Kinetics of Aquation of Tris(5-nitro-1,10-phenanthroline)iron(II) in Hydrogen Peroxide–Water Mixtures†

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Rate constants and activation parameters for the aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in hydrogen peroxide–water mixtures (mole fraction of hydrogen peroxide = 0.015—0.15) have been determined. The variations of these kinetic parameters with solvent composition are discussed in the light of the physical properties of these solvent mixtures. The observed reactivity trends are related to the emerging pattern of reactivities for dissociative solvolyses, particularly of low-spin iron(II) complexes and of t-butyl chloride, in binary water–organic solvent mixtures.

In aqueous solutions, aquation of tris(5-nitro-1,10-phenanthroline)iron(II) [equation (1)] occurs in three

$$[Fe(5\text{-}NO_2phen)_3]^{2+} \longrightarrow Fe^{2+} + 3(5\text{-}NO_2phen) \quad (1)$$

steps, each of which involves loss of one 5-NO_2phen ligand. The rate-determining step in the aquation is loss of the first ligand. In the presence of a sufficiently high concentration of acid the reaction goes to completion, protonation of free ligand inhibiting recombination. The rate of aquation is nearly independent of acid concentration, since protonation of released ligand occurs subsequent to rate-determining ligand loss.[1] Recent work has indicated that the rate-determining step is dissociative, involving fission of the Fe–N bond.[2] The kinetics of aquation are markedly sensitive to added salt[3] and added co-solvent.[4] In this paper we report an extension of these studies to include the effect of added hydrogen peroxide. Hydrogen peroxide–water mixtures have several points of interest, beyond the obvious feature that they belong to the rare group of binary aqueous mixtures in which the non-aqueous component is inorganic. Mixtures of hydrogen peroxide and water are almost isodielectric over the whole composition range,[5] yet there are strong intercomponent interactions, as evidenced by the thermodynamic excess functions of mixing,[6] as well as intracomponent interactions.

Hydrogen peroxide–water mixtures offer one unique advantage over other binary aqueous solvent systems for the study of kinetics of aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$. To make this aquation go to completion it is necessary to have some reagent to scavenge the released ligand or the Fe^{2+}(aq) produced and thus prevent any reformation of the starting complex. Usually this is achieved by the addition of acid to protonate the free ligand;[1] the addition of certain metal ions to complex the released ligand is also effective.[7,8] Scavenging of the ligand, the Fe^{2+}(aq), or

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† No reprints available.

[1] T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 2348; W. W. Brandt and D. K. Gullstrom, *ibid.*, 1952, **74**, 3532.

[2] J. M. Lucie, D. R. Stranks, and J. Burgess, *J.C.S. Dalton*, 1975, 245.

[3] M. J. Blandamer, J. Burgess, and S. H. Morris, *J.C.S. Dalton*, 1974, 1717.

[4] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 385.

[5] P. M. Gross and R. C. Taylor, *J. Amer. Chem. Soc.*, 1950, **72**, 2075.

[6] G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, *J. Amer. Chem. Soc.*, 1952, **74**, 3715; P. A. Giguère and P. Geoffrion, *Canad. J. Res.*, 1950, **B28**, 599; P. A. Giguère, B. G. Monssette, A. W. Olmos, and O. Knop, *Canad. J. Chem.*, 1955, **33**, 804; A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, 1953, **15**, 161.

[7] L. Sieden, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1959, **81**, 3809.

[8] M. J. Blandamer, J. Burgess, and J. R. Membrey, *J.C.S. Faraday I*, 1975, 145.

intermediate complexes also provides a contribution to the overall decomposition of the complex in reaction mixtures containing hydroxide (in the presence of oxygen),[9] cyanide,[10] or peroxodisulphate.[11] In all these cases it is obviously necessary to add the appropriate reagent to the solution of the iron(II) complex in the binary solvent mixture. There is thus the risk of introducing further perturbation of the inter- and intra-solvent interactions especially when, as in the case of the aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$, it is necessary to use relatively high concentrations of acid to force the aquation to completion. Hydrogen peroxide is known to be an effective scavenger of products from dissociation of iron(II) complexes of (substituted) 1,10-phenanthroline and 2,2′-bipyridyl ligands,[12] hence the kinetics of aquation of such complexes can be studied in hydrogen peroxide–water mixtures without the addition of any other reagent. In the present paper we report rate constants and activation parameters for such aquations, in water-rich mixtures in which the mole fraction of hydrogen peroxide is between 0.015 and 0.15.

