Investigation of the Effects of Added Salts on the Rate of Hydrolysis of Sulphur Trioxide–Trimethylamine†

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The first-order rate constant for aquation of sulphur trioxide–trimethylamine, $Me_3N{\cdot}SO_3$, at 336 K increases when tetra-n-butylammonium bromide is added, but decreases when either potassium or lithium bromide is added. This behaviour is examined in the light of similar trends for the dissociative aquation of the tris(5-nitro-1,10-phenanthroline)iron(II) cation.

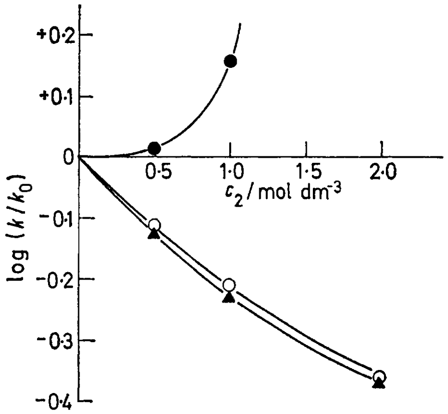
RECENTLY we reported[1] that the rate of aquation of tris(5-nitro-1,10-phenanthroline)iron(II) is increased when tetra-n-butylammonium bromide is added but decreased when potassium bromide, for example, is added. In our analysis of these effects we concluded that the changes in rate are a consequence of the effects of cation–cation interaction in water, which in turn depend on the hydration characteristics of these ions. Further, these salt effects are closely linked with the mechanism of aquation which in this case is dissociative, the leaving group being hydrophobic in character.[1] In order to probe these ideas further we have sought to examine salt effects on the rate of an aquation reaction which involves a neutral molecule and where the mechanism of reaction involves associative attack by water. This information, together with data for the effects of salts on the rate of aquation of t-butyl chloride,[2] where the mechanism is dissociative and the leaving group hydrophobic, would provide a clearer picture of salt effects on reactions in water than was available heretofore. Unfortunately, systems which fit the stated requirements and whose kinetics of reaction can be conveniently followed are difficult to find. The aquation of sulphur trioxide–trimethylamine, $Me_3N{\cdot}SO_3$, in neutral solution appeared a possible candidate for investigation.

RESULTS

Aquation of $Me_3N{\cdot}SO_3$ was very slow; the half-life at 336 K was *ca.* 30 h. Rate constants for aquation at 336 K are given in the Table. Our value for the rate constant at 336 K, 5.86×10^{-6} s^{-1}, is close to that, 5.94×10^{-6} s^{-1}, calculated from the expression given by Ryss and Bogdanova.[3] The pattern of reactivity in the presence of added salts is summarised in the Figure. Addition of lithium bromide resulted in a decrease in the rate constant; added potassium bromide was slightly more effective. However, added tetra-n-butylammonium bromide led to an increase in the rate constant.

Rate constants for aquation of sulphur trioxide–trimethylamine in various aqueous salt solutions at 336 K

Salt	Concentration c_2/mol dm^{-3}	10^6k/s^{-1}
None		5.86
KBr	0.5	4.38
	1.0	3.47
	2.0	2.49
$[Bu^n_4N]Br$	0.5	6.0
	1.0	8.40
LiBr	0.5	4.50
	1.0	3.63
	2.0	2.54



Dependence of the ratio of rate constants, k/k_0, on concentration of added salt, c_2, at 336 K for aquation of sulphur trioxide–trimethylamine (k_0 = rate constant in the absence of salt). Added salts: (▲) KBr, (○) LiBr, and (●) $[Bu^n_4N]Br$

DISCUSSION

The kinetics of hydrolysis of adducts of the type $R_3N{\cdot}SO_3$ have been extensively investigated in acid, neutral, and alkaline solution.[4,5] In alkaline solution the second-order rate law, first order in adduct and first order in hydroxide concentration, indicates a bimolecular mechanism. In neutral solution convincing evidence of the nature of the aquation mechanism is singularly lacking. Associative attack by water at the sulphur is assumed as reasonable in the light of the established bimolecular reaction with hydroxide and the presumed availability of vacant *d* orbitals for easy nucleophilic attack at the sulphur atom. The only real evidence for bimolecular attack by water is derived from the

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† No reprints available.

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dependence of aquation rate on water concentration in acetone–water mixtures.[5] Here there is an apparent first-order dependence on water concentration, though only up to a concentration of *ca.* 2 mol dm^{-3}. Previously published results are therefore not inconsistent with S_N2 aquation in neutral solution, but there is no unequivocal evidence in favour of this mechanism.

The marked difference in the effect of added alkylammonium and alkali-metal salts on the aquation rate cannot be attributed solely to classical ionic-strength effects. There is a striking similarity between the trends in the Table and Figure with those previously reported for the aquation of the tris(5-nitro-1,10-phenanthroline)iron(II) cation.[1] Indeed the plots of $\log(k/k_0)$ against c_2 are almost superimposable. This striking result can be rationalised in one of two ways. The effects of added salts of this type may be almost the same for associative and dissociative aquations. Alternatively, the mechanism for aquation of $Me_3N{\cdot}SO_3$ in neutral solution is dissociative like that of the Fe^{II} complex. We prefer the latter explanation; the reactivity pattern for the allegedly bimolecular hydrolysis of disulphate ion, $[S_2O_7]^{2-}$, in the presence of a similar range of added salts [6] is very different from that reported here. A change in the mechanism of hydrolysis of $Me_3N{\cdot}SO_3$ from associative with hydroxide ion to dissociative in neutral solution is not without parallel in inorganic chemistry. There is just such a change for the analogous reactions of (substituted) 1,10-phenanthroline complexes of Fe^{II}.[7]

EXPERIMENTAL

The salts and water used were purified as described previously.[1] Sulphur trioxide–trimethylamine, $Me_3N{\cdot}SO_3$, was used as purchased (Ralph N. Emanuel). The reaction was followed by titrating aliquot portions of the reaction mixture (initial concentration of $Me_3N{\cdot}SO_3$, 3×10^{-3} mol dm^{-3}) against standard sodium hydroxide solution (1×10^{-3} mol dm^{-3}) using Bromocresol Green–Methyl Red as indicator.[4] The reaction was followed for at least six half-lives; good first-order plots were obtained in all cases. Rate constants were computed (PDP 11) using a standard least-mean-squares program.

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