aquation of the ion $[Co(C_2O_4)_2(H_2O)_2]^-$. Rate enhancement by surfactant-solubilized water in non-aqueous solutions and the utility of these systems in elucidating the mechanistic roles of water are discussed.

DILUTE solutions of alkylammonium carboxylates in non-polar solvents catalyse reactions remarkably.[2] Thus, in benzene rate constants for mutarotation of 2,3,4,6-tetramethyl-α-D-glucose[3] and those for unimolecular decomposition of Meisenhemier complexes, substituted 1,1-dimethoxycyclohexadienylides,[4,5] are factors

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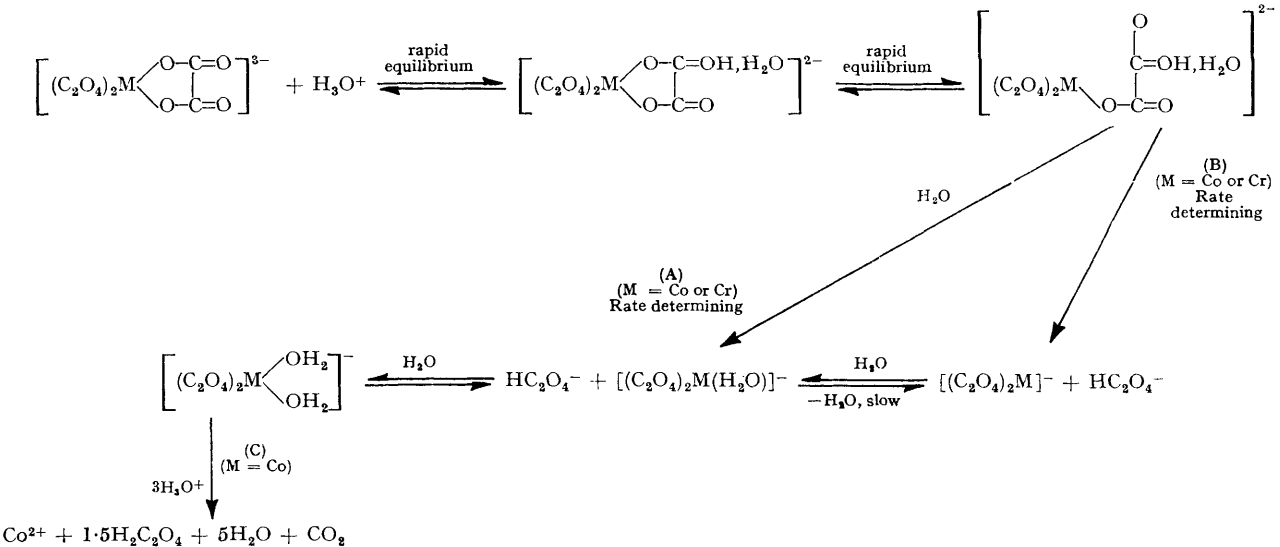
of up to 690 and 62 900 fold greater in the presence of these surfactants than in their absence. Also the observed rate constants for these reactions in the presence of alkylammonium carboxylates in benzene are orders of magnitude greater than those for the corresponding reactions in water.[2-5] We have presented evidence that alkylammonium carboxylates dynamically form small aggregates in non-aqueous solvents in which the carboxylate and ammonium groups are located in the interior forming a polar cavity and the hydrocarbon chain of the surfactants are in contact with the apolar solvent.[6-8] Following the established terminology,[9,10] we have referred to these aggregates as ' reversed ' or ' inverted ' micelles. Addition of water, known to be solubilized in the polar cavity of inverted micelles,[11] can enhance catalysis significantly.[5] Changes in the activity of water, solubilized in the interior of reversed micelles can apparently influence reaction rates. Additionally, the size and nature of both the hydrophilic and hydrophobic parts of the surfactants together with those of the substrate are factors which can influence the efficiency of catalysis by reversed micelles.

