Yields and Decay Processes of the Solvated Electron in Liquid Alcohols at Low Temperature observed by Nanosecond Pulse Radiolysis

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Summary Observations on e_s^- in alcohols are used to show that *ca.* one third of the total electrons produced recombine before solvation, that in the reaction of e_s^- with alcohols neither diffusion nor dielectric relaxation are rate determining, and that the total yield of e_s^- in water may be as high as 5.

RADIOLYSIS of alcohols involves[1] reaction of solvated electrons (e_s^-) which are *either* neutralised by geminate ions ($e_{s,g}^-$):

$$e_{s,g}^- + \overset{+}{\mathrm{R}}\mathrm{OH_2} \rightarrow \mathrm{ROH} + \mathrm{H}\cdot \qquad (1)$$

or escape the Coulombic field of $\overset{+}{\mathrm{R}}\mathrm{OH_2}$ to become free ions ($e_{s,f}^-$) which react with the solvent:

$$e_{s,f}^- + \mathrm{ROH} \rightarrow \mathrm{RO^-} + \mathrm{H}\cdot \qquad (2)$$

$G(e_{s,f}^-)$ is readily determined[1] but much of reaction (1) occurs in < 10 ns at 293 K and $G(e_{s,g}^-)$ has not been measured directly. At *ca.* 185 K these processes are considerably slower and we have observed changes in absorption which are due to the solvation process itself[2] followed by (1) and then by (2). Geminate recombination is now so slow (see Figure) that we can measure $G(e_{s,g}^-)$ and $G(e_{s,f}^-)$ directly.

Pure, deaerated alcohols were irradiated in a variable temperature flow system with 5—10 ns electron pulses from a 12 MeV linear accelerator, and optical absorptions of e_s^- were measured at λ_{max}[3] on equipment with a rise time of *ca.* 1 ns. The Figure shows the initial decay of e_s^- in CH_3OH and $n\text{-}C_4H_9OH$ at 187 K. The solvation process[2] is complete within 5 ns in CH_3OH and 20 ns in $n\text{-}C_4H_9OH$ and is much faster than spur recombination of e^-, *e.g.* in $n\text{-}C_4H_9OH$ the first half-life of reaction (1) is *ca.* 4 μs. The free ions show first-order decay with $t_{\frac{1}{2}}$ *ca.* 1 ms at these temperatures (see below) and extrapolation to zero time gives $G(e_{s,f}^-)$ which subtracted from the total absorption gives $G(e_{s,g}^-)$. Table 1 shows these yields at 293 and *ca.* 185 K.

TABLE 1. *Relative yields of* e_s^- *in alcohols*

	At 293 K		At *ca.* 185 K[a]	
	$10^{-4}G\epsilon(e_{s,f}^-)$[b]	$G(e_{s,g}^-)/G(e_{s,f}^-)$[c]	$10^{-4}G\epsilon(e_{s,f}^-)$[b]	$G(e_{s,g}^-)/G(e_{s,f}^-)$[c]
CH_3OH	1·79	$\geqslant$ 0·24	1·83	1·06
C_2H_5OH	1·52	$\geqslant$ 0·53	1·31	1·04
$n\text{-}C_4H_9OH$	1·31	$\geqslant$ 0·71	1·51	0·90
$(CH_3)_2CHOH$	1·61	$\geqslant$ 0·65	$\sim$1·6	$\sim$1·1

[a] CH_3OH, 187 K; C_2H_5OH, 163 K; $n\text{-}C_4H_9OH$, 188 K; $(CH_3)_2CHOH$, 186 K.
[b] Units: molecules $(100\ \mathrm{eV})^{-1}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. Error *ca.* ±6%.
[c] Error *ca.* ±12%.

We find at *ca.* 185 K $G(e_{s,g}^-) \simeq G(e_{s,f}^-)$, and $G(e_{s,f}) \simeq 1{\cdot}2 \pm 0{\cdot}3$ [1,4] so that the total yield of solvated electrons is $2{\cdot}4 \pm 0{\cdot}6$. Since the total ionization yield $G(e^-) \simeq 4{\cdot}2$—$4{\cdot}6$,[1,4] at least one third of all the electrons produced must recombine as 'dry' electrons before solvation. Previous indirect estimates[1,4] of $G(e_{s,g}^-)$ must include these 'dry' electrons. In fact we have found there is no clear distinction between 'dry' and 'solvated' electrons, and 'solvated' refers here to electrons which have achieved their equilibrium solvent atmosphere. A small fraction of electrons which have not reached this equilibrium state ('damp' electrons!) undergo much more rapid geminate recombination than do solvated electrons.[2]

