Effects of Added Potassium Bromide and Tetra-n-butylammonium Bromide on the Kinetics of Aquation of Tris(5-nitro-1,10-phenanthroline)-iron(II) in Various Binary Aqueous Mixtures

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Rate constants are reported for the aquation of the title complex $[Fe(5NO_2\text{-}phen)_3]^{2+}$ in a series of binary aqueous mixtures at 298.1 K as a function of the concentration of added KBr or $[NBu_4]Br$. The co-solvents are acetone, dimethyl sulphoxide, acetonitrile, and t-butyl alcohol. In each system the first-order rate constant increases when $[NBu_4]Br$ is added but decreases when KBr is added. The results are used to show that salt effects on this reaction are determined to a large extent by the size of the ion, although certain changes in the pattern of kinetic data particularly for t-butyl alcohol mixtures show that hydration and solvation interactions play some part in determining the overall trend.

REACTIVITY trends in series of binary aqueous solvent mixtures have often been used for the diagnosis of mechanisms of substitution reactions of inorganic [1] or of organic [2] compounds. Conversely, reactivity trends for reactions of known mechanism may give information concerning solvent structural properties in mixed aqueous media.[1-3] Similar statements apply to aqueous salt solutions. Classical salt effects have long been used to establish the charge product of the reacting ions,[1,4] while more recent comparisons of alkali-metal and tetra-alkylammonium salt effects have been useful in diagnosis of mechanisms.[5] Again, reactions of known mechanism may be used to probe solute–solvent interaction and consequent structural features of these media. Both for added co-solvents (non-electrolytes) and added salts (electrolytes), the reflection of medium effects in reactivities stems from favourable or unfavourable solute–solvent interaction; the solutes may be broadly classified into structure-breakers and structure-formers. Uncharged solutes such as urea may be considered to link the co-solvent–salt extremes.

Whereas there has been a lot of activity in the areas of kinetic studies in binary solvent mixtures and in salt solutions, there has been very little investigation of ternary solvent media. We felt that it would be of interest to examine such media, to investigate the reinforcement or cancellation of added co-solvent and salt effects. Such an investigation should prove of some value in providing checks on hypotheses of structural modification in binary solvent media. Obviously, for such an investigation one needs a well studied reaction; aquation of the $[Fe(5NO_2\text{-}phen)_3]^{2+}$ cation seemed a good choice for this ($5NO_2$-phen = 5-nitro-1,10-phenanthroline). Trends of rate constants have already been established in many binary aqueous solvent series [6] and in several salt solutions.[7] The reactivity varies markedly with relatively small changes in solvent medium, making this a usefully sensitive probe reaction. The mechanism is known to involve rate-determining loss of the first ligand molecule; moreover, the activation volume for this step establishes that it is dissociative in character.[8] The only drawback to this system is that it is necessary to study kinetics in the presence of acid, albeit in moderately low concentration, in order that the released ligand can be scavenged to prevent re-formation of the complex. Such scavenging is subsequent to the rate-determining step, which obeys simple first-order (in complex) kinetics with rates independent of acid concentration.[9]

On going from the initial state to the transition state there is no overall change in charge of the complex, this being dipositive in both cases. Thus classical analysis of the salt effects on this reaction based on the Brønsted–Bjerrum equation incorporating the Debye–Hückel law would predict that the rate constant would be independent of the total ionic strength of the solution. However, we showed that this is not the case for this reaction.[7] Indeed, for a range of bromide salts, the pattern of salt effects is complicated. Thus added tetra-n-butylammonium bromide increases the first-order rate constant, potassium bromide decreases the rate constant, and tetramethylammonium bromide has relatively little effect. We assigned [7] these trends in part to the different hydration characteristics of the added cation,[3] noting that $[NBu_4]^+$ is a hydrophobic structure-forming ion in water whereas K^+ is an electrostrictive structure-breaker. In addition we discussed how these ions would effect the initial and transition states for the aquation of the iron complex, bearing in mind that the transition state is more hydrophobic than the initial state. More recently [10] we examined the application of the Friedman [11] expression for the dependence of the pair potential on distance apart for two solute species in aqueous solution, in the context of salt effects on the kinetics of reaction. In the case of salt effects on the kinetics of hydrolysis of t-butyl chloride, the analysis showed that the size of the added ion plays an important role in modifying the energies of both initial and transition states. Moreover, since, in both cases, aquation of the iron complex and hydrolysis of Bu^tCl, the substrate increases in size on going to the transition state, the latter should be affected by added salt to a larger extent than the initial state.