EXPERIMENTAL

Solutions.—Aqueous solutions containing tris(5-nitro-1,10-phenanthroline)iron(II) were prepared by dissolving in distilled water ammonium iron(II) sulphate (AnalaR) and a slight excess of the ligand. Hydrogen peroxide solutions (B.D.H. AnalaR) were diluted to the appropriate strength.

Kinetics.—The solutions were contained in 1 cm path length silica cells held in a thermostatted cell holder of a Unicam SP 800 recording spectrophotometer. The progress of the reaction was followed by measuring the change in absorbance at 510 nm with time. The absorbance data were recorded at predetermined time intervals on punched tape (Facit) using a data-logging (Solartron) system. The reaction was monitored sequentially in up to four cells. A troublesome factor in these studies was the tendency for the mixture to decompose, oxygen bubbles (from the H_2O_2) occluding to the inside surface of the spectrophotometer cells. This limited the experiments to mixtures containing low mole fractions of H_2O_2 and to low temperatures.

Rate constants. The method proposed by Moore [13] was used to calculate rate constants for the aquation reaction. In this method the dependence of absorbance, A, on time, t, is fitted using a non-linear least-squares procedure to the first-order rate equation using estimated values of $A(t = 0)$ and $A(t = \infty)$. Improved values for these latter two quantities were calculated from the derived rate constant k and the calculation was then repeated. This analytical procedure was incorporated into an ALGOL computer program (ICL 4130). Less than five cycles were usually required in each calculation for convergence, the program being designed to print out the final values of $A(t = 0)$, $A(t = \infty)$, and k together with calculated values of A at each time t.

The dependence of rate constant on temperature was analysed using the method described by Clarke and Glew,[14] the relevant calculations being incorporated into a computer program (ALGOL). The reference temperature about which the dependence was fitted, θ in ref. 14, was taken as the midpoint of the measured temperature range. The program also provided the activation parameters at 298 K. For the system reported here, the parameters obtained were the Gibbs function, $\Delta G^\ddagger$, the enthalpy of activation, $\Delta H^\ddagger$, and the entropy of activation, $\Delta S^\ddagger$.

RESULTS

Rate constants for the aquation of the iron(II) complex are summarised in Table 1, where each entry represents the mean of at least three satisfactorily consistent determinations. The derived activation parameters are reported in Table 2. The variation of the activation parameters with solvent composition is illustrated in the Figure.

TABLE 1

Mean first-order rate constants, k, for aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$ in hydrogen peroxide–water mixtures (x_2 = mole fraction of hydrogen peroxide)

	$10^4k/s^{-1}$			
x_2	286.2	295.4	298.2	306.1 K
0.015	0.84	3.6	7.2	21.0
0.020	0.75	2.7	6.7	19.3
0.040	0.54	1.7	5.9	12.8
0.057	0.45	1.4	4.4	10.5
0.090	0.21	0.92	2.6	8.2
0.110	0.13	0.66	2.0	6.5
0.150	0.09	0.42	1.4	5.2

TABLE 2

Activation parameters (kJ mol^{-1}) for the aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$ in hydrogen peroxide–water mixtures; $\Delta G^\ddagger$ and $T\Delta S^\ddagger$ were calculated for 298.2 K

x_2	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$T\Delta S^\ddagger$
0.015	90.96	114 ± 2	23
0.020	91.12	115 ± 3	24
0.040	91.43	118 ± 3	26
0.057	92.16	122 ± 3	29
0.090	93.48	132 ± 4	38
0.110	94.14	141 ± 4	47
0.150	95.02	146 ± 5	51

DISCUSSION

When organic co-solvents (*e.g.* monohydric alcohols, acetone, and acetonitrile) are added to water, the relative permittivity of the solvent usually decreases. Quantitative treatments of the dependence of the rate of a given reaction on solvent have often stressed the importance of the solvent permittivity in determining the difference in energies of the initial and transition states.[15] However, this approach has been relatively unsuccessful in the context of aqueous solutions, agreement between observed and predicted trends being poor. Here, other factors must be considered such as the

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[9] D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728; J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697; G. Nord and T. Pizzino, *Chem. Comm.*, 1970, 1633.

