Unexpected selectivity in the oxidation of arylamines with ferrate–preliminary mechanistic considerations

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Ferrate rapidly converts aromatic amines exclusively into either nitro- or azo-compounds under relatively mild conditions.

In order to explore the chemistry of ferrate, and to provide an entry into the general synthesis and reactivity of hypervalent iron complexes, we have initiated a series of kinetic studies of ferrate oxidations. We have reported the kinetics of the ferrate oxidation of sulfite and selenite to sulfate and selenate[1] which appear to involve the formation of ferrate esters, *e.g.* $[O_3Fe^{VI}–O–SO_3]^{4-}$. Recently this group examined the oxidation of hydrazine and monomethylhydrazine with ferrate.[2] In each case, the oxidation process proceeded *via* two electron steps to form diazene and azomethane, respectively. In conjunction with this work, we have also studied the ferrate oxidation of hydroxylamines[3] and thiosulfate,[4] where 2e-oxidations again were again invoked.

As part of our continuing interest in ferrate oxidations of nitrogen containing compounds, we undertook an investigation into the ferrate oxidation kinetics of aniline and its *para*-substituted analogues. When ferrate was added to an alkaline aqueous solution of aniline, a rapid colour change, from purple to orange, was observed. The spent reaction mixtures were extracted with methylene chloride and analysed using GC/FID (Carbowax, 30 m). The product of this reaction was found to be highly dependent on the pH of the medium. Unlike oxidations of aniline with other reagents, where mixtures of products are typically found,[5] conversion to either nitroaniline or azobenzene could be selectively carried out using ferrate ions. The selective oxidation of anilines represents an important class of transformations as pointed out in a recent publication using a chromium silicate to catalyse the peroxide oxidations.[6] The ferrate oxidations of anilines were carried out either in 1 mol dm^{-3} OH^- or at pH 9.

$$FeO_4^{2-} + C_5H_5NH_2 \xrightarrow{1\ \mathrm{mol\ dm^{-3}}} Fe^{2+} + C_5H_5NO_2$$

$$FeO_4^{2-} + C_5H_5NH_2 \xrightarrow{\mathrm{pH}\ 9} Fe^{2+} + C_5H_5N{=}NC_5H_5$$

Under these conditions, the oxidations proceed essentially quantitatively to the products shown. In a previous study,[7] it was reported that aniline (neat) was oxidized to azobenzene using barium ferrate, an insoluble Fe^{VI} salt, as a heterogeneous oxidant. In contrast, the present study uses an aqueous solution of potassium ferrate to provide for a homogeneous oxidation medium. As would be expected, substituted anilines were also found to produce both azobenzenes or nitrobenzenes, dependent upon reaction conditions.

In the production of azobenzene, the reaction was studied at pH 9 (0.05 mol dm^{-3} Na phos buffer) with aniline or substituted anilines in at least ten fold excess over ferrate. Under these pseudo-first-order conditions, azobenzene was produced (with minor contaminants of azoxybenzene but no nitrobenzene). A Hammett type type correlation between the rate constants and σ^+ is observed, Fig. 1. The slope of this, ρ, equals -1.8. Correlations such as this are best interpreted as involving a large buildup of positive charge in the transition state.[8] This is readily accounted for if the ferrate oxidizes the amine nitrogen to form a phenylhydroxylamine in the rate determining step. As precedence, Edwards found a similar value, -1.86, for the conversion of aniline to phenylhydroxylamine by peroxyacetic acid.[9]

$$C_5H_5NH_2 + FeO_4^{2-} \longrightarrow C_5H_5NHOH + Fe^{IV}$$

For aniline, the observed rate constant is 30 dm^3 mol^{-1} s^{-1}. From earlier studies, we know that phenylhydroxylamine is readily oxidized by ferrate to nitrosobenzene, k = 3 800 dm^3 mol^{-1} s^{-1} under identical conditions. At pH 9–10, the condensation of nitrosobenzene with the excess aniline is rapid,[10] compared to the production of hydroxylamine, which results in the production of azobenzene.

$$C_5H_5NHOH \xrightarrow{FeO_4^{2-}} C_5H_5NO \xrightarrow{\mathrm{aniline}} C_5H_5N{=}NC_5H_5$$

In this reaction, the production of phenylhydroxylamine may proceed *via* direct insertion of the oxygen by ferrate during the oxidation procedure, similar to other ferrate oxidations. Currently, ^{18}O labelling studies are underway to determine the source of this oxygen.

In contrast to the above discussion, oxidation of aniline by a slight excess (two to three fold) of ferrate in 1 mol dm^{-3} OH^- produces exclusively nitrobenzene. Prior to the condensation reaction, all the steps are postulated to be the same as for azobenzene, *i.e.* nitrosobenzene is produced as an intermediate. However, instead of condensation with the excess aniline, the ferrate oxidizes the nitrosobenzene to the final nitrobenzene product (k > 0.35 dm^3 mol^{-1} s^{-1}).

$$C_5H_5NO \xrightarrow{FeO_4^{2-}} C_5H_5NO_2$$

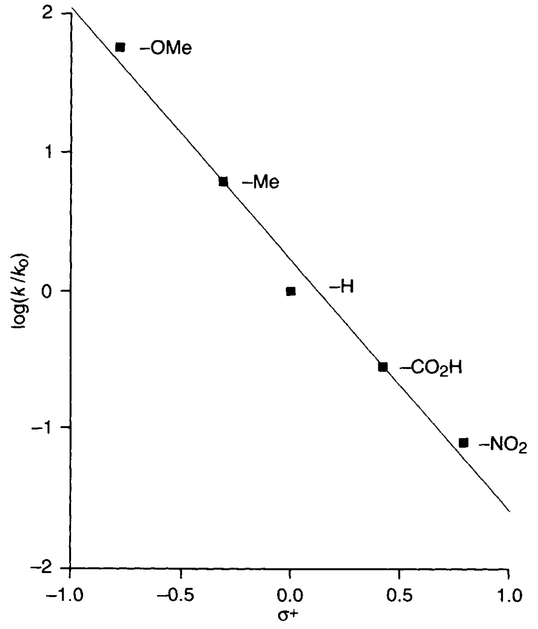

Fig. 1 Hammett plot of the oxidation rates of *para*-substituted anilines with ferrate

Just as the formation of azobenzenes occurred when substituted anilines were oxidized at pH 9, substituted nitrobenzenes are also produced.

Evidence that supports the proposed mechanistic scheme is obtained when mixtures of ferrate and aniline are reacted at 1 : 1 ratios in 1 mol dm^{-3} OH^-. Under these conditions, a mixture of phenylhydroxylamine and nitrosobenzene are produced. This is due to both insufficient oxidant to further convert the nitrosobenzene into nitrobenzene as well as a sluggish rate for this reaction, $k \sim 0.3$ dm^3 mol^{-1} s^{-1}. In these experiments, azoxybenzene is also formed. This is from the condensation of the hydroxylamine and the nitroso intermediate compounds. With excess ferrate present, the oxidation rate of the hydroxylamine is so much faster than this condensation reaction that condensation reactions becomes unimportant.

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