Initial State and Transition State Effects in the Mercury(II)-catalysed Aquation of Chlorotransition-metal Complexes in Binary Aqueous Solvent Mixtures

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Rate constants are reported for the mercury(II)-catalysed equation of the $[Co(NH_3)_5Cl]^{2+}$, *trans*-$[Co(en)_2Cl_2]^+$, and $[ReCl_6]^{2-}$ ions in water-rich methanol–, ethanol–, t-butyl alcohol–, ethylene glycol–, glycerol–, dioxan–, and acetonitrile–water mixtures. The observed reactivity trends are discussed and, as far as possible, analysed into initial- and transition-state components from estimated single-ion Gibbs free energies of transfer. In connection with this analysis the solubilities of the tetraphenylborates of mercury(II) and of caesium in several binary aqueous solvent mixtures are also reported.

THERE have been many attempts to analyse reactivity trends in mixed aqueous solvents or in series of non-aqueous solvents into initial-state and transition-state components, and thus relate such trends to measured or proposed solvation changes for the initial and transition states. Thus for the solvolysis of t-butyl chloride in ethanol–water mixtures this has been achieved (for ΔH) by measuring enthalpies of solution and enthalpies of activation.[1] A thorough analysis of the reactions of tetra-alkyltin compounds with mercury(II) halides in several solvent media (for ΔG, ΔH, and ΔS) has been carried out by Abraham and his co-workers.[2] In these reactions it was found that reactivity trends were dominated by initial-state effects.[3] In general, solvation changes in the initial state can be as important as those in the transition state, and in some cases more important. In the Menschutkin reaction of trimethylamine with methyl iodide again the changes of rate with solvent composition appear to be due predominantly to changes in reactant solvation.[4] Such analyses of rate trends have been rare for transition-metal complexes, although a recent study of the reaction of $[Pt(bipy)Cl_2]$ (bipy = 2,2′-bipyridyl) with thiourea in aqueous dioxan and in aqueous tetrahydrofuran showed that yet again initial-state solvation effects were much more important than transition-state solvation effects.[5] In all these cases the analysis of solvent effects is straightforward in that the reactants are uncharged and hence their enthalpies, entropies, and Gibbs free energies of transfer can be determined directly. In reactions involving ionic reactants analogous analyses of solvent effects on reactivities are rendered more difficult by the impossibility of determining absolute thermodynamic transfer parameters for single ions. Hence discussions of such reactions as those of the $[Fe(bipy)_3]^{2+}$ cation with hydroxide ion [6] or with cyanide ion,[6,7] or of $[Re(CO)_5I]$ with cyanide ion,[8] are complicated by the necessity of making suitable assumptions in order to estimate such quantities as Gibbs free energies of transfer of cyanide or of hydroxide ion from water into binary aqueous mixtures. Of course exactly the same applies to the $[Fe(bipy)_3]^{2+}$ cation in the above example, or to the *cis*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) cation in studies of solvent effects on its dissociative solvolysis.[9] Nevertheless analyses of solvent effects on reactivity of these last reactions have proved informative, and we were encouraged to attempt similar treatments for other types of bimolecular inorganic reactions, for example substitution at square-planar d^8 complexes and metal-ion-catalysed aquation of halogenotransition-metal complexes. Metal-ion-catalysed aquations of carboxylatotransition-metal complexes [10] provide another potential series of reactions for investigation and analysis in this manner.

The main aim of the present paper is to examine solvent effects on the initial state and transition state for mercury(II)-catalysed aquation of several chlorotransition-metal complexes. In pursuance of this objective we have undertaken kinetic studies on such reactions, and solubility studies on compounds containing the reactant ions, in a variety of solvent mixtures. We have also determined solubilities of some ancillary compounds, where such data are needed here in estimating single-ion values. For some series of solvent mixtures there are insufficient basic data on simple compounds and ions for us to carry out the desired analysis. When such data become available it will be possible to complete the analysis of solvent effects on our mercury(II)-catalysed reactions, given the kinetic and solubility results included in this paper.

RESULTS

Kinetics.—All runs were conducted under acidic conditions so that the mercury(II) was all present in the form $Hg^{2+}(aq)$, and not $[Hg(OH)]^+(aq)$ or polynuclear hydroxo-species. The pK_a of $Hg^{2+}(aq)$ probably lies between 2.4 and 3.7 in aqueous solution, slightly lower in mixed aqueous media.[11] Therefore the pH values of our reaction mixtures were kept well below 2 (*cf.* Experimental section and Table captions). All runs were carried out with the mercury(II) present in considerable excess; in all cases the concentration of the transition-metal complex ion decreased according to a first-order pattern [equation (1)] for at least three half-lives.

$$-d[\text{complex}]/dt = k_{\text{obs.}}[\text{complex}] \qquad (1)$$

Observed first-order rate constants [$k_{\text{obs.}}$; equation (1)] for the reactions of the $[ReCl_6]^{2-}$, $[Co(NH_3)_5Cl]^{2+}$, and *trans*-$[Co(en)_2Cl_2]^+$ ions with mercury(II), in large excess, are

TABLE 1

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2, for mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$, $[Co(NH_3)_5Cl]^{2+}$, and *trans*-$[Co(en)_2Cl_2]^+$ ions in binary aqueous mixtures, at 298.2 K

