

SHORT COMMUNICATIONS

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

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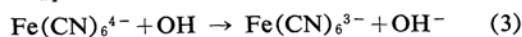
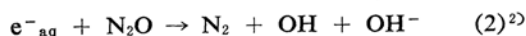
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As has been reported previously,¹⁾ the irradiation of aqueous hexacyanoferrate(II) solutions at 2537 Å results in the formation of hexacyanoferrate(III) ions and hydrated electrons, e^-_{aq} :



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 $\text{Fe(CN)}_6^{4-} - \text{N}_2\text{O}$ systems, the photochemical reaction 1 is followed by:



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



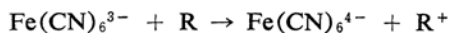
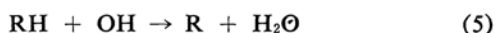
Thus, the relative rates can be obtained. In those cases where the S^- produced reduces the Fe(CN)_6^{3-} ion, the ratio of the rate constants, k_4/k_2 , can also be calculated from the measured hexacyanoferrate(III) yields. Some results obtained are shown in column a of Table I.

In the $\text{Fe(CN)}_6^{4-} - \text{NO}_3^-$ 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 $k(e^-_{aq} + \text{N}_2\text{O}) = 100$ OR $k(e^-_{aq} + \text{NO}_3^-) = 100$

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-}	Unreactive	Cl^-	Unreactive
ClO_4^-		Methanol	

The solutes, RH, which compete with Fe(CN)_6^{4-} in the reaction with OH to yield the reducing radicals, 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, $k(\text{OH} + \text{Fe(CN)}_6^{4-})$ being taken as 100.

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

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

1) S. Ohno and G. Tsuchihashi, This Bulletin, 38, 1052 (1965).

2) F. S. Dainton and D. B. Peterson, Proc. Roy. Soc., A267, 443 (1962).

3) A. Appleby, G. Scholes and M. Simic, J. Am. Chem. Soc., 85, 3891 (1963).