In order to probe further the mechanisms of catalysis by reversed micelles, particularly the role of ' trapped ' water in the polar cavity, we have investigated aquation and other ligand-substitution reactions of cobalt(III) and chromium(III) complexes.[1] An added advantage for studying aquations by micelle-solubilized water in non-polar solvents is that the concentration of water can be controlled and consequently information regarding aquation mechanisms can be gained. Thus, aquation and ligand-substitution reactions of tris(oxalato)-chromate(III) and -cobaltate(III) anions, $[M(C_2O_4)_3]^{3-}$, have been discussed in terms of ' one-ended dissociation ' (Scheme).[12-15] The subsequent fate of the octahedral site on the metal ion vacated by such a dissociation, however, has not been unequivocally established. One school favours a rate-determining step which involves synchronous M–O bond-breaking and nucleophilic attack by water [path (A)],[13,14] while there are arguments in support of an alternative mechanism in which the octahedral site remains vacant during M–O bond-breaking [path (B)].[12,16] Kinetic investigations of the dependence of the rate of aquation on water concentration would provide sufficient evidence to allow a distinction between these alternative paths. In the present paper we report fully rate enhancements for aquation and substitution reactions by micelle-solubilized water and discuss the mechanisms for these reactions and the micellar catalysis.



SCHEME

EXPERIMENTAL

Reagent grade benzene (<0·02% water) was distilled from sodium on to Linde type 5A molecular sieve. Dodecylammonium propionate (dap), octylammonium dodecanoate (oad), octylammonium tetradecanoate (oat), and hexadecyltrimethylammonium butyrate (htab) were prepared

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by the method of Kitahara and purified as previously described.[6-8,17] The surfactants were carefully dried before use. Critical micelle concentrations (c.m.c.s)[6-8] of dap, oad, oat, and htab in benzene were (3—7) × 10^{-3}, (9·3—10) × 10^{-2}, (1·0—1·1) × 10^{-1}, and 1·4 × 10^{-3}M, respectively. Tripotassium tris(oxalato)chromate(III) trihydrate,[12] tripotassium tris(oxalato)cobaltate(III) hydrate (1/3·5),[12] tripotassium azidopentacyanocobaltate(III),[18] *cis*-diazidobis(ethylenediamine)cobalt(III) nitrate,[19] potassium ethylenediaminebis(oxalato)chromate(III) dihydrate,[20] and Durrant's salt, $K_4[Co(C_2O_4)_2(OH)(H_2O)],2H_2O$,[21] were prepared by established methods. In aqueous acid solution Durrant's salt protonates to form the diaquobis(oxalato)cobaltate(III) anion and the absorption spectrum immediately after dissolution in dap-solubilized water in benzene was found to be identical to that reported by Adamson *et al.*[21] The purity of the other complexes and identification of the products of the aquation reactions were determined by u.v.-visible spectroscopy using a Cary 14 spectrophotometer, by comparison, where possible, with known spectra.

Rates of aquation were measured spectrophotometrically by determining the change in absorbance on a Beckman Kintrac VII recording spectrophotometer. The wavelengths used for each complex are as follows: $[Co(C_2O_4)_3]^{3-}$ (416); $[Co(CN)_5N_3]^{3-}$ (285); *cis*-$[Co(en)_2(N_3)_2]^-$ (533); $[Cr(C_2O_4)_2(en)]^-$ (en = ethylenediamine) (530); $[Co(C_2O_4)_3]^{3-}$ (420); and *cis*-$[Co(C_2O_4)_2(H_2O)_2]^-$ (420 nm). Reactions were initiated by injecting known volumes (1—50 μl) of aqueous solutions of complex into thermotatted surfactant solutions (5 cm^3) in carefully dried benzene. Homogeneous solutions were obtained in all cases. Where possible reactions were allowed to run for 8—10 half-lives and good first-order plots were obtained up to 90% completion of reaction, giving rate constants with an error of ±2%. For the slower runs Guggenheim plots[22] were used and the accuracy of the obtained values is ±5%. Aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ in aqueous acid solutions was found not to give linear pseudo-first-order plots[12b] because the rate of secondary aquation of the product, *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$, caused interference. In these reversed micellar systems this secondary aquation is slow enough that it causes no interference with the primary aquation. The temperature of the thermostatted baths and cell compartment was maintained within ±0·05 °C, as monitored by NBS thermometers.

