Unstable Complexes of Iron seen in the Pulse Radiolysis of Aqueous Ferrous Perchlorate

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UNSTABLE products formed by reactions of OH and HO_2 radicals with ferrous ions have been studied by Keene[1] using ferrous sulphate in aqueous sulphuric acid. Effects due to complexing by sulphate have now been eliminated by using ferrous perchlorate in perchloric acid.

Curve A shows the absorption spectrum of an air-saturated solution of ferrous perchlorate (10^{-3} M) in perchloric acid (1 N) at 20 microsec. after a 600 rad pulse of 4 Mev electrons. Down to 260 nm the curve is in agreement with that expected for uncomplexed ferric ions formed from OH radicals ($G = 2{\cdot}9$, $k_{\mathrm{OH}+\mathrm{Fe}^{2+}} > 2 \times 10^{8}$ M^{-1} sec.$^{-1}$), together with a small contribution from HO_2 ($G = 3{\cdot}7$, $k_{\mathrm{HO}_2+\mathrm{Fe}^{2+}} = 2 \times 10^{6}$ M^{-1} sec.$^{-1}$). When a higher concentration of ferrous ions is used (10^{-2}M), the spectrum obtained at 2 microsec., after which all OH radicals have reacted (Curve B, lower), is similar to the previous one above 280 nm, but it drops sharply below 280 nm. The drop is due to spectral impurity in the monochromator output,[1] which becomes serious with 10^{-2} M ferrous perchlorate below about 280 nm because the concentration of ferric ions present as an impurity reduces substantially the transparency of the solution to light of such wavelengths.

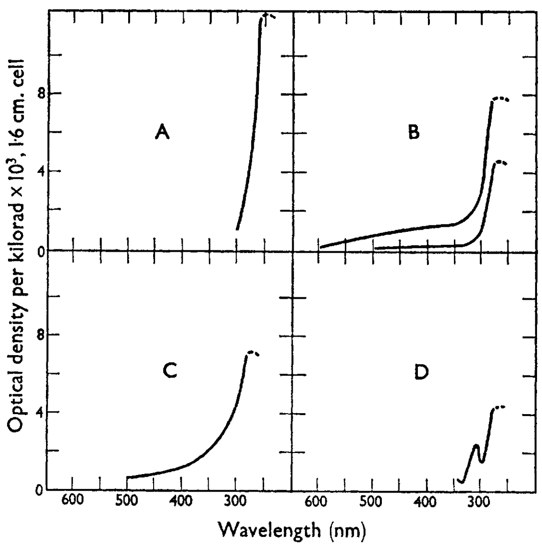

FIGURE. *Observed absorption spectra; A, air-saturated ferrous perchlorate* (10^{-3} M) *in perchloric acid* (1 N), 20 *μsec. after pulse; B, air-saturated ferrous perchlorate* (10^{-2} M) *in perchloric acid* (1 N), *lower curve* 2 *μsec. after pulse, upper curve* 100 *μsec. after pulse; C, air-saturated ferrous perchlorate* (10^{-2} M) *in perchloric acid* (10^{-3} M), 100 *μsec. after pulse; D, deaerated ferrous perchlorate* (10^{-2} M) *in perchloric acid* (1 N), 20 *μsec. after pulse.*

The absorption at 280 nm in this solution rises over a period of microseconds, but there is a bigger proportionate rise in the range 350—600 nm (Curve B, upper). This change is attributed to the action of HO_2 radicals, and the spectrum obtained resembles that previously attributed[2,3] to $Fe^{3+}HO_2^-$. The kinetics of formation and decay of this complex are being studied.

Reduction of the acid concentration to 10^{-3}N ($Fe^{2+} = 10^{-2}$ M) does not greatly affect the absorption at 280 nm or above 400 nm, but results in greater absorption in the region 300—350 nm (Curve C), resembling that seen when uncomplexed ferric is replaced by $Fe^{3+}OH^-$.

A solution of ferrous perchlorate (10^{-2}M) in perchloric acid (1N) has also been pulsed in the absence of oxygen. Under these conditions OH radicals are still present, but HO_2 radicals are replaced by H atoms. As well as the absorption below 300 nm, a new band is now observed in the region 300—350 nm (Curve D) and this is attributed to the formation by the hydrogen atoms of a ferric hydride complex,[4] $Fe^{3+}H^-$.

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