Auto-oxidation of the Tris-(1,10-phenanthroline)iron(II) and Tris-(2,2′-bipyridyl)iron(II) Cations in Aqueous Sodium Hydroxide

By GWYNETH NORD* and TECLA PIZZINO†

(*Chemistry Department* I, *The H. C. Ørsted Institute, Universitetsparken* 5, *Copenhagen, Denmark*)

Summary Oxygen is necessary for the rapid reactions of the tris-(1,10-phenanthroline)iron(II) and of the tris-(2,2′-bipyridyl)iron(II) cations in aqueous sodium hydroxide.

THE dissociation of $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline) in aqueous NaOH has been reported[1] to be dependent on the hydroxide ion concentration according to equation 1,

$$k_0 = k_d + k_1[OH^-] + k_2[OH^-]^2 + k_3[OH^-]^3 \qquad (1)$$

where k_0 is the observed pseudo-first order rate constant with respect to $Fe(phen)_3^{2+}$. The product has been assumed to be an iron(II) hydroxo-species and the precipitation of iron(II) hydroxide to be the "driving force of the reaction".[2,3] This remarkable reaction, which does not occur with $Ni(phen)_3^{2+}$, has been discussed in a recent textbook[4] the authors of which are "tempted to speculate that the redox properties of the central ion are in some way involved." We have found that a solution of $Fe(phen)_3(ClO_4)_2$ in 1M-NaOH prepared under oxygen-free nitrogen exhibits no change in colour after 24 h. When air enters, the rapid reaction reported by previous workers occurs: we have also studied this reaction by their method at 25°. A corresponding solution of $Fe(bipy)_3(ClO_4)_2$ (bipy = 2,2′-bipyridyl) slowly reacts under nitrogen over a period of hours but also

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reacts rapidly in air. Addition of Na_2SO_3 and of $Na_2S_2O_4$ to air-saturated solutions in stoppered cells slows down the reaction of $Fe(bipy)_3^{2+}$ and completely inhibits the reaction of $Fe(phen)_3^{2+}$. The earlier statement[1] that this was not so for $Fe(phen)_3^{2+}$ was due to insufficient reducing agent.[5]

In *air-saturated* solutions the reactions remain first order in complex throughout and the rates are independent of ligand concentration. The ligand is totally unbound when the reaction is complete and the solutions colourless. Under our conditions ($[OH^-]$ 0·05—1·00 M) precipitates of $Fe(OH)_3$ are not perceptible until after the colour has faded. Ionic strengths (*I*) were adjusted with NaCl: for $Fe(phen)_3^{2+}$ at $I = 0{\cdot}15$, $k_0 = k_d + k_1[OH^-]$, $k_d = 5 \times 10^{-3}$ min^{-1}, $k_1 = 0{\cdot}7\ min^{-1}\ mol^{-1}$; at $I = 1{\cdot}0$, $k_0 = k_1[OH^-]$, $k_1 = 0{\cdot}43\ min^{-1}\ mol^{-1}$. Thus, the $[OH^-]$-dependent reaction goes through a transition state of composition $Fe(phen)_3^{2+}OH^-$ and there is a negative kinetic salt effect. The last two terms of equation 1 do not apply to the homogeneous reaction alone, as we find that the red complex precipitates from the $NaOH$–$NaClO_4$ mixtures used by Margerum.[1]

In oxygen-saturated solutions measured under an oxygen pressure of one atmosphere, the reaction rates were the same as those in air-saturated solutions. The rate-determining reaction is therefore not an oxidation, although rapid oxidation of either the reaction product or of intermediates rapidly formed from this must occur. It is possible that species of oxidation state higher than 3 are present in the reacting solutions.

It seems likely that the rate-determining step involves ligand loss. A consequence of this would be an increased rate of racemisation in basic solution in the absence of oxygen and possibly also in the presence of oxygen.

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[1] D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728.

[2] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, **1962**, **84**, **706**.

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

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, **New York**, **1960**.

[5] Professor Dale W. Margerum, personal communication to G.N.