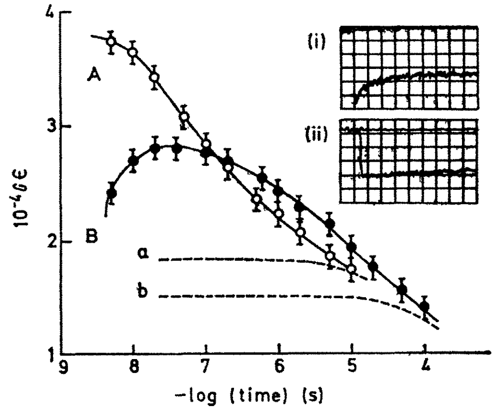

FIGURE. *Initial absorptions of* e_s^- *in alcohols at* 187 K: (A), CH_3OH *and* (B), $n\text{-}C_4H_9OH$. *Curves* a *and* b *show the contributions of* $e_{s,f}^-$ *to the total absorption in each case. Insets:* CRO *traces of decay of absorption at* 187 K *in* (i) CH_3OH, *and* (ii) $n\text{-}C_4H_9OH$, 100 *ns/cm. The increase at short times in curve* (B) *is due to the solvation process.*

Bronskill *et al.*[5] found that the absorption ($G\epsilon$) of e_s^- at 293 K in $(CH_3)_2CHOH$ is 25% that for H_2O at *ca.* 20 ps. We obtain a total $G\epsilon(e_s^-) \geqslant 2{\cdot}6 \times 10^4$ in $(CH_3)_2CHOH$ at *ca.* 10 ns which means that for H_2O at *ca.* 20 ps, $G\epsilon(e_s^-) \geqslant 10{\cdot}4 \times 10^4$. For $e_{s,f}^-$ in H_2O, $G\epsilon = 5{\cdot}1 \times 10^4$ and using the accepted $G(e_{s,f}^-) = 2{\cdot}6$ for H_2O, the total yield $G(e_s^-)$ in H_2O at 293 K is *ca.* 5. This assumes the electron is fully solvated in $(CH_3)_2CHOH$ at *ca.* 20 ps. The data for the other alcohols are also consistent with a higher $G(e_s^-)$ in H_2O than normally assumed, and recently a high value has been observed in alkaline ice.[6]

Analysis of spur decay kinetics in alcohols shows that at 293 K the *observable* fully solvated electrons decay approximately according to $[e^-_{s,s}]$ = constant × $(\text{time})^{-\frac{1}{2}}$, as predicted from current models.[4] At *ca.* 185 K only the last ~60% of $e^-_{s,s}$ decay according to this expression, the initial decay being slower than predicted. Indirect measurements of the temperature dependence of reaction (2) have been used[1] to suggest models for the homogeneous first-order disappearance of $e^-_{s,f}$ in alcohols. Our direct measurements of k_2 between *ca.* 185 and 330 K are closely described by the Arrhenius expression $k_2 = A_2\exp(-E_2/\boldsymbol{R}T)$ with the parameters shown in Table 2. Comparison of E_2 with E_η and E_τ shows that diffusion of e^-_s cannot be rate-determining and that correlations[1] with dielectric relaxation are probably fortuitous.

TABLE 2. *Reactions of e^-_s with alcohols*[a]

	$t_{\frac{1}{2}}$(298K) (μs)	$\log_{10}A_2$ (s^{-1})[b]	E_2 (kJ)[b]	$E\eta$(kJ)[c]	$E\tau$ (kJ)[d]
CH_3OH	7	8·70 ± 0·11	20·2 ± 0·5	11·9	15·5
C_2H_5OH	9	8·45 ± 0·05	20·3 ± 0·2	13·0	18·5
n-C_4H_9OH	8	8·84 ± 0·05	22·4 ± 0·3	19·2	26·3
$(CH_3)_2CHOH$	22	7·60 ± 0·14	17·5 ± 0·7	21·8	26·3

[a] Containing 1 mM-Na alkoxide.
[b] Errors are least-squares standard deviations from measurements at 12—15 temperatures.
[c] Temperature exponent of viscosity.[1]
[d] Temperature exponent of dielectric relaxation time.[1]

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[1] G. R. Freeman, in "Actions chimiques et biologiques des Radiations," ed. M. Haissinsky, Masson et Cie., Paris, 14e Série, 1969.
[2] J. H. Baxendale and P. Wardman, *Nature*, in the press.
[3] S. Arai and M. C. Sauer, jun., *J. Chem. Phys.*, 1966, **44**, 2297.
[4] S. J. Rzad and J. H. Fendler, *J. Chem. Phys.*, 1970, **52**, 5395.
[5] M. J. Bronskill, R. K. Wolff, and J. W. Hunt, *J. Chem. Phys.*, 1970, **53**, 4201.
[6] G. V. Buxton, F. C. R. Cattell, and F. S. Dainton, *Chem. Comm.*, 1971, 23.