RESULTS

Aquation of Tris(oxalato)chromate(III) *Anion.*—Rate constants for aquation of tris(oxalato)chromate(III) anion, $[Cr(C_2O_4)_3]^{3-}$, in the presence of surfactant-solubilized water in benzene, k_4, at 24·5 °C (Table 1) were considerably greater than those in water. From available values at 47 °C[12] and using Arrhenius parameters for the acid-catalysed rate,[12] the estimated rate constant for aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ in water at 24·5 °C is 1·5 × 10^{-9} s^{-1}. The fastest aquation rate, in the presence of 1·1 × 10^{-1}M-water solubilized in 7·58 × 10^{-2}M-oat in benzene at 24·5 °C (k_ψ 8·1 × 10^{-3} s^{-1}, Table 1), therefore represents a 5 × 10^6-fold enhancement with respect to that in water. Catalysis by dap is of similar magnitude (Table 1).

TABLE 1

Rate constants for aquation of the tris(oxalato)chromate(III) anion[a] by surfactant-solubilized water in benzene at 24·5 °C

$10^2[H_2O]$ / M	[dap] / M	10^4k_ψ / s^{-1}	[oat] / M	10^4k_ψ / s^{-1}
5·5	0·0379	13·9	0·0392	56·8
	0·0473	12·2	0·0591	38·4
	0·0947	8·83	0·0784	36·0
	0·189	6·03	0·0984	31·5
	0·331	4·12	0·190	24·0
	0·473	2·88	0·197	23·0
			0·298	20·8
			0·388	19·6
			0·647	12·9
			0·759	11·3
			0·948	8·65
11·0	0·0500	16·9	0·0758	81·3
	0·0750	14·6	0·0946	64·0
	0·0990	14·1	0·199	41·6
	0·125	12·8	0·298	32·5
	0·193	11·3	0·398	25·6
	0·320	9·34	0·473	22·9
	0·376	8·44	0·759	17·0
	0·473	7·63		
16·5	0·189	16·3	0·190	76·8
	0·285	14·6	0·284	54·6
	0·379	13·8	0·285	51·8
	0·473	12·9	0·472	29·6
			0·756	22·6
22·0	0·473	17·8		

[a] Substrate concentration = (1—20) × 10^{-4}M.

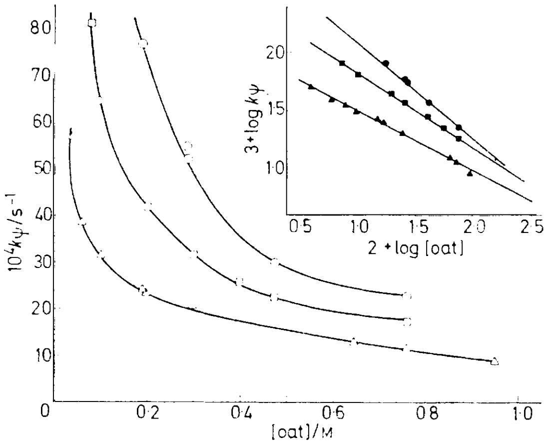

FIGURE 1 Rate constants for hydrolysis of the ion $[Cr(C_2O_4)_3]^{3-}$ by octylammonium tetradecanoate-solubilized water in benzene at 24·5 °C: $[H_2O]$ = 16·5 × 10^{-2} (○); 11·0 × 10^{-2} (□); and 5·5 × 10^{-2}M (△). Inset: logarithmic plots of rate constants for hydrolysis of the ion $[Cr(C_2O_4)_3]^{3-}$ against concentration of octylammonium tetradecanoate in benzene [(●), (■), and (▲): concentrations as above]

At any given water concentration increasing concentrations of surfactant caused an exponential decrease in k_ψ and logarithmic plots of k_ψ against the stoicheiometric surfactant concentration, c_D, were linear (Figure 1). Presumably at sufficiently low surfactant concentrations the

