SHORT COMMUNICATIONS

The Reactivities of Hydrated Electrons and OH Radicals in an Aqueous Hexacyanoferrate(II) Solution

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As has been reported previously,[1] the irradiation of aqueous hexacyanoferrate(II) solutions at 2537Å results in the formation of hexacyanoferrate(III) ions and hydrated electrons, e^-_{aq}:

$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-_{aq} \quad (1)$$

The limiting quantum yield, obtained at high concentrations of an electron scavenger, N_2O or NO_3^-, was 0.35 at 25°C. This communication will present some results of the investigations into the reactivities of hydrated electrons and OH radicals using the above photochemical system.

In the $Fe(CN)_6^{4-}-N_2O$ systems, the photochemical reaction 1 is followed by:

$$e^-_{aq} + N_2O \rightarrow N_2 + OH + OH^- \quad (2)^{2)}$$

$$Fe(CN)_6^{4-} + OH \rightarrow Fe(CN)_6^{3-} + OH^- \quad (3)$$

The addition of other solutes which compete efficiently with N_2O for e^-_{aq} reduces the N_2 yields:

$$e^-_{aq} + S \rightarrow S^- \quad (4)$$

Thus, the relative rates can be obtained. In those cases where the S^- produced reduces the $Fe(CN)_6^{3-}$ ion, the ratio of the rate constants, k_4/k_2, can also be calculated from the measured hexacyanoferrate(III) yields. Some results obtained are shown in column a of Table I.

In the $Fe(CN)_6^{4-}-NO_3^-$ systems containing other electron acceptors, the observed yields of nitrite[1,3] permit us to calculate the rates relative to nitrate. Table I, column b, shows some of these results.

TABLE I. RELATIVE REACTIVITY OF VARIOUS SOLUTES TOWARDS e^-_{aq}, NORMALIZED TO $k(e^-_{aq}+N_2O)=100$ OR $k(e^-_{aq}+NO_3^-)=100$

a		b	
N_2O	=100	NO_3^-	=100
H^+	220	N_2O	35
NO_3^-	286	O_2	250
$Fe(CN)_6^{3-}$	120	CO_2	38
Acetone	150	H_2O_2	210
$H_2PO_4^-$	1.6	Acetone	45
HPO_4^{2-}, ClO_4^-	Unreactive	Cl^-, Methanol	Unreactive

The solutes, RH, which compete with $Fe(CN)_6^{4-}$ in the reaction with OH to yield the reducing radicals, R;

$$RH + OH \rightarrow R + H_2O \quad (5)$$

$$Fe(CN)_6^{3-} + R \rightarrow Fe(CN)_6^{4-} + R^+$$

reduce the yields of hexacyanoferrate(III), and the rate constant ratios, k_5/k_3, can be calculated. Table II shows some of these results, $k(OH+Fe(CN)_6^{4-})$ being taken as 100.

TABLE II. REACTIVITY OF SOME SOLUTES TOWARDS OH RADICALS, NORMALIZED TO $k(OH+Fe(CN)_6^{4-})=100$

$Fe(CN)_6^{4-}$	=100
Methanol	6.1
Ethanol	16
2-Propanol	23
$HCOO^-$	26
Br^-	5.4
Glycine	2.8
D-Glucose	≈8

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