Effects of Micellar Agents on Peroxodisulphate Oxidations and on the Aquation of Cobalt(III) and Iron(II) Complexes

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Effect of micellar agents on reactivities in solution have been much studied for organic systems.[1] There is very much less information on their effect on inorganic reactions. A dramatic increase in the rate of the mercury(II)-catalysed aquation of the $Co(NH_3)_5Cl^{2+}$ cation in the presence of negatively charged surfactants[2] and marked increases in the rate of hydrolysis of the adduct $Et_3N \cdot SO_3$ in the presence of positively or negatively charged surfactants[3] have been described. Polyelectrolytes have also been found to have significant effects on reactivities, as, for instance, in formation reactions of Ni_{aq}^{2+} [4] and in the reduction of cobalt(III) complexes by the $Ru(NH_3)_6^{2+}$ cation,[5] as well as in the above-mentioned mercury(II)-catalysed aquation of the $Co(NH_3)_5Cl^{2+}$ cation.[2,6] These effects of micellar agents or of polyelectrolytes are not strictly catalytic, since the presence of these species may affect the final equilibrium position.[7]

We have been interested for some time in the effects of solvent composition and structure on reactivity in inorganic systems, for example the aquation of cobalt(III),[8] chromium(III),[9] and low-spin iron(II)[10] complexes and oxidations by peroxodisulphate[11] in aqueous organic mixed solvents, and in

reactions of low-spin iron(II) complexes in alkyl-ammonium salt solutions[12] and in aqueous sols and gels.[13] There appears to be no information published on the effects of micellar agents on these types of reaction. We have therefore investigated the effects of the micellar agents sodium lauryl sulphate (SLS) and cetyltrimethylammonium bromide (CTAB) on some of these reactions, to see whether marked effects on reactivities or equilibria could be observed. We have looked at peroxodisulphate oxidations of iodide and of hexacyanoferrate(II), since these reactions involving the approach of ions of like charge should be particularly susceptible to micellar catalysis.[14] We have also examined the effects of added micellar agents on two types of aquation of established dissociative mechanism, of the familiar cobalt (III) complexes *cis*- and *trans*-$Co(en)_2Cl_2^+$ and of the tris-5-nitro-1,10-phenanthroline complex of iron(II), $Fe(5NO_2phen)_3^{2+}$. This last-named cation was chosen in the light of the known sensitivity of its aquation rate to solvent environment.

Results and Discussion

Peroxodisulphate Oxidations

Oxidation of iodide or of hexacyanoferrate(II) by peroxodisulphate is a bimolecular process. We have followed these reactions spectrophotometrically (Unicam SP800A recording instrument fitted with a thermostatted cell holder) under first-order conditions by having one of the reactants in relatively large excess. In practice it is necessary to work with low concentrations of both reactants in order not to overwhelm the micellar agent. The conditions used

TABLE 1. Observed First-order Rate Constants, k_{obs}, for the Oxidation of Iodide and of Hexacyanoferrate(II) by Peroxodisulphate in Aqueous Media in the Presence of Cetyltrimethylammonium Bromide (CTAB), at 298.2K.

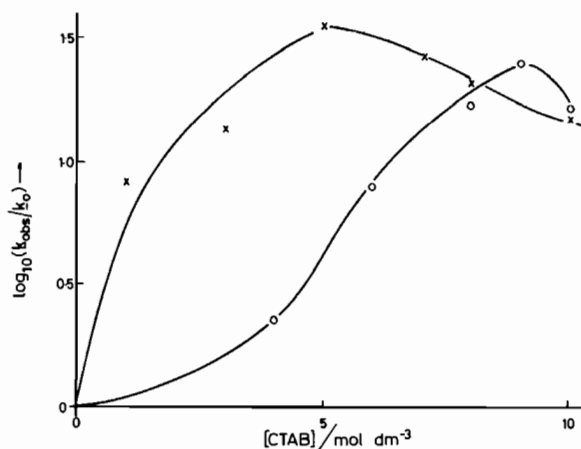| Initial $[I^-]$/mol dm^{-3}		4.0×10^{-3}		
Initial $[Fe(CN)_6^{4-}]$/mol dm^{-3}				1.33×10^{-4}
Initial $[S_2O_8^{2-}]$/mol dm^{-3}		1.0×10^{-4}		2.0×10^{-3}
$[KOH]$/mol dm^{-3}				6.0×10^{-4}
	10^5 [CTAB]/mol dm^{-3}	$10^4 k_{obs}$/s^{-1}	10^5 [CTAB]/mol dm^{-3}	$10^4 k_{obs}$/s^{-1}
	0	2.2	0	0.5
	4.0	5.0	1.0	4.0
	6.0	17	3.0	7.0
	8.0	37	5.0	16
	9.0	55	7.0	12
	10.0	36	8.0	9.3
			10.0	6.6

Fig. 1. Dependence of the decadic logarithms of the ratios of rate constants for peroxodisulphate oxidation in the presence and absence of CTAB, $\log_{10}(k_{obs}/k_0)$, on the concentration of CTAB; o iodide, + hexacyanoferrate(II).

and first-order rate constants determined are reported in Table I. The dependences of reactivity on micelle concentration are depicted in Figure 1. Kinetic studies at higher CTAB concentrations were precluded by the opalescence of such reaction mixtures. The overall pattern shown in Figure 1 closely resembles that described for mercury(II)-catalysed aquation of the $Co(NH_3)_5Cl^{2+}$ cation,[2] although the rate enhancements for these peroxodisulphate oxidations in the presence of CTAB are less dramatic. The magnitudes of the effect of CTAB on reactivities are similar for the two peroxodisulphate oxidations, but the critical micelle concentrations differ, as one would expect.