In summary, therefore, we have two possible causes for the differences between added KBr and added $[NBu_4]Br$ on the kinetics of aquation of the iron complex. These are (*i*) hydration characteristics or (*ii*) size of the added cation. In order to probe these alternatives in more detail we measured the rate of aquation in a series of aqueous mixtures as a function of added KBr or $[NBu_4]Br$. Thus, in aqueous solution K^+ is an electrostrictive structure-breaking ion but $[NBu_4]^+$ is a hydrophobic structure-forming ion.[3] We reasoned that if the special characteristics of ionic hydration of the two cations is the important factor then discrimination between the two salts would become less marked as more co-solvent is added. On the other hand, if ion size is the dominant influence then the discrimination would remain. We have measured the first-order rate constant for the aquation reaction in aqueous binary mixtures, containing either KBr or $[NBu_4]Br$. The co-solvents in these mixtures are acetone, dimethyl sulphoxide (dmso), acetonitrile, and t-butyl alcohol.

TABLE 1

Observed first-order rate constants, *k*, for aquation of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation in aqueous Bu^tOH in the presence of various concentrations of KBr or $[NBu_4]Br$. All runs were in the presence of 0.20 mol dm^{-3} HBr, at 298.2 K

Mol fraction Bu^tOH		[Salt]/mol dm^{-3} 0	0.20	0.40	0.67	0.80	1.00
0.021	$10^4k(KBr)/s^{-1}$	5.4	4.6	3.9			3.0
	$10^4k(NBu_4Br)/s^{-1}$				8.4	10.7	
0.087	$10^4k(NBu_4Br)/s^{-1}$	11.4				18	
0.112	$10^4k(KBr)/s^{-1}$	16.5				9.5	
	$10^4k(NBu_4Br)/s^{-1}$			17	23		

TABLE 2

Observed first-order rate constants, *k*, for aquation of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation in aqueous Bu^tOH in the presence of various concentrations of KBr or $[NBu_4]Br$. These runs were in the presence of 0.20 mol dm^{-3} HCl, at 298.2 K

Mol fraction Bu^tOH		[Salt]/mol dm^{-3} 0	0.42	0.50	0.83	1.00	1.17	1.20	1.25	1.50
0.021	$10^4k(KBr)/s^{-1}$	6.5		5.1		3.9				3.7
	$10^4k(NBu_4Br)/s^{-1}$		7.5		10		13		14	
0.045	$10^4k(KBr)/s^{-1}$	11		8.7		7.1				6.0
	$10^4k(NBu_4Br)/s^{-1}$		12		15				16	
0.075	$10^4k(KBr)/s^{-1}$	14		11		8.5		7.0		
	$10^4k(NBu_4Br)/s^{-1}$		17		19				21	
0.112	$10^4k(KBr)/s^{-1}$	24		14		8.6				
	$10^4k(NBu_4Br)/s^{-1}$		25		27					

The outcome of the analysis of these data shows that, in most cases, the discrimination between the two salts is not lost. Thus, the dominant influence appears to be ion size. However, there are sufficient differences in detail to show that hydration and solvation characteristics play their part.

EXPERIMENTAL

Details of the preparation of the complex and solutions have been given previously.[6,7]

Kinetic Measurements.—The aquation reaction was monitored spectrophotometrically by following the decrease in absorbance at 510 nm.[12] The apparatus has been described previously, together with details for the calculations of the rate constants.[7,10]