Solvent [a]	$[Hg^{2+}]$/mol dm^{-3} 0.003	0.005	0.010	0.015	0.020	k_2/dm^3 mol^{-1} s^{-1}
	$10^3k_{obs.}$/s^{-1}					
(*a*) For $[ReCl_6]^{2-}$ [b]						
Water	0.061	0.106	0.21	0.31		0.021
10 % methanol	0.108	0.190	0.39	0.58		0.039
20	0.32	0.54	1.07	1.61		0.107
30	0.69	1.06	2.3	3.5		0.23
40	1.90	3.1	6.2	9.2		0.61
10 % ethanol	0.14	0.22	0.45	0.68		0.046
20	0.40	0.67	1.35	2.02		0.135
30	1.07	1.86	3.6	5.5		0.36
40	4.4	7.3	14.8	22		1.49
10 % t-butyl alcohol	0.19	0.31	0.62	0.93		0.062
20	0.50	0.65	1.70	2.5		0.176
30	1.9	3.0	6.1	9.1		0.60
40	4.7	7.9	15.6	24		1.57
10 % ethylene glycol	0.16	0.27	0.54	0.80		0.053
20	0.21	0.36	0.72	1.08		0.072
30	0.34	0.57	1.14	1.72		0.114
40	0.45	0.78	1.54	2.3		0.155
10 % dioxan	0.27	0.44	0.89	1.33		0.088
20	1.41	2.2	4.6	6.8		0.46
30	3.2	5.5	11.0	16.6		1.12
40	5.0	6.5	17.0	26		1.78
10 % acetonitrile	0.18	0.40	0.60	0.87		0.054
20	0.61	0.93	1.91	2.9		0.196
30	2.2	3.6	7.4	11.1		0.75
40	5.5	9.2	18.2	27		1.80
(*b*) For $[Co(NH_3)_5Cl]^{2+}$ [c]						
Water		0.49	0.95	1.47	1.91	0.095
10 % methanol		0.47	0.97	1.45	1.93	0.096
20		0.52	1.07	1.52	2.09	0.102
30		0.53	1.09	1.63	2.15	0.106
40		0.57	1.12	1.70	2.27	0.112
10 % ethanol		0.49	0.98	1.50	1.95	0.097
20		0.53	1.10	1.66	2.21	0.113
30		0.57	1.18	1.71	2.32	0.121
40		0.61	1.26	1.85	2.51	0.128
10 % t-butyl alcohol		0.57	1.08	1.69	2.22	0.110
20		0.67	1.28	2.01	2.61	0.130
30		0.80	1.68	2.41	3.3	0.163
40		0.99	2.04	2.88	4.1	0.203
10 % ethylene glycol		0.43	0.89	1.29	1.75	0.087
20		0.46	0.85	1.40	1.71	0.090
30		0.45	0.92	1.41	1.82	0.092
40		0.47	0.99	1.47	2.06	0.098
10 % glycerol		0.40	0.85	1.17	1.66	0.082
20		0.39	0.73	1.22	1.51	0.077
30		0.42	0.73	1.23	1.42	0.075
40		0.40	0.79	1.26	1.63	0.081
10 % acetonitrile		0.41	0.78	1.20	1.53	0.080
20		0.35	0.73	1.02	1.37	0.070
30		0.32	0.65	0.95	1.31	0.064
40		0.25	0.58	0.80	1.12	0.055

(*c*) For *trans*-$[Co(en)_2Cl_2]^+$ [d]	$[Hg^{2+}]$/mol dm^{-3} 0.004	0.008	0.012	0.016	0.020	
	$10^3k_{obs.}$/s^{-1}					
Water	1.13	2.1	3.3	4.6	5.5	0.28
40% t-butyl alcohol	1.62	3.4	5.6	7.4		0.49
40% acetonitrile	0.75	1.48	2.5	3.6	4.4	0.24

[a] Solvent compositions by volume before mixing. [b] Initial $[ReCl_6^{2-}] = 10^{-4}$, $[HClO_4] = 0.025$, $I = 0.040$ mol dm^{-3} ($Mg[ClO_4]_2$). [c] Initial $[Co(NH_3)_5Cl^{2+}] = 5 \times 10^{-4}$, $[HClO_4] = 0.20$, $I = 0.24$ mol dm^{-3} ($Mg[ClO_4]_2$). [d] Initial [*trans*-$Co(en)_2Cl_2^+$] $= 10^{-3}$, $[HClO_4] = 0.03$, $I = 0.10$ mol dm^{-3} ($Mg[ClO_4]_2$).

recorded in Tables 1 and 2. The dependence of $k_{obs.}$ on mercury(II) concentration is illustrated, for the $[ReCl_6]^{2-}$ anion, in Figure 1. Similar plots are obtained for the cobalt(III) complexes. Over the concentration range studied, the rate law is thus that shown in equation (2).

$$-d[\text{complex}]/dt = k[\text{complex}][Hg^{2+}] \qquad (2)$$

The reaction sequence for reactions of this type is set out in equation (3). Here the binuclear species M–X–Hg may be

$$M{-}X^{n+} + Hg^{2+} \underset{K_{eq}}{\overset{\text{fast}}{\rightleftharpoons}} [M{-}X{-}Hg]^{(n+2)+} \xrightarrow{\text{slow}} M^{(n+1)+} + [HgX]^{+} \qquad (3)$$

a transient intermediate, possibly of such short lifetime that it approximates to a transition state, or it may have a lifetime sufficiently long to have kinetic consequences. The rate laws corresponding to these cases are shown in equations (4) and (5) respectively. Figure 1 and Table 1 indicate that the mercury(II)-catalysed aquations of the $[ReCl_6]^{2-}$, $[Co(NH_3)_5Cl]^{2+}$, and *trans*-$[Co(en)_2Cl_2]^+$ ions follow equation (4) rather than (5), at least at the relatively low mercury(II) concentrations employed in our study. The absence of intermediates of significant concentration and lifetime is supported by the observation of isosbestic points in repeat-scan spectra of runs. Thus there is a clear isosbestic point at 260 nm for the reaction of $[ReCl_6]^{2-}$ with Hg^{2+}(aq). Values of k_2 [equation (4)], computed for least-mean-squares plots of $k_{obs.}$ against $[Hg^{2+}]$, are quoted in Table 1. It may be added that these plots all pass through the origin; there is no kinetic evidence for a significant parallel mercury(II)-independent solvolysis path.

