Evidence for the Production of an Oxidising Radical on Pulse-radiolysis of Methanol

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IRRADIATION of aqueous systems causes the formation of approximately equal numbers of reducing ($H\cdot$ and e_{aq}) and oxidising ($OH\cdot$) radicals.[1] Hitherto the radiation chemistry of the alcohols has been explicable exclusively in terms of the formation of reducing species (e_s^-, $H\cdot$, and $R\dot{C}HOH$).[2] We now report data which prove that an oxidising species, probably $MeO\cdot$, is formed during the radiolysis of de-aerated methanol.

Solutions of potassium iodide or ammonium thiocyanate in dry methanol were irradiated with 0·6 μsec. pulses of 3 Mev electrons and any transient species was detected by kinetic absorption spectroscopy methods already described.[3,4]

The absorption spectra observed for a 0·1M-KI solution and a 0·1M-NH_4CNS solution following a *ca.* 5 krad electron pulse are shown in Figure 1. The end-of-pulse spectrum for the iodide solution comprises two peaks with λ_{max} 380 ± 5 nm. and 630 nm., which decay at different rates. The peak with λ_{max} 630 nm. decays by a first-order rate law with $t_{\frac{1}{2}}$ *ca.* 2·5 μsec. and can be confidently assigned to the solvated electron, e_s^-.[5] The peak with λ_{max} 380 nm. correlates well with the absorption spectrum of I_2^- radical ion,[6] and this assignment has been confirmed by direct observation of the spectrum of I_2^- when resolutions of iodine in methanol are pulse radiolysed. Similarly, the peak at 470 nm. in the thiocyanate solutions can be identified with the analogous $(SCN)_2^-$ radical ion.[7,8] The formation of these light-absorbing species is attributable to the reaction of I^- or SCN^- ions with the product formed by the oxidation of I^- or SCN^- by an oxidant generated by irradiation of methanol. Equations (1) and (2) are the equilibria by which $I_2^-\cdot$ and $(SCN)_2^-$ are formed from their precursors.

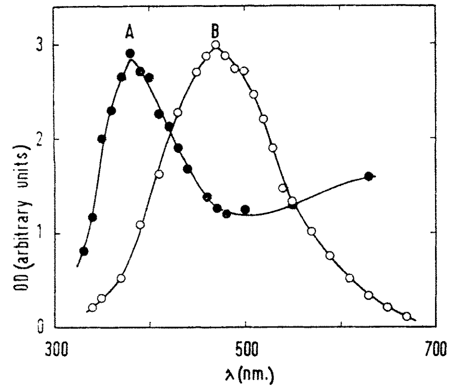

FIGURE 1. *End-of-pulse absorption spectra.* (A) *Methanolic* 0·1M-KI *solution*; (B) *Methanolic* 0·1M-NH_4SCN *solution.*

$$I\cdot + I^- \rightleftharpoons I_2^- \quad K_1 \qquad (1)$$

$$SCN\cdot + SCN^- \rightleftharpoons (SCN)_2^- \quad K_2 \qquad (2)$$

The oxidant is probably the methoxy-radical ($MeO\cdot$), which is formed together with $\cdot CH_2OH$ radicals by the ion–molecule reactions (3a) and (3b), and which is expected to react readily with I^- and SCN^- according to equations (4) and (5).

$$MeOH^+ + MeOH \rightarrow MeO\cdot + MeOH_2^+ \qquad (3a)$$

$$\rightarrow \cdot CH_2\cdot OH + MeOH_2^+ \qquad (3b)$$

$$MeO\cdot + I^- \rightarrow MeO^- + I\cdot \qquad (4)$$

$$MeO\cdot + SCN^- \rightarrow MeO^- + SCN\cdot \qquad (5)$$

The initial yields of $MeO\cdot$ and $\cdot CH_2\cdot OH$ are probably about equal.[4] In the absence of a sufficient concentration of an oxidisable solute the $MeO\cdot$ radicals are converted into the thermodynamically more stable $\cdot CH_2\cdot OH$ radicals, either by the rearrangement reaction (6) or more probably by the hydrogen atom abstraction reaction (7), which has been estimated

$$MeO\cdot \rightarrow \cdot CH_2\cdot OH \qquad (6)$$

$$MeO\cdot + MeOH \rightarrow \cdot CH_2\cdot OH + MeOH \qquad (7)$$

to have a rate constant *ca.* $10^4 M^{-1}$ sec.$^{-1}$ and hence a half-life in liquid methanol of about 4 μsec.