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rate enhancements are even greater. The inability of the surfactants to solubilize sufficient water in benzene at low surfactant concentration, however, precluded the observation of rate maxima. The presence of such maxima in the surfactant concentration–rate profiles is inferred from the lack of aquation in benzene in the absence of surfactants: 5 μl of a saturated solution of the complex $K_3[Cr(C_2O_4)_3]$,$3H_2O$ in dmso (dimethyl sulphoxide) added to pure benzene (5·0 cm²) produced no change in the visible spectrum at 39·8 °C for 6 h, and similarly no change occurred in the spectrum of tris(oxalato)chromate(III) anion when water was solubilized in 0·091M-htab in benzene. The reaction product of aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ in dap- and oat-solubilized water in benzene was identified as $[Cr(C_2O_4)_2(H_2O)_2]^-$ from its known spectrum.[13]

Aquation of Tris(oxalato)cobaltate(III) *and* cis-*Diaquobis(oxalato)cobaltate*(III) *Anions and the Subsequent Electron-transfer Process.*—Rate constants, k_ψ, for aquation of the tris(oxalato)cobaltate(III) anion, $[Co(C_2O_4)_3]^{3-}$, in surfactant-solubilized water in benzene at 38·0 °C are given in Table 2 and those for diaquobis(oxalato)cobaltate(III) anion, *cis*-$[Co(C_2O_4)_2(H_2O)_2]^-$, in Table 3. Figure 2 shows plots of k_ψ' values for both these reactions against stoicheiometric dap concentration in the presence of 1·1 × 10^{-1}M solubilized water. It can be seen that at [dap] ⩽ 0·3M the rate constants are virtually identical for both the tris and bis oxalato-complexes, and comparison of the data in Tables 2 and 3 shows that this is also true for the case of 2·2 × 10^{-1}M-H_2O in the 0·3—0·5M-dap range.

TABLE 2

Rate constants for aquation of the tris(oxalato)cobaltate(III) anion [a] in surfactant-solubilized water in benzene at 38·0 °C [b,c]

$10^2[H_2O]$ / M	[dap] / M	10^5k_ψ / s^{-1}	$10^2[H_2O]$ / M	[dap] / M	10^5k_ψ / s^{-1}
1·1	0·00410	15·4	5·5	0·0712	6·39
	0·00715	13·5			
	0·0102	9·33	11·0	0·0712	7·45
	0·0410	6·45		0·103	6·44
	0·0712	5·58		0·205	5·32
	0·205	3·39		0·307	4·01
	0·309	3·35		0·408	2·53
	0·412	3·89		0·512	1·25
	0·515	5·18			
			22·0	0·329	3·14
				0·438	2·98
	0·180 [e]	57·7		0·547	2·65

[a] Substrate concentration = (2—20) × 10^{-4}M. [b] In 0·05M-H_2SO_4, 10^5k_ψ = 23·1 s^{-1}. [c] In water, 10^5k_ψ = 0·417 s^{-1}. [d] Unless specified otherwise. [e] oad.

TABLE 3

Rate constants of aquation of the *cis*-diaquobis(oxalato)cobaltate(III) anion [a] in surfactant-solubilized water in benzene at 38·0 °C [b,c]

$10^2[H_2O]$ / M	[dap] / M	10^5k_ψ / s^{-1}	$10^2[H_2O]$ / M	[dap] / M	10^5k_ψ / s^{-1}
11·0	0·0723	7·78	22·0	0·207	3·46
	0·107	6·56		0·310	3·14
	0·207	4·85		0·413	2·94
	0·310	3·92		0·516	2·65
	0·413	3·23			
	0·516	2·87	55·0	0·329	2·96
				0·438	2·74
16·5	0·207	3·69		0·547	2·58

[a] Substrate concentration = (1·5—4) × 10^{-4}M. [b] In 0·05M-H_2SO_4, 10^5k_ψ = 380 s^{-1}. [c] In water, 10^5k_ψ = 4·97 s^{-1}.