TABLE 2

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, $k_2 = k_{obs.}/[Hg^{2+}]$, for mercury(II)-catalysed aquation of the *trans*-$[Co(en)_2Cl_2]^+$ cation in binary aqueous mixtures, at 298.2 K. Initial [complex] = 10^{-3}, initial $[Hg^{2+}] = 10^{-2}$, $[HClO_4]$ = 0.03, and I = 0.053 mol dm^{-3} ($Mg[ClO_4]_2$)

Solvent	$10^3k_{obs.}/s^{-1}$	k_2/dm^3 mol^{-1} s^{-1}
Water	3.50	0.35
10% methanol	3.85	0.39
20% methanol	4.04	0.40
30% methanol	3.61	0.38
10% ethanol	4.14	0.41
20% ethanol	4.40	0.44
30% ethanol	3.99	0.40
40% ethanol	3.57	0.36
10% ethylene glycol	3.60	0.36
20% ethylene glycol	3.26	0.33
30% ethylene glycol	2.94	0.29
40% ethylene glycol	2.42	0.24
10% glycerol	3.37	0.34
20% glycerol	3.12	0.31
30% glycerol	2.54	0.25
40% glycerol	2.06	0.21
10% acetonitrile	3.56	0.36
20% acetonitrile	2.55	0.26
30% acetonitrile	1.99	0.26
40% acetonitrile	1.31	0.13

$$-d[\text{complex}]/dt = k_2[\text{complex}][Hg^{2+}] \qquad (4)$$

$$-d[\text{complex}]/dt = \frac{(k_1 + K_{eq}[Hg^{2+}])[\text{complex}]}{1 + K_{eq}[Hg^{2+}]} \qquad (5)$$

The products of the mercury(II)-catalysed aquations of the cobalt(III) complexes are the respective aquocobalt(III) complexes. For the mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$ anion the final rhenium-containing product was the $[ReO_4]^-$ anion, here as in the uncatalysed aquation of the $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ anions.[12] As discussed in our earlier paper on the uncatalysed aquation, present knowledge of the solution chemistry of rhenium is insufficient to allow us to elucidate the full reaction sequence, but the rate-determining step both in the uncatalysed and in the mercury(II)-catalysed aquation must involve the loss of the first halide ion from the hexahalogeno-anion. Oxidation of rhenium(IV) to rhenium(VII), relatively rapidly by dissolved oxygen, occurs in a subsequent step involving an aquohalogeno-intermediate or even the as-yet-uncharacterised Re^{4+}(aq) cation.

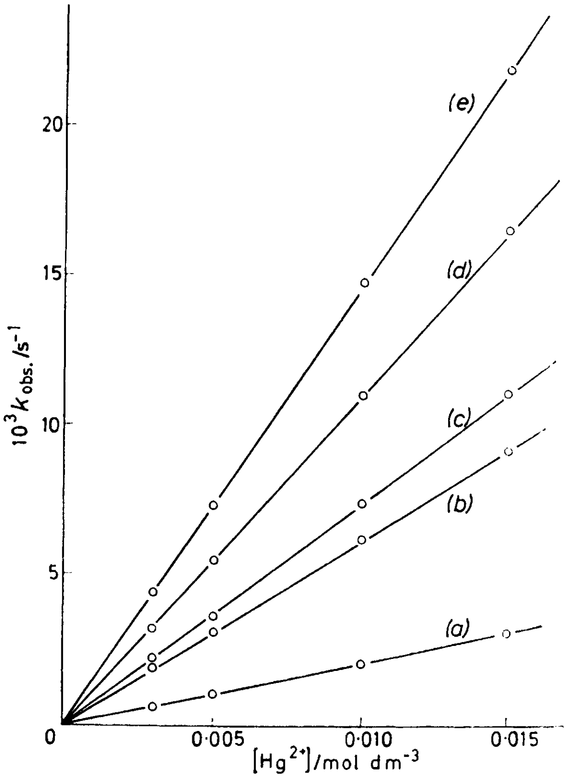

FIGURE 1 Dependence of the observed first-order rate constant, $k_{obs.}$, for catalysed aquation of the $[ReCl_6]^{2-}$ anion on mercury(II) concentration at 298.2 K. Solvents: (*a*) water (*y* scale expanded 10 times); (*b*) 40% methanol; (*c*) 30% acetonitrile; (*d*) 30% dioxan; and (*e*) 40% ethanol

For *trans*-$[Co(en)_2Cl_2]^+$ it was confirmed that plots of $k_{obs.}$ *vs.* $[Hg^{2+}]$ were linear in water, in 40% t-butyl alcohol, and in 40% acetonitrile (respective k_2 values in Table 1). For other solvent mixtures k_2 values were determined simply as $k_{obs.}/[Hg^{2+}]$ at one mercury(II) concentration (Table 2).

