Intermediates in the Oxidation of Thiocyanate Ions by Hydroxyl Radicals

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Summary Optical absorption spectra of precursors of $(\mathrm{CNS})_2^-$ in the pulse radiolysis of aqueous CNS^- solutions are reported, it is concluded that the reaction of OH radicals with CNS^- leads to the intermediate formation of CNSOH^-

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IN pulse-radiolysis studies of aqueous CNS^- solutions Adams, Boag, and Michael[1] observed a transient species with a maximum optical absorption around 480 nm Although this absorption was initially attributed to the CNS radical, formed according to reaction (1), subsequent

$$\mathrm{CNS}^- + \mathrm{OH} \rightarrow \mathrm{CNS} + \mathrm{OH}^- \qquad (1)$$

kinetic analysis[2] indicated the participation of *two* transients in the oxidation process, the 480 nm absorption being shown to be due to the $(\mathrm{CNS})_2^-$ radical-ion, formed by process (2)

$$\mathrm{CNS} + \mathrm{CNS}^- \overset{K_2}{\rightleftharpoons} (\mathrm{CNS})_2^- \qquad (2)$$

In view of the suggestion[3] that complex radical-ions can be formed as a consequence of reaction of O^- with CNS^- in irradiated alkaline glasses at low temperature, we have re-investigated the pulse radiolysis of aqueous CNS^- solutions, both under neutral and alkaline conditions Solutions of KCNS were saturated with $\mathrm{N_2O}$ (to convert the radiation-produced solvated electrons into OH radicals) and subjected to 0·1 μs pulses of electrons (5—10 MeV) from a linear accelerator The transient optical absorption spectra in the region 280—540 nm were recorded at various times after the pulse and the Figure shows some results obtained from solutions (10^{-4}M) at pH 7 and 13 The recorded difference spectra correspond to the precursors of $(\mathrm{CNS})_2^-$ and are different in these solutions of differing pH [$\lambda_{\max}$ (neutral) 330 nm, $\lambda_{\max}$ (alkaline) 390 nm] It is clear therefore, that a simple oxidation mechanism involving only reactions (1) and (2) is inadequate to account for these observations An alternative scheme, involving an OH adduct to CNS^-, could comprise reactions (3) and (4)

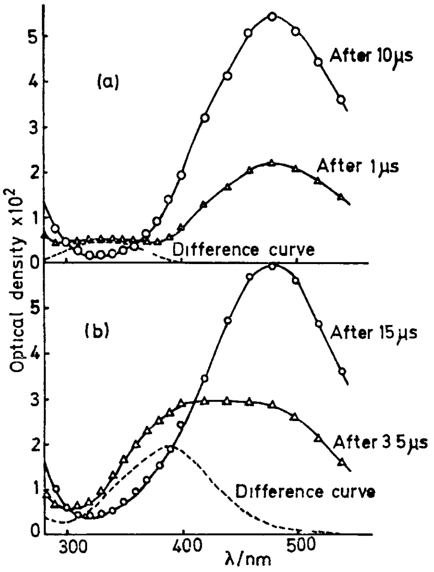

FIGURE *Transient absorption spectra in pulsed aqueous thiocyanate solutions* (10^{-4}M) *saturated with* $\mathrm{N_2O}$ (a) *Neutral* (b) *Alkaline* (10^{-1}M-NaOH)

$$\mathrm{CNS}^- + \mathrm{OH} \rightarrow \mathrm{CNSOH}^- \qquad (3)$$

$$\mathrm{CNSOH}^- \overset{K_4}{\rightleftharpoons} \mathrm{CNS} + \mathrm{OH}^- \qquad (4)$$

followed by reaction (2). If D represents the optical density due to $(CNS)_2^-$ at equilibrium, where CNS, $CNSOH^-$, and $(CNS)_2^-$ co-exist, and D_0 the absorption where final oxidation to $(CNS)_2^-$ has occurred, it can be shown that expression (5) applies. If, in addition, one includes

$$D_0/D = 1 + 1/(K_2[CNS^-]) + [OH^-]/(K_4K_2[CNS^-]) \quad (5)$$

reaction (6) as a possible process at high pH, then K_4K_2 is

$$CNSOH^- + CNS^- \overset{K_6}{\rightleftharpoons} (CNS)_2^- + OH^- \quad (6)$$

replaced by K_6. In either instance, $1/D$ should vary linearly with $[OH^-]$, and this has been found to be the case experimentally, using solutions of fixed CNS^- concentration ($7{\cdot}8 \times 10^{-5}$M) in which $[OH^-]$ was varied from 0·1 to 0·8 M.

Under strongly alkaline conditions reaction (2) will be replaced by reaction (7) since $pK(OH) = ca.\ 12$. However,

$$O^- + CNS^- \rightarrow CNSO^{2-} \quad (7)$$

production of $(CNS)_2^-$ from the doubly charged transient species according to reaction (8) must be ruled out, since

$$CNSO^{2-} + CNS^- \overset{H_2O}{\rightleftharpoons} (CNS)_2^- + 2OH^- \quad (8)$$

this would lead to a dependence of $1/D$ upon $[OH^-]^2$. It follows, therefore, that if $CNSO^{2-}$ exists, it has $pK > 14$, and that under the above conditions is rapidly converted into $CNSOH^-$.

According to our proposed mechanism we assign the species absorbing at 330 nm to CNS, and that absorbing at 390 nm to $CNSOH^-$. Thus, the rate of formation of $(CNS)_2^-$ in neutral solution depends upon K_2 as previously indicated,[2] but in alkaline solutions will depend upon K_4 and possibly also K_6.

The transient production of such complex radical-ions from reactions involving OH and O^- should be a rather more general phenomenon and, indeed, has already been the subject of some speculation in the radiation chemistry of halide solutions.[4] Preliminary pulse-radiolysis studies of iodide solutions[5] have indeed revealed the presence of precursors of I_2^-. In alkaline solutions the precursor has λ_{max} *ca.* 340 nm whereas under neutral conditions the absorption of the precursor increases continuously below 300 nm; by analogy with the thiocyanate system, it is possible that these absorptions correspond to IOH^- and I respectively.

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[1] G. E. Adams, J. W. Boag, and B. D. Michael, *Proc. Chem. Soc.*, 1964, 411.

[2] J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, 1968, **64**, 2389.

[3] D. V. Bent, N. B. Nazhat, and G. Scholes, 4th International Congress of Radiation Research, Evian, 1970, Abstract 74.

[4] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 3829; M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *ibid.*, 1966, **70**, 2092.

[5] In collaboration with M. Ebert.