RESULTS

In aqueous solution containing no co-solvent the kinetics were first order in the presence of 0.2 mol dm^{-3} HBr or HCl. The reaction proceeded to completion and it was confirmed that the rate constant was independent of acid concentration over the range $0.2 \leqslant [H^+] \leqslant 0.5$ mol dm^{-3}. There was a slight difference between the values calculated for solutions containing either HCl or HBr. In solutions containing HBr, $k_{obs.} \simeq 6 \times 10^{-4}$ s^{-1} and in solutions containing HCl, $k_{obs.} \simeq 4.5 \times 10^{-4}$ s^{-1}. However, this difference is much smaller than that produced when either KBr or $[NBu_4]Br$, $c_2 > 0.2$ mol dm^{-3}, was added. Rate constants for the aquation reaction in a range of co-solvents containing different concentrations of the salts are summarised in Tables 1—5. Where the data overlap with those previously reported, there is satisfactory agreement. It was important in this study to monitor closely the total extent of chemical reaction. For most systems, the aquation reaction proceeded to completion as judged by the final absorbance. However, at high mol fractions of co-solvent, particularly Bu^tOH, this was not always the case. Although the analysis of kinetic data yielded in these cases a first-order rate constant which satisfactorily accounted for the dependence of absorbance on time, nevertheless, these particular rate constants were rejected.

The general pattern of rate constants for all systems was remarkably similar. Thus, added $[NBu_4]Br$ increased *k* in all solvent mixtures but added KBr produced a decrease in *k*. These trends are summarised in Figure 1 for a range of solvent mixtures. In these plots we show the dependence

TABLE 3

Observed first-order rate constants, *k*, for aquation of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation in aqueous acetone in the presence of various concentrations of KBr or $[NBu_4]Br$. All runs were in the presence of 0.20 mol dm^{-3} HBr at 298.2 K

Mol fraction acetone		[Salt]/mol dm^{-3} 0	0.25	0.51	0.80	1.00	2.00
0	$10^4k(KBr)/s^{-1}$	4.8		4.0		2.8	2.8
	$10^4k(NBu_4Br)/s^{-1}$		4.9	5.6	6.1		
		0	0.25	0.51	0.80	1.00	1.33
0.017	$10^4k(KBr)/s^{-1}$	5.3		4.3		3.7	3.5
	$10^4k(NBu_4Br)/s^{-1}$		5.7	6.5	8.4		
0.036	$10^4k(KBr)/s^{-1}$	6.2		5.0		4.3	3.9
	$10^4k(NBu_4Br)/s^{-1}$		7.0	8.1	11.1		
0.069	$10^4k(KBr)/s^{-1}$	7.5		6.0		5.4	5.0
	$10^4k(NBu_4Br)/s^{-1}$		8.8	11.3	15.9		
0.118	$10^4k(KBr)/s^{-1}$	11.2		9.9		8.7	8.3
	$10^4k(NBu_4Br)/s^{-1}$		16	24			

TABLE 4

Observed first-order rate constants, k, for aquation of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation in aqueous acetonitrile in the presence of various concentrations of KBr or $[NBu_4]Br$. All runs were in the presence of 0.20 mol dm^{-3} HBr, at 298.2 K

Mol fraction MeCN		[Salt]/mol dm^{-3}						
		0	0.25	0.50	0.70	1.10	1.50	2.00
0	$10^4k(KBr)/s^{-1}$	4.6	4.5		3.9	3.4		2.6
	$10^4k(NBu_4Br)/s^{-1}$		4.7	5.0	6.1	6.7	8.6	
		0	0.25	0.33	0.50	0.67	1.00	
0.01	$10^4k(KBr)/s^{-1}$	5.0	4.5		3.5		3.3	
	$10^4k(NBu_4Br)/s^{-1}$			5.6		6.3	8.2	
0.05	$10^4k(KBr)/s^{-1}$	5.9	5.7		5.0		4.3	
	$10^4k(NBu_4Br)/s^{-1}$			7.3		8.1	11	
0.10	$10^4k(KBr)/s^{-1}$	7.6	6.5		5.6		4.5	
	$10^4k(NBu_4Br)/s^{-1}$			9.7		12	14	
0.16	$10^4k(KBr)/s^{-1}$	8.7	8.4		7.8		6.7	
	$10^4k(NBu_4Br)/s^{-1}$			11		15		

on concentration of added salt, c_2, on log (k/k_0) where k is the observed rate constant and k_0 is the rate constant for aquation in the same solvent but when $c_2 = 0$. For comparison, Figure 1 includes the line summarising the trends when $x_2 = 0$. For the three solvent systems examined, the change on going to an aqueous mixture is more marked when the added salt is $[NBu_4]Br$. In Figure 2 we summarise the data for mixtures where the co-solvent is Bu^{t}OH. With increase in x_2, there is an interesting reversal in order of the curves. Thus, a low mol fraction of Bu^{t}OH produces a sharp increase in gradient of the plot, but when $x_2 > 0.1$ the data curve now falls close to that for systems where $x_2 = 0$. In contrast, the curves formed by the data points for KBr solutions show a smooth change in gradient as x_2 increases.