Solubilities.—Solubilities of mercury(II) tetraphenylborate, caesium tetraphenylborate, and tris(1,10-phenanthroline)iron(II) hexachlororhenate in water and in some binary aqueous mixtures at 298.2 K are reported in Table 3. In order to prevent complications from the hydrolysis $Hg^{2+}(aq) \rightleftharpoons [Hg(OH)]^+(aq) + H^+(aq)$ solubilities were measured in 10^{-2} mol dm^{-3} perchloric acid. It was necessary to keep the acid strength as low as possible and to equilibrate the mixtures quickly in order to prevent significant decomposition of the tetraphenylborate anion.[13]

TABLE 3

Solubilities (S) of $Hg[BPh_4]_2$, $Cs[BPh_4]$, and $[Fe(phen)_3]$-$[ReCl_6]$ in binary aqueous solvent mixtures at 298.2 K

Solvent *	$Hg[BPh_4]_2$ 10^5S/mol dm^{-3}	$Cs[BPh_4]$ 10^4S/mol dm^{-3}	$[Fe(phen)_3]$ $[ReCl_6]$ 10^6S/mol dm^{-3}
Water	5.09	1.00	5.1
10% methanol	5.20	1.87	8.0
20% methanol	5.80	2.17	10.6
30% methanol	6.65	3.33	18.0
40% methanol	6.70	3.67	26.0
10% ethanol	5.25	2.10	
20% ethanol	5.70	3.17	
30% ethanol	7.25	4.5	
40% ethanol	10.7	5.8	
10% t-butyl alcohol	5.35		
20% t-butyl alcohol	6.85		
30% t-butyl alcohol	10.5		
40% t-butyl alcohol	14.6		
10% acetonitrile	7.0		
20% acetonitrile	11.7		
30% acetonitrile	15.5		
40% acetonitrile	19.2		

* Solvent compositions by volume before mixing.

DISCUSSION

Mercury(II) is generally the best metal-ion catalyst for halogeno-complexes, apart from fluoro-derivatives. Its catalytic properties are compared with those of the next most effective catalyst, Tl^{3+}(aq), in Table 4. Mercury(II) is also to be preferred to thallium(III) in the light of the oxidising properties of the latter. It should be mentioned here that mercury(II) is a catalyst for the aquation of a variety of compounds. In particular it catalyses the aquation of acetonitrile; we are able to use acetonitrile as a cosolvent in our investigation as mercury(II) catalysis of our complexes is much faster than its catalysis of acetonitrile hydrolysis.[14]

TABLE 4

Relative effectiveness of Hg^{2+}(aq) and Tl^{3+}(aq) as aquation catalysts for chlorotransition-metal complexes, expressed as the ratio of the second-order rate constants, $k_2(Hg^{2+})/k_2(Tl^{3+})$, under comparable conditions

Complex	$k_2(Hg^{2+})/k_2(Tl^{3+})$	Ref.
$[ReCl_6]^{2-}$	8.7	20
$[Co(NH_3)_5Cl]^{2+}$	16.2	*a*
cis-$[Co(en)_2Cl_2]^+$	11.8	14,16, *b*
trans-$[Co(en)_2Cl_2]^+$	8.4	

[a] I. V. Kozhevnikov and E. S. Rudakov, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 571. [b] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

The relative effects of different cosolvents on the mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$ anion are illustrated in Figure 2, where k_2 is shown as a function of x_2, the mole fraction of the organic cosolvent. This diagram resembles the analogous plot for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide ion.[6]

There is a striking difference between the solvent sensitivities of our three mercury(II)-catalysed aquations. Thus k_2 for the $[Co(NH_3)_5Cl]^{2+}$ complex is only *ca.* 1.25 times greater in 40% ethanol than in water, whereas k_2 for the $[ReCl_6]^{2-}$ anion is 75 times larger in 40% ethanol than in water. At this stage of our discussion this difference can be qualitatively ascribed to the difference between reactant charge products; it will be analysed in detail towards the end of this paper. The importance of charge product in determining solvent sensitivities of substitution rates has long been recognised, as, for instance, in Ingold's discussion of organic substitution.[15]

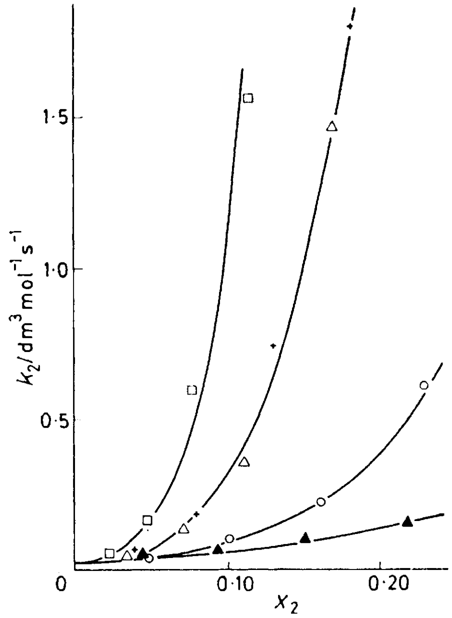

FIGURE 2 Variation of the second-order rate constant, k_2, for mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$ anion at 298.2 K with mole fraction organic component, x_2; (□), t-butyl alcohol; (△), ethanol; (+), acetonitrile; (○), methanol; (▲), ethylene glycol

Grunwald–Winstein analyses [16] of solvent dependences of rates of substitution reactions have proved useful in the classification and mechanism diagnosis both of organic [17] and of inorganic [18] reactions. Good correlations of logarithms of rate constants with solvent Y values (defined from relative rates of S_N1 solvolysis of t-butyl chloride [16]) are expected for dissociative solvolyses of organic and inorganic halides; they are also sometimes found for bimolecular reactions. Thus we have found that second-order rate constants for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide ion, and for mercury(II)-catalysed aquation of the $[Co(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Cl]^{2+}$ cations, correlate tolerably well with solvent Y values, with slopes (m) of the respective plots being *ca.* −1.0 to −1.1,[7] −0.35, and −0.25 (ref. 19) respectively. For the iron(II) complex the cosolvents included methanol, ethanol, acetone, and dioxan; for these cobalt(III) and rhodium(III) complexes, rate constants were only determined over the short solvent range 0—25% ethanol. Grunwald–Winstein plots of our present results for mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$ and $[Co(NH_3)_5Cl]^{2+}$ ions are shown in Figure 3. The degree of correlation, and the curvature of the best correlation line, are similar for $[ReCl_6]^{2-} + Hg^{2+}$ to $[Fe(bipy)_3]^{2+} + CN^-$. However, the high sensitivity of the former reaction to solvent variation is reflected in an *m* value of -1.7 for water-rich mixtures. Our present results for the mercury(II)-catalysed aquation of the $[Co(NH_3)_5Cl]^{2+}$ cation, relating both to more co-solvents and to a greater composition range than our earlier study,[19] now suggest an *m* value of *ca.* -0.2 for this reaction. A Grunwald–Winstein plot for the mercury(II)-catalysed aquation of the *trans*-$[Co(en)_2Cl_2]^+$ cation shows markedly less correlation than for the other two complexes.

