Photoreduction of Iron(III) Chloride in Aqueous Media

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Summary A study of the photoreduction of iron(III) to iron(II) in aqueous iron(III) chloride as a function of hydrochloric acid and chloride ion concentrations indicates that $Fe^{3+}OH^-$, and not $Fe^{3+}Cl^-$, is the photoactive species.

IT was reported that the photoactive species in aqueous solutions of iron(III) chloride is $Fe^{3+}Cl^-$,[1,2] and that the primary photoprocess is as shown in (1). However results reported here are not in agreement with this conclusion.

$$Fe^{3+}Cl^- \xrightarrow{h\nu} Fe^{2+} + \cdot Cl \qquad (1)$$

An aqueous solution of iron(III) chloride contains, in addition to $Fe^{3+}Cl^-$,[3,4] an appreciable concentration of $Fe^{3+}OH^-$, dependent on the pH of the solution.[5] The ion-pair $Fe^{3+}Cl^-$ has a charge-transfer band at 340 nm,[4,6] and its concentration increases directly with the concentration of chloride ions.[3,4] If $Fe^{3+}Cl^-$ were the photoactive species in aqueous solutions of ferric chloride, there would be an increase in quantum yield of iron(II) on increasing chloride ion concentration. However, the observed quantum yields for 340 nm irradiation (incident light intensity $1{\cdot}0 \times 10^{14}$ quanta s^{-1}) of $3{\cdot}5 \times 10^{-3}$M iron(III) chloride at pH $2{\cdot}5 \pm 0{\cdot}1$ (adjusted with perchloric acid) and [NaCl] values of 0·00, 0·01, 0·05, 0·30, 0·50, and 1·00 M were respectively 3·2, 2·8, 2·2, 1·3, 1·0, and $0{\cdot}7 \times 10^{-2}$ (all $\pm\, 0{\cdot}1 \times 10^{-2}$). Under similar conditions when NaCl is replaced by HCl to give pH 0·00, 1·00, 1·50, 2·00, 2·50, and 2·80, with [Cl^-] values 1·010, 0·110, 0·042, 0·020, 0·013, and 0·010, quantum yields $\times 10^2$ were respectively $0{\cdot}10 \pm 0{\cdot}05$, $0{\cdot}30 \pm 0{\cdot}10$, $1{\cdot}2 \pm 0{\cdot}10$, $2{\cdot}10 \pm 0{\cdot}10$, $2{\cdot}10 \pm 0{\cdot}10$, and $1{\cdot}2 \pm 0{\cdot}20$. Since hydrochloric acid increases the concentration of $Fe^{3+}Cl^-$, while decreasing that of $Fe^{3+}OH^-$, an increase in quantum yield may be expected if $Fe^{3+}Cl^-$ is the photoactive species. The results do not support this conclusion. $Fe^{3+}Cl^-$ is therefore not the photoactive species. In aqueous solutions of iron(III) chloride, the primary photoprocess is probably as shown in (2).

$$Fe^{3+}OH^- \xrightarrow{h\nu} Fe^{2+} + \cdot OH \qquad (2)$$

The results on radical scavenging experiments using benzoic acid, a hydroxy-radical scavenger,[7] are in agreement with equation (2). Salicyclic acid was formed when iron(III) chloride was irradiated at 300—350 nm in the presence of benzoic acid, while no detectable amount of chlorobenzoic acids were formed.

Quantum yield shows a maximum in the pH range 2·0—2·5. It is to be expected that the concentration of $Fe^{3+}OH^-$ is maximum at this pH range. A substantial decrease in the concentration of $Fe^{3+}OH^-$ occurs below pH 2·0. The decrease in quantum yield above pH 2·5 may be due to the formation of higher association species of Fe^{3+} with OH^-, *i.e.*, $Fe(OH)_2^+$ or the binuclear species $Fe_2(OH)_2^{4+}$.[8,9]

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