Pulse Radiolysis of Aqueous CNS$^-$ Solutions and the Rates of Hydroxyl-radical Reactions

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PULSE-RADIOLYSIS studies of thiocyanate solutions[1,2] have shown that oxidation by the radical OH gives a transient species which absorbs strongly in the visible (λ_{max} *ca.* 500 mμ; $\epsilon_{500} = 7 \times 10^3$ mole^{-1}). It was presumed to be the radical CNS· although the possibility was considered[2] that, as with the halogen atoms in similar circumstances, combination with the original ion may occur to give $(CNS)_2^-$. This absorption is readily measured since it decays relatively slowly, and it has provided a convenient and widely adopted method for obtaining rates of reaction of hydroxyl radicals with solutes using conditions in which the solutes compete with CNS$^-$ for the radicals.[3] The measured rate constant for the appearance of the absorption ($6{\cdot}6 \times 10^9$ mole^{-1} sec.$^{-1}$), presumed to be that for the OH + CNS$^-$ reaction, in conjunction with the decrease in absorption produced by the solute allows the rate constant for the OH + solute reaction to be calculated.

We have now observed that at constant electron-pulse intensity such that the initial OH concentration is much smaller than the CNS$^-$ concentration, the absorption produced begins to decrease when the latter is decreased sufficiently (see Figure). Calculation shows that reactions of OH other than that with CNS$^-$ (*e.g.*, OH + OH) must be negligible in these conditions and are therefore not responsible for this behaviour.

The observations are quantitatively explained if the absorption is due entirely to the species $(CNS)_2^-$ present in equilibrium with CNS·, *i.e.*, if the reactions occurring are:

$$\mathrm{OH} + \mathrm{CNS}^- \xrightarrow{k_1} \mathrm{CNS}\cdot$$

$$\mathrm{CNS}\cdot + \mathrm{CNS}^- \underset{k_3}{\overset{k_2}{\rightleftharpoons}} (\mathrm{CNS})_2^- \qquad K = k_2/k_3$$

The results in the Figure give $K \simeq 3 \times 10^5$ mole^{-1} at 20°. Considering the rate of formation of the absorption, the exact kinetic analysis of these three reactions shows that if k_1 is appreciably larger than k_2, when $[\mathrm{CNS}^-] \gg [\mathrm{OH}]$ and $k_1[\mathrm{CNS}^-] \gg k_3$, the observed rate constant for the first-order formation of the absorption (measured in the usual way as $d \log [D_\infty - D_t]/dt$ where D is optical density) will be $k_2[\mathrm{CNS}^-]$. Thus the bimolecular constant obtained in such conditions *viz.* $6{\cdot}6 \times 10^9$ mole^{-1} sec.$^{-1}$, will be k_2. On the other hand at lower $[\mathrm{CNS}^-]$ where $k_3 \gg k_1[\mathrm{CNS}^-]$, the observed rate constant will approach $k_1[\mathrm{CNS}^-]$, *i.e.*, the bimolecular rate constant will increase to k_1. We have observed such an increase, and at 1μM-CNS$^-$, the lowest at which we can make useful measurements, the bimolecular constant is 2×10^{10} mole^{-1} sec.$^{-1}$, which we conclude is approximately the value of k_1.

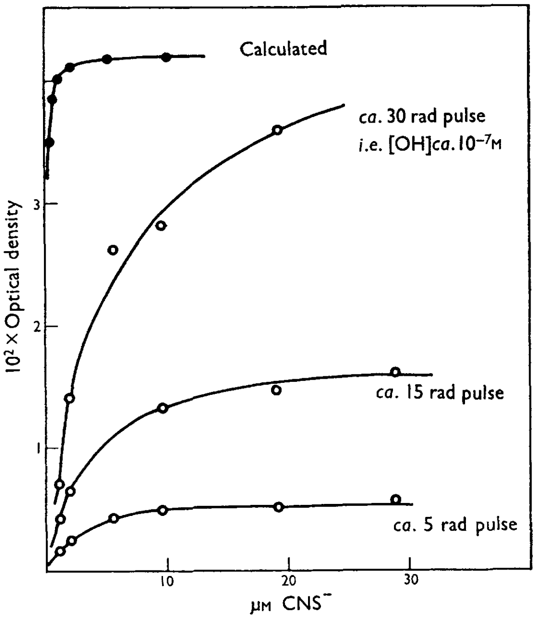

FIGURE. *Extent of the transient absorption at* 5000 Å *produced by a* 2μsec. *pulse of* 4Mev *electrons in aqueous thiocyanate solutions. Optical densities are those given in a cell of path length about* 60 cm. *The calculated curve* (*O.D. scale arbitrary*) *is obtained assuming that reactions* OH + OH *and* OH + CNS$^-$ *are competing, with rate constants* 10^{10} mole^{-1} sec.$^{-1}$ *and initial* [OH] = 10^{-7}M.

In view of this it would appear that the rate constants of HO reactions previously obtained using the thiocyanate system are too small by a factor of about three since they have been referred to k_2 and not k_1. Furthermore, when using thiocyanate in this way it is possible that reactions of the radical CNS· with the solute may complicate the system.

Recent pulse-radiolysis studies[4] of aqueous nitrobenzene confirm the above conclusions. It is found that there is a discrepancy between the rate of the HO reaction measured directly and that obtained by competition with thiocyanate if $6{\cdot}6 \times 10^9$ mole^{-1} sec.$^{-1}$ is used for the thiocyanate rate-constant. The higher value given above would remove the discrepancy.

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[1] G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 1674.

[2] G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis", Academic Press, London 1965, p. 117.

[3] Ref. 2, p. 131.

[4] Private communication from B. Cercek and M. Ebert.