The addition of a negatively charged micellar agent to these peroxodisulphate oxidations should have no effect on rates. We have confirmed that this is so, for the case of sodium lauryl sulphate.

Aquation of Cobalt(III) Complexes

Rates of aquation of the *cis*- and *trans*-isomers of the bis-ethylenediaminedichlorocobalt(III) cation, $Co(en)_2Cl_2^+$, in the presence of various concentrations of sodium lauryl sulphate* are reported in Table II. The results for the *cis*-compound are illustrated in Figure 2. Obviously the effects are very much less pronounced here than for bimolecular reactions between like-charged species, but the presence of the micellar agent does have a significant effect on reac-

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*The onset of opalescence precluded kinetic studies of the aquation of *cis*-Co(en)$_2$Cl$_2^+$ at concentrations of SLS greater than 20×10^{-5} mol dm^{-3}, and of the *trans*-isomer between 7 and 100×10^{-5} mol dm^{-3}.

TABLE II. Observed First-order Rate Constants, k_{obs}, for the Aquation of the *cis*- and of the *trans*-Co(en)$_2$Cl$_2^+$ Cations in Aqueous Media in the Presence of Sodium Lauryl Sulphate (SLS), at 308.2K. Initial [complex] = 3.0×10^{-3} mol dm^{-3} in each case.

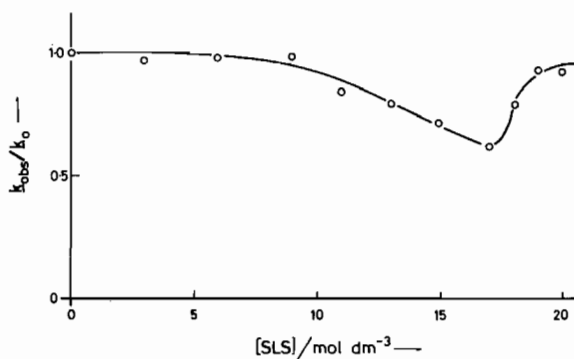| *cis*-Co(en)$_2$Cl$_2^+$		*trans*-Co(en)$_2$Cl$_2^+$	
10^5 [SLS] / mol dm^{-3}	$10^4 k_{obs}$/s^{-1}	10^5 [SLS] / mol dm^{-3}	$10^4 k_{obs}$/s^{-1}
0	3.6	0	1.5$_5$
3.0	3.3	1.0	1.4$_4$
6.0	3.4	4.0	1.4$_5$
9.0	3.4	7.0	1.4$_5$
11	3.0		
13	2.8		
15	2.5		
17	2.2	100	1.5$_0$
18	2.8	400	1.3$_6$
19	3.3	700	1.0$_5$
20	3.2		

Fig. 2. Dependence of the ratios of rate constants for aquation of the *cis*-Co(en)$_2$Cl$_2^+$ cation in the presence and absence of SLS, k_{obs}/k_o, on the concentration of SLS.

tivities. Presumably this effect arises from small differences in solvation of the intial and transition states for these complexes when they are in close proximity to the micelles. It is interesting to compare the reactivity changes here with those in mixed solvents, to get the two types of effect into perspective. The aquation rate of the *cis*-Co(en)$_2$Cl$_2^+$ cation is about 40% less in the presence of SLS at the critical micelle concentrafion than in pure water; a similar reduction in rate results from a change in solvent from pure water to solvent mixtures containing about 20% by volume of methanol or ethanol.[8] Again the obvious expectation that a positively charged micellar agent would have no effect on reactivity for a positively charged complex has been confirmed, using cetyltrimethyltriammonium bromide as micellar agent.

Aquation of Iron(II) Complexes

Here there appears to be no significant effect on micellar agent on reactivity, at least for the aquation of the $Fe(5NO_2phen)_3^{2+}$ cation in the presence and absence of sodium lauryl sulphate (or of cetyltrimethyltriammonium bromide). However there is a small effect on equilibria here. The aquation of the $Fe(5NO_2phen)_3^{2+}$ cation does not go to completion in very dilute acid. Under such conditions the addition of sodium lauryl sulphate causes the equilibrium to be displaced somewhat further towards complete aquation. As initial rates of aquation of the complex are unaffected by the addition of sodium lauryl sulphate, this small change in the equilibrium position must reflect a correspondingly small change in the fourth-order rate constant[15] for the formation of the complex.

Acknowledgement

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