TABLE 5

Observed first-order rate constants, k, for aquation of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation in aqueous dimethyl sulphoxide in the presence of various concentrations of KBr or $[NBu_4]Br$. All runs were in the presence of 0.20 mol dm^{-3} HBr, at 298.2 K

Mol fraction dmso		[Salt]/mol dm^{-3}					
		0	0.26	0.53	0.80	1.07	1.60
0.018	$10^4k(KBr)/s^{-1}$	6.0		4.6		4.0	3.6
	$10^4k(NBu_4Br)/s^{-1}$		5.8	7.1	7.8		
0.038	$10^4k(KBr)/s^{-1}$	6.9		5.4		4.7	4.2
	$10^4k(NBu_4Br)/s^{-1}$		7.2	8.2	10		
0.072	$10^4k(KBr)/s^{-1}$	9.5		6.9		6.2	5.7
	$10^4k(NBu_4Br)/s^{-1}$		9.7	12	14		
0.112	$10^4k(KBr)/s^{-1}$	10.9		9.3		7.6	7.4
	$10^4k(NBu_4Br)/s^{-1}$		16	20			

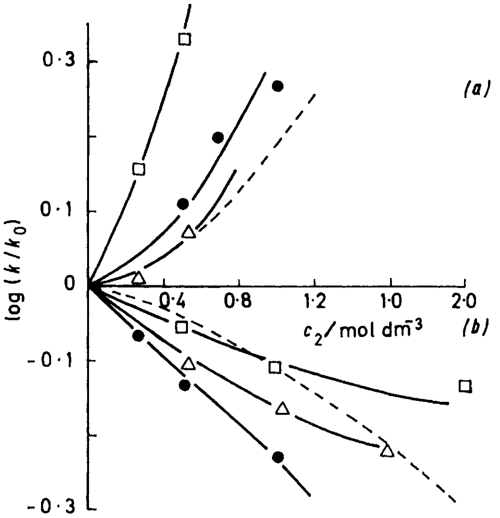

FIGURE 1 Dependence of log (k/k_0) for the aquation of $[Fe(5NO_2\text{-phen})_3]^{2+}$ on the concentration of added salt [(*a*) $[NBu_4]Br$, (*b*) KBr] at 298.2 K in various aqueous solutions: water (– – – –); water–acetonitrile, $x_2 = 0.1$ (●); water–acetone, $x_2 = 0.12$ (□); and water–dmso, $x_2 = 0.04$ (△)

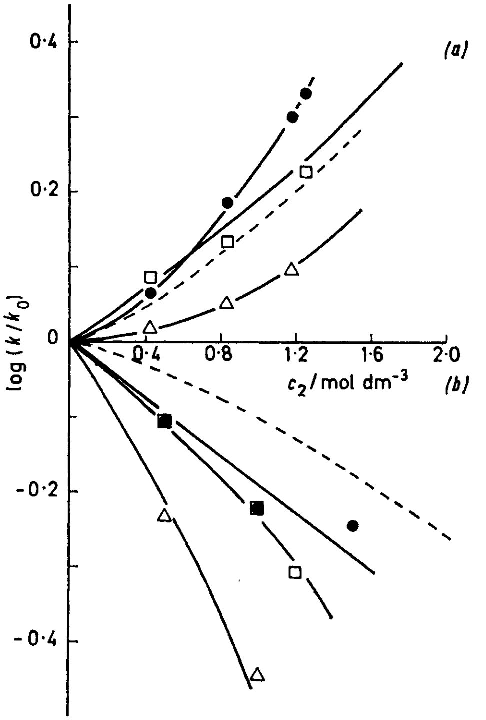

FIGURE 2 Dependence of log (k/k_0) for the aquation of $[Fe(5NO_2\text{-phen})_3]^{2+}$ on the concentration of added salt [(*a*) $[NBu_4]Br$, (*b*) KBr] at 298.2 K in t-butyl alcohol–water mixtures: $x_2 = 0$ (———), 0.02 (●), 0.07 (□), or 0.11 (△)