The rate-determining step for aquation of the ion $[Co(C_2O_4)_3]^{3-}$ by surfactant-solubilized water in benzene is probably the electron transfer [path (C) in Scheme] rather than formation of diaquobis(oxalato)cobaltate(III) as occurs in aqueous acid solutions.[15] Kinetic determinations of the rate of aquation of the ion $[Co(C_2O_4)_3]^{3-}$ to *cis*-$[Co(C_2O_4)_2(H_2O)_2]^-$ are precluded by similarities in the absorption spectra of these species [ε(605) 170 and ε(420 nm) 220 l mol^{-1} cm^{-1} for the former and ε(600) 124 and ε(420 nm) 160 l mol^{-1} cm^{-1} for the latter]. During aquation of the ion $[Co(C_2O_4)_3]^{3-}$ a slight initial decrease in the absorbance at 420 nm was noted. Subsequent to this 'initiation time' absorbances were found to decrease more rapidly to nearly complete transmittance. The data quoted in Table 2 were calculated from linear Guggenheim [22] plots over this larger decrease in absorbance. In the presence of 1·1 × 10^{-1}M solubilized water the initiation time varied from 25 min for 0·0712M-dap to 11 h for 0·512M-dap. If this initiation time is regarded as the time taken for formation of the bis(oxalato) species [path (A) or (B) in Scheme] then the estimated rate constant for aquation of the ion $[Co(C_2O_4)_3]^{3-}$ by 1·1 × 10^{-1}M-water solubilized in 0·0712M-dap in benzene ($k_\psi \simeq 6 \times 10^{-3}$ s^{-1}) is *ca.* 1 500- and 25-fold greater than that in pure water or in 0·05M-H_2SO_4 respectively (Table 2). The spectrum of the solutions at the end of the initiation time appeared to be predominantly that of the diaquobis(oxalato)cobaltate(III) anion. In the presence of 1·1 × 10^{-2}M-water, the initiation time could not be clearly distinguished because the total change in absorbance over the whole reaction was governed by an electron-transfer rate-determining step [path (C) in Scheme].

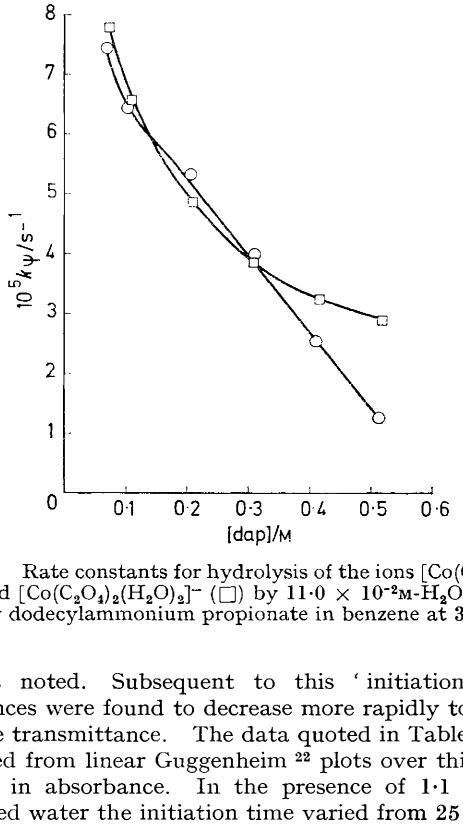

FIGURE 2 Rate constants for hydrolysis of the ions $[Co(C_2O_4)_3]^{3-}$ (○) and $[Co(C_2O_4)_2(H_2O)_2]^-$ (□) by 11·0 × 10^{-2}M-H_2O solubilized by dodecylammonium propionate in benzene at 38·0 °C

At constant water concentration increasing concentration of surfactant caused an exponential decrease in the rate of directly measured aquation of the ion *cis*-$[Co(C_2O_4)_2$-

