Electron Yields and the Early Stages of Radiolysis in Aqueous Systems

By G. V. BUXTON, F. C. R. CATTELL, and F. S. DAINTON*

(*The University of Leeds, Cookridge High Energy Radiation Research Centre, Cookridge Hospital, Leeds* LS16 6QB)

Summary Pulse radiolysis of 10 M OH^- solution between 300 and 77 K shows (i) that the maximum yield of solvated electrons is 5, 30% of which do not escape from the spurs; (ii) that this medium is rigid below 135 K, and (iii) that diffusion-controlled reactions in this medium obey the equation $\ln k = \ln A - E/\boldsymbol{R}(T - 135)$, values of A lying in the range 10^{11} to 10^{12} M^{-1} s^{-1} and E from 6·4 to 7·4 kJ $mole^{-1}$.

10^{-10} SECONDS after the passage of a fast charged particle through fluid aqueous systems solvated electrons, e_s^-, H atoms and OH radicals are non-uniformly distributed. Theory indicates[1] that small volume elements exist called spurs, blobs, and short tracks, the centres of which contain a variable number of H_{aq}^+, H, and OH whilst e_s^- are more widely distributed. Subsequently inter-radical reactions leading to the formation of H_2 and H_2O_2 and the reconstitution of water compete with the diffusive escape of e_s^-, H, and OH into the bulk solution where they can react with solutes present in low concentrations. Since e_s^- has a high extinction coefficient for visible light use of the technique of pulse radiolysis should, in principle, enable these processes to be explored, but in practice the time resolution of existing apparatus prevents this. If, however, the diffusion of the intermediates could be decelerated these processes might be explored with existing equipment. We report that this has been fully achieved by using concentrated alkaline aqueous solutions which on cooling form transparent glasses.

The values of $G\epsilon$ at λ_{max} for e_s^- at the end of a 0·2 μs pulse of 3 Mev electrons are shown as a function of temperature in Figure 1 for 10 M OH^- solution. As the temperature is lowered from 300K the first-order decay of e_s^- becomes slower and an early second-order component becomes increasingly prominent. The spectra immediately after the pulse and at all subsequent observable stages indicate that the absorbing species are always solvated electrons. For many liquids, including aqueous 10 M KOH solution, which on cooling ultimately become glasses rather than crystalline solids, viscosity, η, may be represented[2] by an equation of the form

$$\eta = \eta_0 e^{B/(T-T_\infty)} \qquad (1)$$

where T_∞ is the temperature at which these glasses become rigid. As diffusion-controlled reactions are dependent on viscosity the temperature dependence of their rate constants might be expected to obey equation (2)

$$\ln k = \ln A - E/\boldsymbol{R}(T - T_\infty) \qquad (2)$$

As illustrated in Figure 2, this equation is obeyed exactly for T_∞ = 135K over a wide temperature range, and the parameters of this equation are given in the Table.

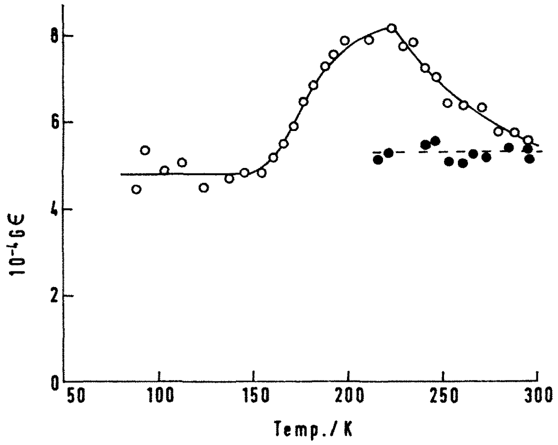

FIGURE 1. *Dependence of* $G\epsilon$ *for* e_s^- *in* 10 M-OH^- *on temperature*: (○) *end of pulse;* (●) *first-order component extrapolated to end of pulse.* G = *yield per* 100 ev, ϵ = *extinction coefficient at* λ_{max} *in* M^{-1} cm^{-1}. *Ordinate:* 10^{-4} $G\epsilon$. *Abscissa: Temperature*/K.

