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Activation Volume for the Peroxodisulphate Oxidation of the Tetracyano-2,2'-bipyridylferrate(II) Anion

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Volumes of activation have provided valuable information for the diagnosis of mechanism in many systems. However for reactions involving charged species, as reactants or as leaving groups, in polar solvents intrinsic volumes of activation can be affected markedly by volume changes due to solvation changes in going from the initial state to the transition state. One of the most dramatic illustrations of this is afforded by nucleophilic attack, by cyanide or hydroxide, at the low-spin iron(II) diimine complexes $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ [1]. In aqueous solution these reactions have activation volumes between +19 and +22 $cm^3 mol^{-1}$. Such volumes differ strikingly from the negative values expected for a bimolecular process; the mechanism of these reactions may involve initial attack of nucleophile at the iron or at the coordinated ligand but is bimolecular in either case [2]. The assignment of the positive activation volumes to release of electrostricted water on incorporation of hydroxide or cyanide into the transition state has been supported by the establishment of activation volumes [3] of +4 and −9 $cm^3 mol^{-1}$ respectively for the reaction of $Mo(CO)_4(bipy)$ with cyanide in methanol (cyanide lightly solvated) and in dimethyl sulphoxide (cyanide effectively not solvated) [4]. We are investigating these surprisingly large solvation contributions in related reactions, and in this letter we report the activation volume for peroxodisulphate oxidation of the $Fe(bipy)(CN)_4^{2-}$ anion.

We have reported elsewhere details of the kinetics of peroxodisulphate oxidation of the $Fe(bipy)(CN)_4^{2-}$ in water and in some binary aqueous solvent mixtures [5]. The rate law is first-order in each reactant, the mechanism presumably involving simple bimolecular outer-sphere electron transfer as rate-determining step. We have measured rate constants under pressures up to 1.01 kbar at the conditions stated in Table I. A trace of the disodium salt of EDTA was added to reaction mixtures (10^{-5} mol dm^{-3}) to sequester any traces of interfering metal ions. Runs were conducted at 293.0 K as rates were a little too fast at 298 K for monitoring with our present high pressure apparatus [6].

TABLE I. Observed First-order Rate Constants for Peroxodisulphate Oxidation of the $Fe(bipy)(CN)_4^{2-}$ Anion in Water at 293.0 K; initial $[K_2Fe(bipy)(CN)_4] = 1.4 \times 10^{-4}$ mol dm^{-3}, initial $[K_2S_2O_8] = 3.3 \times 10^{-3}$ mol dm^{-3}, I = 0.033 mol dm^{-3} (K_2SO_4); rates monitored at 485 nm.

Pressure/kbar	$10^4\ k_{obs}/s^{-1}$
0.001	3.5[a]
0.34	3.3
0.67	3.6
0.84	3.6
1.01	3.3

[a] *Cf.* $k = 7 \times 10^{-4}\ s^{-1}$ at 298.2 K (ref. [5]).

TABLE II. Activation Volumes for Bimolecular Reaction between Ions of Like Charge in Aqueous Solution.

Reaction[a]	$\Delta V^{\neq}/cm^3\ mol^{-1}$
$Fe(bipy)(CN)_4^{2-} + S_2O_8^{2-}$	0
$Fe(fz)_3^{4-} + OH^-$	−2[b]
$Cr(NH_3)_5Cl^{2+}$ $Co(NH_3)_5X^{2+}$ [c] + Hg^{2+} $Rh(NH_3)_5Cl^{2+}$	−2 to +1[d]
$Co(NH_3)_5Br^{2+} + Pb^{2+}$	+2.5[e]

[a] fz = ferrozine(3-(2-pyridyl)-5,6-bis-(4-sulphophenyl)-1,2,4-triazine). [b] J. Burgess and R. Sherry, unpublished observations. [c] X = Cl, Br. [d] Ref. [8]. [e] In an aqueous polyelectrolyte solution, ref. [9].

The kinetic results in Table I indicate an activation volume of 0 ± 1 $cm^3 mol^{-1}$. Clearly some contribution from solvation changes on forming the transition state is balancing the intrinsic negative volume change (about −10 $cm^3 mol^{-1}$ [7]) for a bimolecular process. The present reaction involves two ions of like charge; the peroxodisulphate anion is hydrophilic and the iron(II) complex has a 2− charge and a largely hydrophilic periphery. It is interesting to compare our zero activation volume with values for other bimolecular reactions involving like-charged ions (Table II) [8, 9]. All are close to zero, as indeed is the volume change for the model reaction $Fe(OH)^{2+}aq + H^+aq = Fe^{3+}aq$, where ΔV^θ =

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-1.2 cm^3 mol^{-1} [10]. In all these processes the expected loss in volume as the reactants come together is balanced by an increase in volume arising from the release of some electrostricted water from reactant shells to bulk solvent.

The activation volume for peroxodisulphate oxidation of the $Fe(4\text{-}Mephen)_3^{2+}$ cation is also approximately zero in aqueous solution [4]. Here, as in the reactions of $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ with hydroxide or cyanide, the iron(II) complex has a hydrophobic periphery and release of electrostricted water can only come from the hydrated anion.

It is interesting that activation volumes close to zero are also found for bimolecular reactions of nonelectrolytes in non-polar solvents. Thus the activation volume for attack of triphenylphosphine on triruthenium dodecacarbonyl in decalin [11] is 0 ± 2 cm^3 mol^{-1} (at 303 K) [12]. Here the explanation is probably that steric crowding prevents the triphenylphosphine from approaching the ruthenium closely enough for the volume of the system to decrease markedly on forming the transition state.

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