$(H_2O)_2]^-$ (Figure 2). In dap, plots of log k_ψ against log [dap] were linear with negative gradients as observed for the aquation of tris(oxalato)chromate(III) anion. With increasing water concentration the gradients of these lines approached zero. Values for dlog k_ψ/dlog [dap] are $-0·50$, $-0·28$, and $-0·24$ for water concentrations of $1·1 \times 10^{-1}$, $2·2 \times 10^{-1}$, and $5·5 \times 10^{-1}$M, respectively. Behaviour of the rate constants as functions of solubilized water concentration was, however, more complex At low dap concentration k_ψ values increased with increasing water concentration, at intermediate surfactant concentration they decreased going through a minimum, while at the highest surfactant concentrations they were essentially independent of the concentration of water. As had been found for the aquation of tris(oxalato)chromate(III) anion, the nature of the surfactant appreciably altered the reaction rate. In 0·180M-oad the rate constant was 15 times greater than that in dap under comparable conditions.

Aquations of cis-*Diazidobis*(*ethylenediamine*)*cobalt*(III) *Nitrate*.—Although base-catalysed hydrolysis of the ion *cis*-$[Co(en)_2(N_3)_2]^+$ has been studied,[19] no information is available on the acid-catalysed rate. We have determined rate constants for aquation of this cation in water and in 0·05M-H_2SO_4 at 38·0 °C (Table 4). Water solubilized by dap in benzene enhanced the rate of aquation with respect to that in pure water, but not with respect to the acid-catalysed rate (Table 4). Increasing concentration of surfactant caused a decrease in the rate constant as observed in the other systems. The absence of substantial micellar effects did not warrant more detailed investigations of this reaction.

TABLE 4

Rate constants for aquation of *cis*-diazobis(ethylenediamine)cobalt(III) nitrate at 38·0 °C [a]

Conditions	$10^7 k_\psi$/s^{-1}
Water (pH *ca.* 5·5)	6·06
0·05M-H_2SO_4-H_2O	3 780
$1·10 \times 10^{-1}$M-H_2O-benzene-$6·4 \times 10^{-2}$M-dap	112
$1·10 \times 10^{-1}$M-H_2O-benzene-$8·5 \times 10^{-2}$M-dap	67·2
$5·50 \times 10^{-1}$M-H_2O-benzene-$1·07 \times 10^{-1}$M-dap	38·0

[a] Substrate concentration = (1—5) × 10^{-4}M.

Aquation of Tripotassium Azidopentacyanocobaltate(III) *Anion*.—The aquation of $[Co(CN)_5N_3]^{3-}$ is acid catalysed.[18] In the absence of added thiocyanate ions, the products of the reaction are the ion $[Co(CN)_5(H_2O)]^{2-}$ and HN_3. In the presence of added thiocyanate ions some $[Co(CN)_5(NCS)]^{3-}$ is formed but the rate of the acid-catalysed aquation is unaltered. These results yielded strong support for an S_N1 mechanism involving five-co-ordinate $[Co(CN)_5]^{2-}$. We anticipated confirming this mechanism by the absence of an increase in rate with increasing concentration of surfactant-solubilized water. However, rate constants for aquation of tripotassium azidopentacyanocobaltate(III) at 38·0 °C in water (k_ψ $2·2 \times 10^{-6}$ s^{-1}) and in 0·05M-H_2SO_4 (k_ψ $1·8 \times 10^{-3}$ s^{-1}) were higher than those obtained in the reversed micellar system. (Only 5—10% reaction occurred in 6 days at 38 °C in benzene in the presence of $1·1 \times 10^{-1}$M-water solubilized in 0·1—0·5M-dap.) More detailed investigations of this system were, therefore, not carried out.

Aquation of Potassium Ethylenediaminebis(*oxalato*)*chromate*(III) *Dihydrate*.—Although quantitative measurements of the rate of aquation have not been made, Bushra and Johnson reported that absorption coefficients of an aqueous solution markedly diminished in the neighbourhood of the maximum at 530 nm after several hours in the dark at room temperature and that alkalis accelerated the decomposition.[20] We expected that aquation would also be acid catalysed and found this to be true. (At 38·0 °C, k_ψ = $4·31 \times 10^{-5}$ and $1·6 \times 10^{-6}$ s^{-1} in 0·05M-H_2SO_4 and water respectively.) We had anticipated that this reaction would also be catalysed by reversed micelles, but unfortunately the complex was insufficiently soluble in water to carry out the investigation. The maximum absorbance that could be obtained using a 11×10^{-2}M-H_2O solution (saturated in complex) in dap was only 0·02.