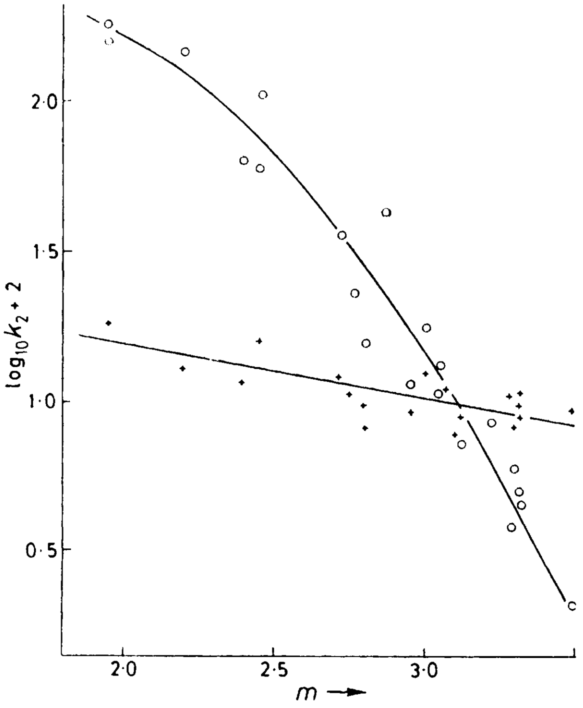

FIGURE 3 Grunwald–Winstein plots of decadic logarithms of second-order rate constants, k_2, for the mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$ anion (○) and the $[Co(NH_3)_5Cl]^{2+}$ cation (+) against solvent *Y* values, for binary aqueous mixtures and water

We have found that there is a close correlation between the kinetic parameter $\delta_m\Delta G^\ddagger$ (*i.e.* the medium effect, δ_m, on the activation Gibbs function $\Delta G^\ddagger$) and the excess Gibbs free energy of mixing, G^E, of the solvent mixture for the (dissociative) solvolysis of t-butyl chloride, aquation of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation ($5NO_2$-phen = 5-nitro-1,10-phenanthroline),[19] and substitution at pentacyanoiron(II) complexes $[Fe(CN)_5L]^{3-}$,[20] for reaction in 'typically aqueous' ($|TS^E| > |H^E|$) binary aqueous solvent mixtures. There is a tolerable correlation of $\delta_m\Delta G^\ddagger$ with G^E for the second-order mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$ anion in the 'typically aqueous' solvent mixtures we have used, *viz.* methanol–, ethanol–, and t-butyl alcohol–water, although the plot for t-butyl alcohol deviates from those for the other two alcohols beyond a mole fraction of *ca.* 0.09 t-butyl alcohol.

A recent examination[21] of the endostatic analysis of activation parameters[22] has identified certain problems of definition with reference to endostatic conditions. Consequently we have not extended our previous application of this model approach[23] to the systems reported here. Rather we have attempted to determine explicitly the solvent effects on initial and transition states, as set out in the paragraphs which follow.

Both the Grunwald–Winstein analysis and the comparison with excess Gibbs free energies of mixing concern just reaction rates, and thus include both initial- and transition-state solvation contributions. To separate these we need to establish solvent effects on the initial states, $\delta_m\mu^\ominus$(i.s.), and on reactivity, and thence by arithmetic obtain the transition-state contribution, $\delta_m\mu^\ominus$(t.s.) [equation (6)]. We have $\delta_m\Delta G^\ddagger$ values for all

$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ominus(\text{t.s.}) - \delta_m\mu^\ominus(\text{i.s.}) \qquad (6)$$

three second-order mercury(II)-catalysed reactions in several series of binary aqueous mixtures. We shall now derive such values of $\delta_m\mu^\ominus$ (reactants) as we can, so that we can calculate $\delta_m\mu^\ominus$(t.s.) for at least some solvent mixtures and thus compare initial-state and transition-state solvation effects in determining reactivity trends. The most difficult and contentious aspect of establishing $\delta_m\mu^\ominus$(ions) is the splitting of whole-salt values into single-ion contributions. There are a variety of ways of doing this, which unfortunately do not always give consistent results when they can be compared directly. The two commonest approaches are to estimate $\delta_m\mu^\ominus$(ion) for one ion, and thence derive $\delta_m\mu^\ominus$ values for all other ions from appropriate experimental $\delta_m\mu^\ominus$ (salt) values, and to assume that $\delta_m\mu^\ominus$ values for a selected cation and a selected anion are equal. We shall use Wells's version of the first approach, which involves Born calculations on the transfer of the proton,[24] and versions of the latter approach in which it is assumed that the thermodynamic transfer parameters for large and allegedly lightly solvated anions and cations are equal [*e.g.* $\delta_m\mu^\ominus(PPh_4^+$ or $NR_4^+) = \delta_m\mu^\ominus(BPh_4^-)$].[25] It is unfortunate that the latter attractive approach, much used recently for single solvents, has been used very little in work and calculations on the properties of ions in binary aqueous mixtures.