[10] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706; J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[11] J. Burgess and R. H. Prince, *J. Chem. Soc.* (*A*), 1970, 2111.

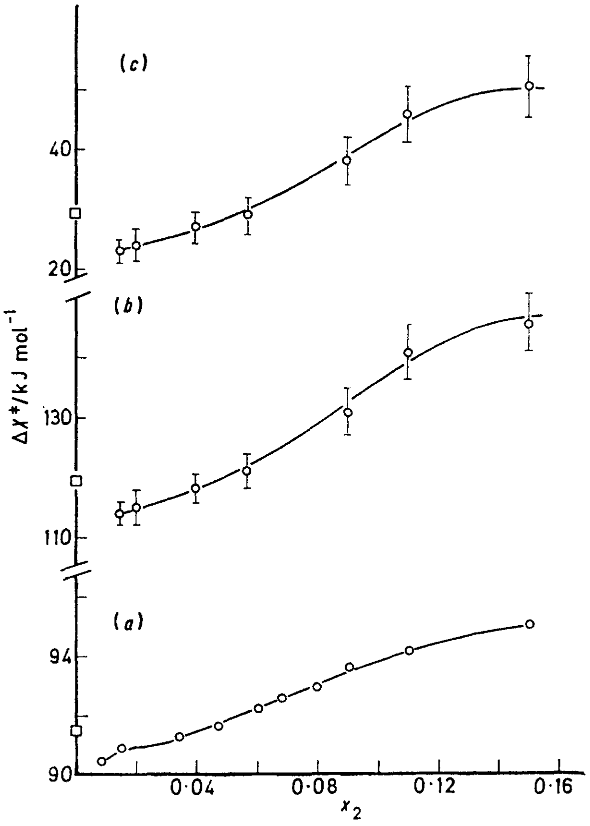
[12] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061.

[13] P. Moore, *J.C.S. Faraday I*, 1972, 1890.

[14] E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

[15] E. S. Amis, ' Solvent Effects on Reaction Rates and Mechanisms,' Academic Press, London, 1966.

effect of added solvent on the structure of water. Nevertheless both factors, changes in solvent permittivity and solvent structure, will probably have to be considered in the final analysis particularly for reactions involving ions. It is in this context that the solvent system, hydrogen peroxide–water, is important when it is recalled that these aqueous mixtures are almost isodielectric. Clearly, therefore, changes in kinetic parameters resulting from changes in solvent composition must stem from effects other than a change in solvent permittivity. The properties of hydrogen peroxide–water mixtures are controlled to a considerable extent by intercomponent association as shown by the molar excess thermodynamic function of mixing. Thus the mixing is exothermic and the excess Gibbs function of mixing is negative.[6] Intercomponent hydrogen bonding results in a decrease in the extent of water–water hydrogen bonding so that hydrogen peroxide can be classed as a ' typically non-aqueous (t.n.a.) co-solvent '[16] and a water-structure breaker.



Dependence on mole fraction of hydrogen peroxide, x_2, of (a) the Gibbs function, $\Delta G^{\ddagger}$, (b) the enthalpy, $\Delta H^{\ddagger}$, and (c) the entropy, $T\Delta S^{\ddagger}$, of activation for aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$ at 298 K. The points at $x_2 = 0$ (□) denote activation parameters for aquation in acid solution

The Figure shows that the rate constant for aquation decreases, in other words that $\Delta G^{\ddagger}$ increases, continuously as the mole fraction of hydrogen peroxide increases from 0.015 to 0.15 (the practical maximum, *cf.* Experimental section). The change in rate constant is *ca.* 4—8 times, which is of the same order of magnitude as that observed for the same reaction in analogous series of water–organic solvent mixtures, despite the very small variation in solvent permittivity. Unfortunately, it is not possible to make an estimate of the change in rate constant to be expected from the known small change in solvent permittivity, since for such an estimate it is necessary to know the differences between the dipole moments and between the effective radii of the initial and transition states. Nevertheless, the observed variation in aquation rate constant is markedly larger than one would expect from the very small variation in solvent permittivity. We prefer to attribute the observed rate variation to the effects of intercomponent interactions on initial-state and transition-state solvation.