DISCUSSION

When water and a Cr^{III} or Co^{III} complex are localized in the polar cavity of reversed alkylammonium carboxylate micelles in benzene they undergo measurable, and indeed, in some cases, extremely rapid, aquation. At a given temperature, rates of these aquations depend on the nature of the substrate, the type and concentration of micelle-forming surfactant, and the concentration of solubilized water (Tables 1—4 and Results section). Observed rate constants for aquation of the ions $[Cr(C_2O_4)_3]^{3-}$, $[Co(C_2O_4)_3]^{3-}$, and $[Co(en)_2(N_3)_2]^+$ by surfactant-solubilized water in benzene are factors of up to 5×10^6, *ca.* 1 500, and 11 greater than those for the same reactions in pure water. Conversely, the rate constant for aquation of the ion $[Co(CN)_5N_3]^{3-}$ is considerably faster in pure water than in surfactant-solubilized water in benzene. Focusing primarily on the data concerning aquation of the ion $[Cr(C_2O_4)_3]^{3-}$, where the micellar effect is the most spectacular, mechanisms for aquation and micellar catalysis will now be discussed.

Aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ by water solubilized in dap represents a relatively simple situation. In all cases the surfactant concentration is at least a 100-fold greater than the c.m.c. (see Experimental section and Table 1) and therefore, subsequent to reaching maximum catalysis, values of k_ψ are expected to be independent of surfactant concentration. This type of saturation kinetic behaviour has often been observed in aqueous micellar systems.[23-27] Experimental results, however, do not bear out this expectation. Lack of solubilization of water at sufficiently low surfactant concentration prevents observation of rate maxima. Furthermore, increasing surfactant concentration, at constant water concentration, causes an exponential decrease in k_ψ values (Figure 1 and Table 1). The most probable explanation is that subsequent to optimum saturation of the polar cavity of the reversed micelle by water,

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increasing surfactant concentration results in a decrease in the effective water concentration per micelle and hence a decrease in the rate of aquation. Since the concentrations of oat used are less than 10 times greater than the c.m.c. (Experimental section and Table 1), the effective water concentration per micelle may be greater than that for dap and the highest observed value of k_ψ is probably close to the rate maximum. Not unexpectedly, therefore, the observed maximum-rate enhancement for oat (5×10^6-fold) is greater than that for dap (1×10^6-fold).

At constant surfactant concentration there is a linear dependence of the observed aquation rate, k_ψ, on the concentration of water solubilized both by oat and dap (see insert in figure in ref. 1). Furthermore, this dependence of k_ψ on solubilized-water concentration is the same for micellar oat and dap giving an apparent second-order rate constant of 1×10^{-2} l mol^{-1} s^{-1} with respect to water concentration. Comparing this value with those available for perchloric-acid-catalysed aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ in water at the same temperature (by calculating an apparent second-order rate constant from the linear plot of log k_ψ against $-H_0$),[12a] establishes this reaction to be *ca.* 100-fold faster in the reversed micellar system in benzene than in aqueous perchloric acid solutions. The observed linear dependency of the aquation rate on surfactant-solubilized-water concentration implies, of course, an aquation mechanism in which Cr–O bond-breaking is synchronous with the nucleophilic attack by water. In other words, path (A) in the Scheme prevails. It is realized that the environment of the ion $[Cr(C_2O_4)_3]^{3-}$ in the polar cavity of the reversed micelles in non-polar benzene differs considerably from that in pure water and consequently different mechanisms [path (A) or (B)] may well predominate in the two media.