$\delta_m\mu^\ominus(Hg^{2+})$.—Estimates of values for $\delta_m\mu^\ominus(Hg^{2+})$ from water into 10—40% methanol can be obtained from our solubility results (Table 3) and appropriate literature data, as shown in Table 5. Agreement between $\delta_m\mu^\ominus(Hg^{2+})$ values derived by different routes for ethanol–water mixtures is not good (columns VII and VIII of Table 5 have to agree fairly well as their underlying assumptions are almost identical). The assumption $\delta_m\mu^\ominus(BPh_4^-) = 0$, after Abraham's hypothesis of $\delta_m\mu^\ominus(NMe_4^+) = 0$,[26] gives a very different set of results (*cf.* column IV of Table 5), is less attractive, and is therefore not used in deriving $\delta_m\mu^\ominus(Hg^{2+})$ values in

Table 5. Our values of $\delta_m\mu^\ominus(Hg^{2+})$ for transfer into methanol–water mixtures are compared with selected $\delta_m\mu^\ominus$(ion) values in Table 6. The surprising feature of this comparison is that the trend for Hg^{2+} is similar to that for K^+ and for halides, and in the opposite direction to that for the more closely related 'soft'[27] cations Cd^{2+} and Ag^+. It should be added here that all the values in Table 6 have been derived by the use of very similar assumptions.[24] At least our $\delta_m\mu^\ominus(Hg^{2+})$ values (columns VII and VIII of Table 5) are of the same sign for methanol–water and for ethanol–water mixtures and, as expected, increase more rapidly with increasing proportion of organic cosolvent in the latter series of mixtures.

Table 5

Gibbs free energies of transfer, $\delta_m\mu^\ominus$, of mercury(II) and caesium tetraphenylborates, and of the ions Cs^+, Hg^{2+}, and BPh_4^-, at 298.2 K (molar scale) *

		$\delta_m\mu^\ominus$/kJ mol^{-1}								
		$Hg[BPh_4]_2$	$Cs[BPh_4]$	Cs^+	BPh_4^-			Hg^{2+}		
Cosolvent	% (v/v)	I	II	III	IV	V	VI	VII	VIII	IX
Methanol	10	−0.15	−3.10	−0.38	−2.72			3.2		
	20	−0.97	−3.84	−0.08	−3.76			3.9		
	30	−1.99	−5.97	+0.42	−6.39			6.6		
	40	−2.05	−6.44	+1.05	−7.49			6.9		
Ethanol	10	−0.23	−3.68	+0.67	−4.35	−1.8	−1.0	6.0	3.2	1.8
	20	−0.84	−5.72	+1.38	−7.10	−3.6	−2.2	9.3	6.4	3.6
	30	−2.63	−7.46	+2.09	−9.55	−6.9	−3.6	11.4	11.2	4.6
	40	−5.49	−8.73	+2.93	−11.05	−11.3	−5.0	16.1	17.1	4.5

* Sources: I and II calculated from Table 4 solubilities; III from ref. 24; IV from II and III; V from ref. 24; VI estimated assuming $\delta_m\mu^\ominus(AsPh_4^+) = \delta_m\mu^\ominus(BPh_4)$, ref. 25; VII from I and IV; VIII from I and V; IX from I and VI.

$\delta_m\mu^\ominus(ReCl_6^{2-})$.—Two routes have been used to estimate values for $\delta_m\mu^\ominus(ReCl_6^{2-})$. One set of values has been obtained directly from published solubilities of caesium hexachlororhenate(IV)[28] and published estimates of $\delta_m\mu^\ominus(Cs^+)$.[24] The second set of values was obtained by a slightly more tortuous route, from the solubilities of $[Fe(phen)_3][ReCl_6]$ (Table 3). The required values of $\delta_m\mu^\ominus[Fe(phen)_3^{2+}]$ were calculated from known solubilities of $[Fe(phen)_3][ClO_4]_2$[29] and published estimates of $\delta_m\mu^\ominus(ClO_4^-)$.[24] The two sets of values for $\delta_m\mu^\ominus(ReCl_6^{2-})$ are listed in Table 7; they agree well for methanol–water mixtures where direct comparison is possible. The Gibbs free energy of transfer, or $\delta_m\mu^\ominus$ value, for the hexachlororhenate(IV) anion becomes more positive as the solvent mixture contains more of the organic component. This is the expected behaviour; $\delta_m\mu^\ominus(ReCl_6^{2-})$ *ca.* 6 kJ mol^{-1} for 30% methanol (Table 7), whereas $\delta_m\mu^\ominus(Cl^-)$ *ca.* 4 kJ mol^{-1} for the same solvent mixture.[7]

Table 6

Comparison of $\delta_m\mu^\ominus(Hg^{2+})$ values with other $\delta_m\mu^\ominus$(ion) values for transfer from water into aqueous methanol, at 298.2 K. Values are taken from ref. 24, and are in kJ mol^{-1} (mole fraction scale except where indicated otherwise)

		% Methanol			
	v/v	10	20	30	40
Ion	w/w	8.1	16.5	25.3	34.5
Hg^{2+}		3.2 *	3.9 *	6.6 *	6.9 *
		2.1	2.6	4.6	4.9

	% (w/w) Methanol						
	10	20	30	33.4	40	43.1	50
Ba^{2+}	0.13	−0.01			−1.55		
Cd^{2+}	−0.50	−1.01			−3.28		
Zn^{2+}	−0.77	−1.46	−2.11				
K^+	0.46	0.68	1.05		1.10		0.81
Ag^+	−0.10	−0.38		−0.99		−1.76	
Cl^-	1.27	2.69			6.24		8.59

* Molar scale, from Table 5, column VII.