DISCUSSION

The non-aqueous components of the aqueous mixtures used in this study have been chosen to cover a range of types, based on the classification of aqueous mixtures according to their thermodynamic properties. Thus, acetone–water and t-butyl alcohol–water are typically aqueous mixtures where the excess molar Gibbs function, G^E, is positive and the mixing process is determined by changes in entropy. Dimethyl sulphoxide–water and acetonitrile–water are typically non-aqueous mixtures but they differ because for dmso mixtures $G^E < 0$ while for acetonitrile mixtures, $G^E > 0$. Thus, our aim was to ensure as far as possible that a complete range of modifications to hydration interactions would be covered.

Comparison of the effects of added salt on the reaction in different solvent mixtures is not, however, straightforward. The curves given in Figures 1 and 2 are in effect projections on one plane, normalised to a common origin, of extremely complex surfaces in the three-dimensional plot showing the dependence of rate constant on x_2 and on c_2. Many factors contribute to this complexity. For example, the properties of aqueous mixtures are often extremely sensitive to added salt and the changes are rarely additive. Indeed, addition of a salt can often produce partial miscibility. In the present context, we have the added complication that the rate constant is determined by the difference in energies of initial and transition states which potentially are affected differently by the salt and solvent. Therefore, we suggest that it is dangerous to read too much into the trends, although a broad pattern emerges. Interestingly, a pattern of additivity of effects is beginning to emerge for solubilities of some non-electrolytes in ' ternary ' solvent mixtures of the water + organic solvent + salt type, specifically for ethyl acetate [13] and for the uncharged inorganic complex $[Fe(bipy)_2(CN)_2]$ [14] (bipy = 2,2′-bipyridine). We hope to extend this investigation to sparingly soluble electrolytes such as the perchlorates of complexes of the $[Fe(bipy)_3]^{2+}$ type, thus providing some information germane to the initial state of our present kinetic study.

It is indeed striking that in all systems addition of $[NBu_4]Br$ produces an increase in rate constant whereas the reverse trend occurs when KBr is added. Thus, in agreement with the conclusions, based on the statistical thermodynamic calculations, the dominant factor appears to be the size of the added ion. This conclusion is re-enforced by the observation that at a given value of c_2 the effectiveness of the co-solvent is enhanced in the presence of $[NBu_4]Br$. In other words, the size of the $[NBu_4]^+$ ion is more effective in a mixture than when $x_2 = 0$. In an aqueous solution of this hydrophobic ion the alkyl chains are held in cavities formed by hydrogen-bonded water molecules, similar to those observed in the corresponding solid hydrates. Addition of a co-solvent which disrupts water–water interactions (*e.g.* dmso or acetonitrile) will lead to an increase in the effective size of these ions. Thus, we still argue that the hydration and solvation characteristics of the added ion play some, if only secondary, part. Otherwise, it would be difficult to account for the data obtained for mixtures containing Bu^tOH (Figure 2). This co-solvent generally exhibits in a striking fashion the behaviour of typically aqueous mixtures. At low mol fractions, $x_2 < 0.04$, t-butyl alcohol enhances water–water interactions. In terms of the liquid clathrate model for these mixtures,[3] the alkyl chains occupy voids in the water structure in a manner similar to that discussed above for $[NBu_4]^+$ ion. Thus, when this ion is added there is a competition for these voids with the result that the effective size of the ion increases more rapidly when $x_2 > 0$. However, when $x_2 > 0.04$ the co-solvent disrupts water structure and the curve for log (k/k_0) against c_2 falls back and eventually crosses the curve containing the points for $x_2 = 0$. The quite different trend for solutions containing KBr in t-butyl alcohol mixtures lends support to the proposal that hydration characteristics play some part in determining the salt effects.

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