The origin of the catalysis by reversed micelles is clearly not favourable partitioning, since the rate of aquation both in pure benzene and water is negligible (see Results section) compared to that observed in surfactant-solubilized water (Table 1). A rate enhancement, resulting largely from favourable partitioning, has been recently described for imidazole-catalysed hydrolysis of *p*-nitrophenyl acetate in 'water pools' solubilized in octane by sodium di-2-ethylhexyl sulphosuccinate surfactants.[27] Micellar catalysis in the present system is probably the consequence of hydrogen bonding between oxygen atoms of the substrate and the ammonium ion of the surfactant, thereby facilitating proton transfer and increasing the concentration of the one-ended dissociated species in the pre-equilibria steps. The lack of detectable aquation by water solubilized in the cavity of htab micelles in benzene (see Results section), a surfactant in which proton donation is not feasible, substantiates this interpretation. An increase in effective water activity in the polar micellar cavity over that in bulk water is quite plausible[10] and would also contribute to the overall rate enhancement by accelerating the rate-determining step [path (A)]. The decrease in k_ψ values with decreasing surfactant concentration (*vide infra*) is in agreement with this postulate.

In the light of the rate enhancement observed for the $[Cr(C_2O_4)_3]^{3-}$ aquation, aquation of the ion $[Co(C_2O_4)_3]^{3-}$ was also expected to be catalysed by water solubilized in the polar interior of reversed micelles in benzene; but such catalysis would predictably be smaller since aquation of the ion $[Co(C_2O_4)_3]^{3-}$ in pure water relative to that in 0·50M-H_2SO_4 is appreciable. Indeed the rate constant for primary aquation of the ion $[Co(C_2O_4)_3]^{3-}$ [path (A)] is *ca.* 1 500-fold greater than that in pure water. In aqueous solutions the electron-transfer reaction [path (C)] is 20 times faster than the primary-aquation reaction of the tris(oxalato) complex [path (A)];[15] but in surfactant-solubilized water in benzene (Tables 2 and 3 and Figure 2), the situation is reversed and the rate of the electron-transfer reaction is essentially identical to that for the directly measured aquation of the ion *cis*-$[Co(C_2O_4)_2(H_2O)_2]^-$. Observed rate constants in surfactant-solubilized water are comparable to that in pure water and less than that in aqueous acids (Table 3). The role of water in the electron-transfer process in the *cis*-diaquobis(oxalato)cobaltate(III) system is complex (Table 3). At high surfactant concentrations the rate is independent of water concentration whilst at low surfactant concentrations increasing amounts of water increase k_ψ. Additionally, at constant water concentration increasing surfactant concentration decreases the electron-transfer rate (Figure 2).

Catalysis of aquation of the ion $[Cr(C_2O_4)_3]^{3-}$ in water solubilized in the polar interior of reversed micelles is 10^3 times more favourable than that of $[Co(C_2O_4)_3]^{3-}$, illustrating the influence of the central metal atom in this reaction. The oxalato-ligand is strongly basic with a large tendency to hydrogen bond, and this tendency is promoted in a reversed-micellar environment. In aqueous-acid-catalysed hydrolysis reactions, the primary factor to be considered is the nature of the ligand being replaced. We had hoped that introduction of other strongly basic ligands with strong hydrogen-bonding tendencies, *e.g.* azido or cyano, into the co-ordination sphere of octahedral chromium(III) complexes, would again lead to rate enhancements of their aquations in water solubilized by surfactants in non-aqueous solvents. Although rate enhancement for aquation of *cis*-diazidobis(ethylenediamine)cobalt(III) nitrate was observed, the micellar affect was considerably smaller than that found for the oxalato-complexes. In the case of the azidopentacyanocobaltate(III) anion, a rate deceleration was observed. Thus, the nature of the ligand as a factor in the reactivity is even more critical under these circumstances than in an aqueous environment. Since the observed rate constants are much larger for bound oxalate than for the other ligands, the dominating factor must be interaction of the alkylammonium moiety of the surfactant with the free oxygen atom of a bound carboxylate group subsequent to solubilization. We are currently investigating ligand interactions and catalyses of these and similar types of reactions in both normal and reversed micellar systems which may serve to elucidate the relative importance of the energetic and configurational factors involved.

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