$\delta_m\mu^\ominus[Co(NH_3)_5Cl^{2+}]$.—Values of $\delta_m\mu^\ominus[Co(NH_3)_5Cl^{2+}]$ were obtained directly from published solubilities of the chloride salt of this complex cation[30] and published values for $\delta_m\mu^\ominus(Cl^-)$.[24] The chemical potential of this cobalt(III) complex cation increases rapidly as the proportion of ethanol in ethanol–water mixtures increases; $\delta_m\mu^\ominus[Co(NH_3)_5Cl^{2+}]$ * = 2.0, 3.6, 7.0, and 9.6 kJ mol^{-1} at 298.2 K for transfer from water to 10, 20, 30, and 40% (v/v) ethanol.

$\delta_m\mu^\ominus$[*trans*-$Co(en)_2Cl_2^+$].—From published solubilities of *trans*-$[Co(en)_2Cl_2][ClO_4]$[31] and estimates of $\delta_m\mu^\ominus(ClO_4^-)$[24] it is possible to estimate that $\delta_m\mu^\ominus$[*trans*-$Co(en)_2Cl_2^+$] * is 0.1, 0.5, 0.7, and 0.6 kJ mol^{-1} at 298.2 K for transfer from water to 10, 20, 30, and 40% (v/v) ethanol. These values may be compared with $\delta_m\mu^\ominus$[*cis*-$Co(en)_2Cl_2^+$] = 12.5 kJ mol^{-1} for transfer from water to

* Molar scale.

pure ethanol.[32] The smaller change of chemical potential with solvent composition for *trans*-$[Co(en)_2Cl_2]^+$ than for $[Co(NH_3)_5Cl]^{2+}$ (*cf.* above) is reasonable from a simple electrostatic viewpoint.

Initial- and Transition-state Effects.—Having obtained values of $\delta_m\mu^\ominus$ for the reactants (initial state), we can now combine these with values of $\delta_m\Delta G^\ddagger$ calculated from the appropriate rate constants using normal transition-state kinetic theory to obtain values of $\delta_m\mu^\ddagger$, the transfer function for the transition state. These calculations and results are summarised in Table 8, for all three mercury(II)-catalysed aquations in water–ethanol mixtures.

TABLE 7

Values for $\delta_m\mu^\ominus(ReCl_6^{2-})$, molar scale, estimated by the two routes described in the text [a]

	$\delta_m\mu^\ominus(ReCl_6^{2-})$/kJ mol^{-1}	
Solvent [b]	I	II
Methanol		
10%	2.8	1.8
20%	5.5	3.7
30%	6.7	5.0
40%	8.6	7.9
Ethanol		
10%	0.7	
20%	2.8	
30%	2.6	
40%	5.2	

[a] Column I values derived *via* solubilities of the caesium salt, column II *via* solubilities of the $[Fe(phen)_3]^{2+}$ salt. [b] Solvent compositions are by volume before mixing.

TABLE 8

Gibbs free energies of transfer of the initial (i.s.) and transition states (t.s.) and Gibbs activation free energies of transfer for mercury(II)-catalysed aquation of the $[ReCl_6]^{2-}$, $[Co(NH_3)_5Cl]^{2+}$, and *trans*-$[Co(en)_2Cl_2]^+$ ions, at 298.2 K, in ethanol–water mixtures. The values given are for transfer from water; units are kJ mol^{-1}

	% (v/v) Ethanol			
	10	20	30	40
$\delta_m\mu^\ominus(Hg^{2+})$	3.2	6.4	11.2	17.1
(*a*) For $[ReCl_6]^{2-}$				
$\delta_m\mu^\ominus(ReCl_6^{2-})$	0.7	1.6	2.6	5.2
$\delta_m\mu^\ominus$(i.s.)	3.9	8.0	13.8	22.3
$\delta_m\Delta G^\ddagger$	−2.0	−4.7	−7.1	−10.6
$\delta_m\mu^\ddagger$	1.9	3.3	6.7	11.7
(*b*) For $[Co(NH_3)_5Cl]^{2+}$				
$\delta_m\mu^\ominus[Co(NH_3)_5Cl^{2+}]$	2.0	3.6	7.0	9.6
$\delta_m\mu^\ominus$(i.s.)	5.2	10.0	18.2	26.7
$\delta_m\Delta G^\ddagger$	−0.1	−0.4	−0.6	−0.7
$\delta_m\mu^\ddagger$	5.3	10.4	18.8	27.4
(*c*) For *trans*-$[Co(en)_2Cl_2]^+$				
$\delta_m\mu^\ominus$[*trans*-$Co(en)_2Cl_2^+$]	0.1	0.5	0.7	0.6
$\delta_m\mu^\ominus$(i.s.)	3.3	6.9	11.9	17.7
$\delta_m\Delta G^\ddagger$	−0.4	−0.6	−0.3	−0.1
$\delta_m\mu^\ddagger$	3.7	7.5	12.2	17.8

In the reaction with the $[ReCl_6]^{2-}$ anion, the marked increase in rate with increasing ethanol proportion can be ascribed to the much greater destabilisation of the initial state (charges +2 and −2 separately) than of the transition state (electrically neutral overall) [Figure 4(*a*)].

The much smaller variations in rate constants with solvent composition for the mercury(II)-catalysed aquations of the two cationic cobalt(III) complexes arise from near compensation of initial- and transition-state chemical-potential variations [Figure 4(*b*)]. Figure 5 presents a comparable analysis for solvolysis of the *cis*-$[Co(en)_2Cl_2]^+$ cation in various non-aqueous solvents.[32] Here the rate represents a relatively small difference between initial- and transition-state effects, with both these effects closely paralleling the solvent effect on $\delta_m\mu^\ominus(Cl^-)$.