Extrapolation of the trend of aquation rate constants for mole fractions from 0.15 to 0.015 of H_2O_2 back to pure water produces a value markedly greater than that reported for aquation in acidic aqueous solution; indeed rate constants for aquation in low mole fractions of H_2O_2 (up to x_2 *ca.* 0.06) are also greater than that for an acidic aqueous medium.[4] At first sight this might seem to suggest an extremum at a very low mole fraction of H_2O_2; but in fact such a conclusion would be erroneous. It is not permissible to compare rate trends in hydrogen peroxide–water mixtures (no acid) with a value in acid–water, for ionic strength and solvent structural effects will be somewhat different. The trend in rate constant from $x_2 = 0$ to $x_2 = 0.225$ for hydrogen peroxide–water mixtures, all containing 0.54 mol dm^{-3} H_2SO_4 is one of continuous decrease.[4] We are not able to suggest a plausible explanation for the difference between the rate constant for aquation extrapolated from our hydrogen peroxide–water results and that reported for an aqueous acid medium. Although rationalisation would be possible for the particular case of this 5-NO_2phen complex, it would be difficult to use the same rationalisation for other complexes of substituted phen and bipy ligands. The ratios of rate constants extrapolated from hydrogen peroxide–water mixtures to those for aqueous acid vary from *ca.* 0.8 : 1 to *ca.* 1.1 : 1, with no pattern apparent in the variation of this ratio with substituent nature.[12] Such ratios must represent the resultants of several effects.

The trend of decreasing rate constant with increasing mole fraction of H_2O_2 for aquation of this iron(II) complex in hydrogen peroxide–water mixtures is the opposite of that reported for solvolysis of t-butyl chloride.[17] This pattern of behaviour parallels that observed for these two reactions in other solvent mixtures, *e.g.* alcohols–, acetone–, dioxan–, or acetonitrile–water.[4] The only anomaly in this overall pattern

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[16] F. Franks, in ' Hydrogen-bonded Solvent Systems,' eds. A. Covington and P. Jones, Taylor and Francis, London, 1968, p. 31.

[17] M. J. Blandamer and J. R. Membrey, *J.C.S. Perkin II*, 1974, 1400.

of opposite reactivity trends for t-butyl chloride solvolysis and $[Fe(5\text{-}NO_2phen)_3]^{2+}$ aquation is the glycerol–water system.[4] The opposite trends have been ascribed to the contrast between chloride leaving from carbon, where a more hydrophilic transition state is generated, and phen leaving from iron, when more of the hydrophobic periphery of the organic ligand is exposed in the transition state. The trends observed for hydrogen peroxide–water systems are consistent with the operation of a dissociative mechanism of aquation of the iron(II) complex in such solvent mixtures as in aqueous solution.[2]

The activation parameters $\Delta H^\ddagger$ and $T\Delta S^\ddagger$, like $\Delta G^\ddagger$, show a continuous trend with solvent-composition variation, with no evidence for extrema within the H_2O_2 mole fraction range 0.015—0.15. This lack of extrema for the ' typically non-aqueous negative (t.n.a.n.) ' system hydrogen peroxide–water contrasts with the situation for ' typically aqueous (t.a.) ' systems. In the latter cases, as for example for alcohol–water systems, there are marked extrema at relatively low mole fractions of organic co-solvent. The parameters $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ for aquation of this iron(II) complex in hydrogen peroxide–water mixtures show considerable compensation, to give a less rapidly varying $\Delta G^\ddagger$ (*cf.* Figure). In this respect hydrogen peroxide–water mixtures show similar behaviour to t.a. mixed-solvent systems.

We thank the S.R.C. for support.

[5/2391 *Received, 10th December,* 1975]