Electron and Radical Scavenging by Acrylamide, m_1, in Aqueous Solution

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ABSOLUTE rate constants (M^{-1} sec.$^{-1}$) for the reaction of m_1 with e^-_{aq} [$= (2{\cdot}1 \pm 0{\cdot}4) \times 10^{10}$], hydroxy-radicals [$= (7{\cdot}2 \pm 1{\cdot}3) \times 10^9$], and hydrogen atoms [$= (1{\cdot}8 \pm 0{\cdot}2) \times 10^9$] have been determined in these laboratories.[1] It was previously proposed[1a] that the species formed by the reaction of e^-_{aq} with m_1 and responsible for the intense absorption at 275 nm. observed in pulse radiolysis is the radical anion, $\cdot m_1^-$. The lack of effect of ionic strength on the rate constant of the dimerisation of this species, together with other observations, have now shown that the radical anion is rapidly protonated during the pulse to form the radical $\cdot m_1H$ of formula $CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}C(OH)NH_2$ which has an absorption maximum for which $\epsilon_{275} = 7300 \pm 800$ M^{-1} cm.$^{-1}$. In contrast, the radicals $Rm_1\cdot$ ($\equiv RCH_2\text{—}CH\overset{\cdots}{-}\underset{\substack{|\\ NH_2}}{C}\overset{\cdots}{-}O$) have an absorption maximum for which $\epsilon_{370} = 640 \pm 60$ M^{-1} cm.$^{-1}$ for R = H or OH. Taking measured values of $G\epsilon$ at 275 nm. and assuming that ϵ is constant at 7300 M^{-1} cm.$^{-1}$, $G(\cdot m_1H)$ can be obtained as a function of $[m_1]$ (see Figure 1). The value at $[m_1] = (1\text{—}5) \times 10^{-4}M$ is assumed to be 2·3, *i.e.* the yield of electrons which escape the spur without any penetration of the spurs by m_1. When $[m_1] \geqslant 10^{-3}M$ the measured yield $G(e^-_{aq})$ increases owing to capture by m_1 within spurs of electrons which would otherwise enter into recombination or reconstitution reactions. As would be expected, m_1 is more effective than N_2O in this respect (*cf.* Buxton[2]). The diminution in $G(\cdot m_1H)$ at $[m_1] > 3 \times 10^{-2}M$ cannot be due to a decrease in $G(e^-_{aq})$ and is attributed to the first propagation step (1) competing increasingly with the protonation of $\cdot m_1^-$ so that at the end of the pulse the yield

$$\cdot m_1^- + m_1 \longrightarrow m_2\cdot^- \qquad (1)$$

of $\cdot m_1H$ (which is the only species present which can absorb at 275 nm.) is diminished. This implies that the propagation rate constant for reaction (1), $k_{p,1} \geqslant 3 \times 10^7$ M^{-1} sec.$^{-1}$. Since the chromophore responsible for the band at 370 nm. is $\text{–}CH\overset{\cdots}{-}\underset{\substack{|\\ NH_2}}{C}\overset{\cdots}{-}O$ and is likely to be present in $m_2\cdot^-$ as well as in all species $Rm_j\cdot$ where $j \geqslant 1$, the propagation reactions (1) and (2) will not cause loss of absorption in this region. Consequently, $(G\epsilon)^{370}_{Rm_1}$

$$Rm_1\cdot + m_1 \longrightarrow Rm_2\cdot \qquad (2)$$

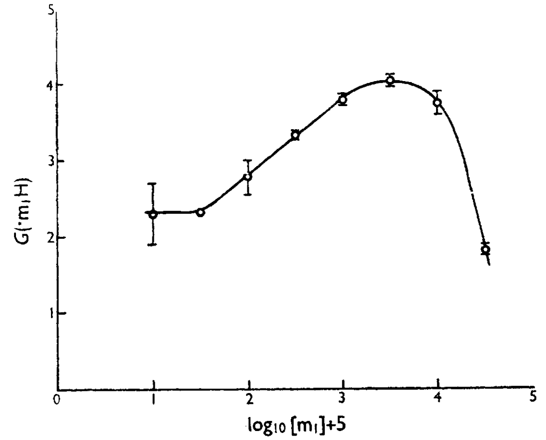

FIGURE 1. *Variation of* G(·m_1H) *with acrylamide concentration.*

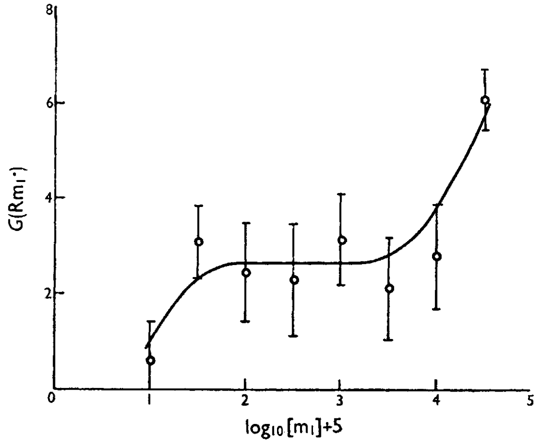

FIGURE 2. *Variation of* G($Hm_1\cdot + HOm_1\cdot$) *with acrylamide concentration.*

is expected to show no maximum as [m_1] is increased and Figure 2 shows this to be the case. Previous observations[3] that scavenging by m_1 of precursors of the "molecular" products H_2 and H_2O_2 occurs when [m_1] $> 10^{-3}$ is in accordance with this conclusion.

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[1] (*a*) K. W. Chambers, E. Collinson, F. S. Dainton, W. A. Seddon, and F. Wilkinson, *Trans. Faraday Soc.*, 1967, **63**, 1699; (*b*) K. W. Chambers, E. Collinson, and F. S. Dainton, unpublished results.

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

[3] E. Collinson, F. S. Dainton, and G. S. McNaughton, *Trans. Faraday Soc.*, 1957, **53**, 357.