These are consistent with diffusion-controlled mechanisms, a conclusion supported by very similar values of E and T_∞ for the diffusion of oxygen in highly alkaline aqueous solutions. It should be noted that A should have a magnitude identical with the frequency factor in diffusion controlled reactions at temperatures where $T \gg T_\infty$ and therefore when equation (2) becomes the Arrhenius equation. Therefore if, as the value of E and other considerations suggest, the last reaction is also diffusion-controlled, the anomalously high A factor implies that the reacting species are in high local concentrations (*ca.* 10^{-2} M), and we therefore identify this process as the disappearance of e_s^- in spur reactions. Moreover, calculation shows that in the time to complete these reactions spur overlap cannot occur under the conditions of our experiments.

Values of A *and* E *for some reactions of* e_s^- *in aqueous* 10 M-OH^- *solution.*

Reaction		$\log_{10} A$ (M^{-1} s^{-1})	E (kJ mole^{-1})
$e_s^- + NO_3^-$	..	12·02 ± 0·04	7·42 ± 0·08[a]
$e_s^- + CrO_4^{2-}$	..	12·00 ± 0·08	6·24 ± 0·08
$e_s^- + NO_2^-$	..	12·05 ± 0·09	7·00 ± 0·04
$e_s^- + WO_4^{2-}$	..	10·97 ± 0·11	6·50 ± 0·13
e_s^- + impurity	..	7·8 ± 0·06[b]	7·08 ± 0·04
Spur reaction	..	14·85[c]	6·40 ± 0·38

[a] Quoted errors are standard deviations from least-squares fits.
[b] Units of A are s^{-1} in this case.
[c] Taking ϵ = 17,000 M^{-1} cm^{-1}.

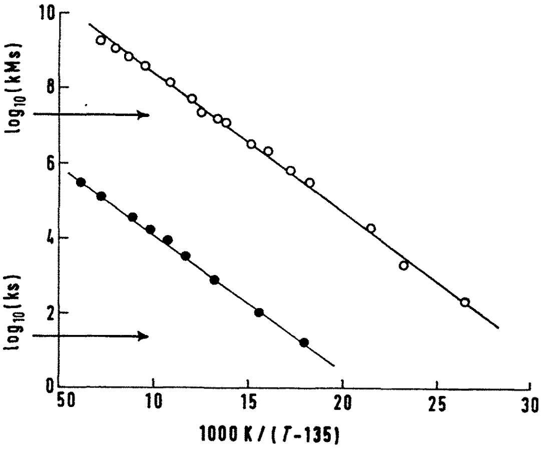

FIGURE 2. *Plot of* $\log_{10}$ k *against* 100/(T − 135) *for reactions of* e_s^- *in* 10 M-OH^-: (●) *first-order decay in absence of added solutes;* (○) *reaction with* NO_2^-. *Ordinate:* $\log_{10}$ (ks) (*for* ●), $\log_{10}$ (kMs) (*for* ○). *Abscissa:* 1000 K/(T − 135).

As the temperature is reduced the extent of the second-order spur reaction which can be measured increases to a maximum at 220K, but the yield of electrons which decay in the first-order process remains constant (see Figure 1). Below 220K the increasing rotational relaxation time of the water molecules combined with the decreasing dielectric constant, and therefore increasing Onsager escape radius, so diminish the trapping probability that the observed end-of-pulse yields decrease. Below *ca.* 140 K the medium is a rigid glass with a constant number of trapping sites and constant dielectric constant so that $G\epsilon$ is invariant. Taking ϵ = 17,000 M^{-1} cm^{-1} [3] gives $G(e_s^-)$ = 3·3 at 300K, 5 at 220K, and 2·7 below 140K.

These and other results to be reported elsewhere carry many implications for the radiation chemistry of aqueous systems, of which the two most important are (i) that the total radiation yield of e_s^- and H (since all H are converted into e_s^- in these strongly alkaline media) is $\geqslant 5$, and (ii) that recent theories[4,5] which assume that most, if not all, electrons entering spur reactions do not become solvated are incorrect.

(*Received, July 8th,* 1970; *Com.* 1092.)

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