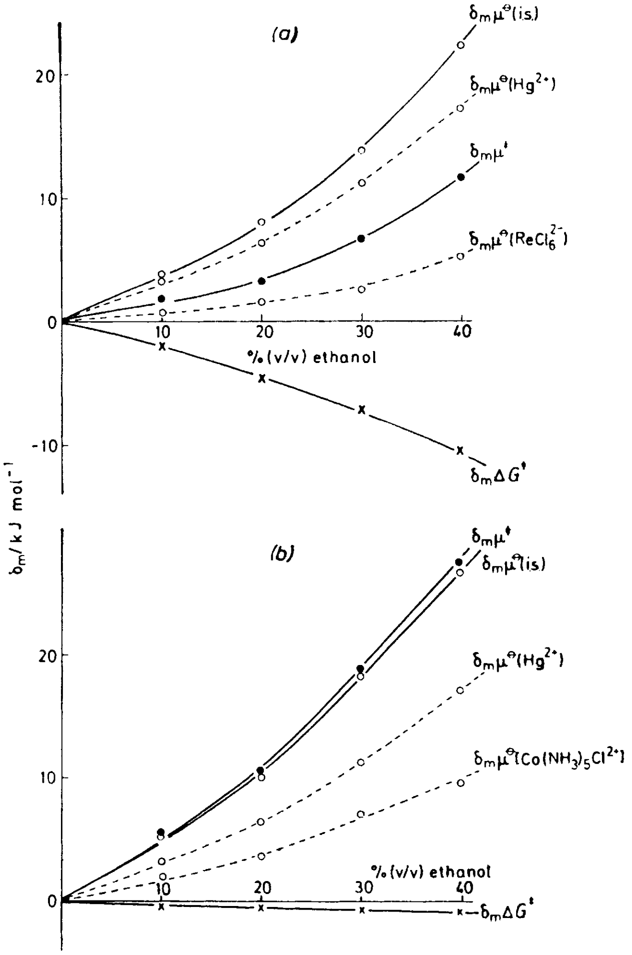

FIGURE 4 Analysis of solvent effects on reactivity into initial- and transition-state contributions for mercury(II)-catalysed aquation of (*a*) $[ReCl_6]^{2-}$ and (*b*) $[Co(NH_3)_5Cl]^{2+}$ in ethanol–water mixtures. The plots show the dependence of transfer parameters on solvent composition for the individual reactants (– – O – –), the initial state (— O —), the Gibbs free energy of activation (– × –), and the transition state (– ● –)

Conclusions.—In the previous paragraphs we have shown a significant difference in behaviour between the reaction of $[ReCl_6]^{2-}$ on the one hand, and of $[Co(NH_3)_5Cl]^{2+}$ and *trans*-$[Co(en)_2Cl_2]^+$ on the other, with mercury(II). We have shown how the observed reactivity trends can be explained in terms of initial- and transition-state chemical potentials, themselves determined by solvation changes. What is disappointing is that our analysis can only be carried out in one series of solvent mixtures, ethanol–water, for all three reactions. This restriction is imposed by the paucity of single-ion parameters for aqueous mixtures. When more data in this area eventually become available it will be possible to analyse more of our kinetic data and test the generality of our preliminary conclusions.

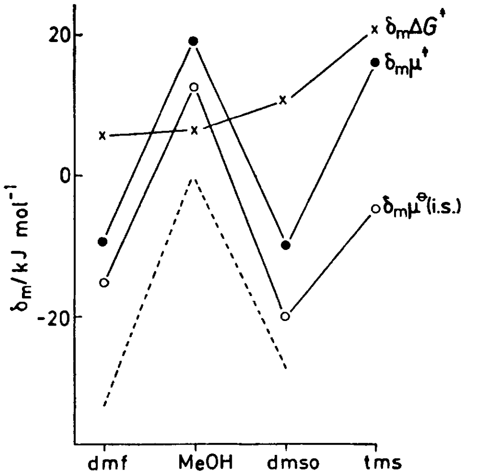

FIGURE 5 Analysis of solvent effects on reactivity into initial- and transition-state contributions for solvolysis of the *cis*-$[Co(en)_2Cl_2]^+$ cation in dimethylformamide (dmf), methanol (MeOH), dimethyl sulphoxide (dmso), and tetramethylene sulphone (tms). The plots show transfer parameters from water into these solvents for the cobalt(III) complex (○), the Gibbs free energy of activation (×), and the transition state (●). The dashed line shows the Gibbs free energies of transfer of chloride (shifted by 17 kJ mol^{-1} for convenience) for comparison

We have restricted our present investigation to mercury(II) catalysis. A variety of cations can catalyse aquation of halogenometal complexes. For example, thallium(III) and cadmium(II) as well as mercury(II) catalyse aquation of the $[ReCl_6]^{2-}$ anion;[33] thallium(III) catalyses the equation of many chlorocobalt(III) complexes.[34] Such ions as silver(I),[35] copper(II),[36] iron(II),[37] cadmium(II), and lead(II) [38] can also act as catalysts for aquation of chloro-, bromo-, and thiocyanato-complexes. These ions are, of course, ineffective as catalysts for aquation of fluoro-complexes, where compounds of aluminium(III), thorium(IV), or zirconium(IV) [39] are more suitable; the 'hard and soft acids and bases' collation approach [27] provides a good guide in this area.

EXPERIMENTAL

The salts $K_2[ReCl_6]$,[40] $[Co(NH_3)_5Cl]Cl_2$,[41] and *trans*-$[Co(en)_2Cl_2]Cl$,[42] were prepared by published methods. Methanol was treated with magnesium and iodine and redistilled before use.[43] 1,4-Dioxan was freed from peroxides by passing down an alumina column, and was then distilled. Other solvents were AnalaR materials, used as received. Mercury(II) perchlorate and nitrate were purchased from K & K Laboratories and from B.D.H. respectively, and used as received. Mercury(II) solutions were prepared freshly each day to avoid any formation of polynuclear mercury species; they were made up in aqueous acid. Kinetic runs were carried out in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer, at wavelengths corresponding to maximum absorption of the respective complexes. Reaction conditions are specified in the respective Table headings.

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