The dependences of the yields of I_2^- and $(SCN)_2^-$ on $[I^-]$ and $[SCN^-]$ respectively are shown in Figure 2 as the product of the G value (molecules/100 ev) and the molar decadic extinction coefficient at λ_{max}. The yield of I_2^- achieves a plateau value when $[I^-] \simeq 0\cdot1$ M, and this suggests that at this concentration of iodide scavenging of $MeO\cdot$ radicals is complete, *i.e.* $k_4 \geqslant 2 \times 10^6$ M^{-1}sec.$^{-1}$ and that the equilibrium (1) lies largely to the right. If I_2^- has the same extinction coefficient[9] as in water (14,000 M^{-1} cm.$^{-1}$) then $G(MeO\cdot) \simeq 2\cdot0$ which is close to the value suggested by Theard and Burton[10] to account for the effect of iodide ion on the yields of ethylene glycol and formaldehyde from γ-irradiated methanol. The lack of attainment

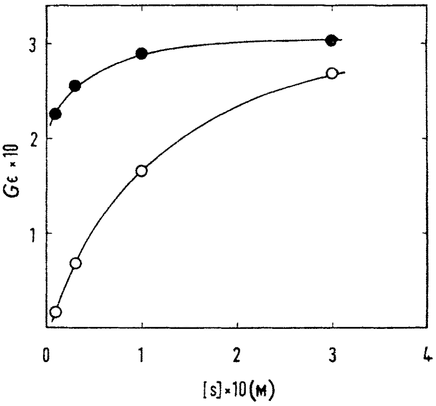

FIGURE 2. *Variation of* $G\epsilon$ *for* I_2^- (●) *and* $(SCN)_2^-$ (○) *with* $[I^-]$ *and* $[SCN^-]$ *respectively.*

of a plateau in the dependence of the yield of $(SCN)_2^-$ on $[SCN^-]$ may be due to either $k_5 < k_4$ or a smaller value of the equilibrium constant, K_2.

The absorption due to $(SCN)_2^-$ decayed by complex kinetics with a first half-life of about 18 μsec. at the dose used, and within the wavelength region studied no permanent absorption remained after the irradiation. The decay of I_2^- followed approximately a second-order law with $(k/\epsilon) = 1{\cdot}4 \times 10^6$ cm.sec.$^{-1}$, but unlike the situation following irradiation of aqueous iodide solutions[9] no absorption due to I_3^- or I_2 was detectable after the decay. This result is in accord with the earlier work of Theard and Burton,[10] who observed that no iodine was produced on irradiation of methanolic KI solutions. I_2^- apparently disappears by reaction with $\cdot CH_2{\cdot}OH$ according to reaction (8) rather than by the combination reaction (9)

$$I_2^- + \cdot CH_2{\cdot}OH \rightarrow HCHO + H^+ + 2I^- \qquad (8)$$

$$2\,I_2^- \rightarrow I_3^- + I^- \qquad (9)$$

The lack of absorption due to e_s^- in the ammonium thiocyanate solutions is very probably due to the reaction of e_s^- with NH_4^+ at the high concentrations of NH_4^+ used in this study.

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[1] G. V. Buxton, *Radiation Res. Rev.*, 1968, **1**, 209.

[2] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," Wiley, 1964.

[3] T. J. Kemp, J. P. Roberts, G. A. Salmon, and G. F. Thompson, *J. Phys. Chem.*, 1968, **72**, 1464.

[4] F. S. Dainton, G. A. Salmon, and P. Wardman, in course of publication.

[5] F. S. Dainton, J. P. Keene, T. J. Kemp, G. A. Salmon, and J. Teply, *Proc. Chem. Soc.*, 1964, 265.

[6] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, 1958, **61**, 1089.

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

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

[9] J. K. Thomas, *Trans. Faraday Soc.*, 1965, **61**, 702.

[10] L. M. Theard and M. Burton, *J. Phys. Chem.*, 1963, **67**, 59.