Processes in γ-irradiated Methanol Glass

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WE have extended our observations on the γ-radiolysis at 77°K of methanol glass containing 2·3 vol. % water and are now able to present a mechanism which with those for other low-temperature glasses forms a consistent pattern. The relevant observations are:

(i) The continuous absorption band due to trapped electrons has $G\epsilon = (3{\cdot}0 \pm 0{\cdot}4) \times 10^4$ molecules (100 ev)$^{-1}$ M^{-1} cm.$^{-1}$ at $\lambda_{\max}$ 526 ± 5 nm.[1] The width of the band at half height is 1·00 ± 0·05 ev which is almost two thirds that of the band in n-propanol glass,[2] but, despite the narrower distribution of trap depths in methanol thereby implied, selective thermal and photobleaching of the shallower traps can be achieved.[2]

(ii) The continuum[3] beginning about 450 nm. and increasing steadily to give $G\epsilon = (1{\cdot}1 \pm 0{\cdot}2) \times 10^4$ at 200 nm. is attributable to the superimposed absorption of the $\dot{C}H_2OH$[4] and $\dot{C}H_2O^-$ radicals,[4,5] together with that of any residual absorption of e_t^- at this short wavelength. The e.s.r. spectrum[6,7] of $\dot{C}H_2O^-$ is likely to be very similar to that of $\dot{C}H_2OH$ in methanol glass at 77°K.[7] Photolysis with light of λ 254 nm. after photobleaching e_t^- results in the destruction of the optical and e.s.r. absorption of $\dot{C}H_2OH$ (and probably $\dot{C}H_2O^-$), with the formation of the formyl radical ($\lambda_{\max}$ 515 ± 10 nm., 134 G e.s.r. doublet) without loss of spin.

(iii) The following reactions can compete with the electron trapping process

$$e_m^{-*} + C(NO_2)_4 \longrightarrow NO_2 + \underline{C(NO_2)_3^-} \qquad (1)$$

$$e_m^{-*} + N_2O \longrightarrow N_2 + O^- \qquad (2)$$

$$e_m^{-*} + PhCH_2Cl \longrightarrow \underline{PhCH_2\cdot} + Cl^- \qquad (3)$$

$$e_m^{-*} + CH_3I \longrightarrow \underline{CH_3\cdot} + \underline{I^-} \qquad (4)$$

$$e_m^{-*} + Ag_n^{n+} \longrightarrow \underline{Ag_n^{(n-1)+}} \quad n = 1, 2 \text{ or greater} \qquad (5)$$

$$e_m^{-*} + C_6H_6 \longrightarrow C_6H_6^- \ (+ MeOH \longrightarrow \underline{C_6H_7\cdot} + MeO^-) \qquad (6)$$

where e_m^{-*} denotes the mobile electron before trapping and the underlined symbol represents that product identified by optical or e.s.r. spectroscopy or chemical analysis.

(iv) On warming an irradiated glass the trapped electrons decay by a first-order law[1] [$\log_{10} k_{uni}$ (sec.$^{-1}$) = (14 ± 1·5) − (7·7 ± 0·7 kcal.)/2·303 RT] with *no increase* in the $\dot{C}H_2OH$ radical concentration. This is in marked contrast to the behaviour of trapped electrons produced by reaction of sodium atoms with methanol in the rotating cryostat.[8] In the latter case the glass contains no $Me\overset{+}{O}H_2$ ions and we assume the relevant bleaching reaction to be decomposition of the trap (7) whereas in our

$$e_t^- \xrightarrow{kT} \dot{C}H_2O^- + H_2, \text{ or } \dot{C}H_2OH + CH_3O^- + H_2 \qquad (7)$$

case where $CH_3\overset{+}{O}H_2$ ions are present the reaction can be represented by equation (8) where e_m^-

$$e_t^- \xrightarrow{kT} e_m^-;\ e_m^- + Me\overset{+}{O}H_2 \longrightarrow MeOH + H\cdot \qquad (8)$$

represents an electron which is capable of diffusion and $Me\overset{+}{O}H_2$ a solvated proton. There is evidence that H atoms diffuse through, rather than react with, alcohol matrices and ultimately disappear by reaction with themselves or other radicals.[9] Alternatively it is possible that H atoms are not intermediates in the formation of H_2 but that reaction (9) can occur.

$$e_t^- \xrightarrow{kT} e_m^-;\ e_m^- + e_t^- \longrightarrow H_2 \qquad (9)$$

(v) Although the detailed mechanism of the diffusion process implied in equation (8) is unknown it follows that if sufficient of any of the solutes in equations (1) to (6) is present to prevent formation of some trapped electrons slight warming of the glass after irradiation should cause formation of more of the relevant product. This effect has been observed.

(vi) In striking contrast to the thermal bleaching, photobleaching using light $\lambda > 460$ nm. causes the conversion of e_t^- to $\dot{C}H_2OH$ and this reaction appears to be stoicheiometric because the ratio of spins before photobleaching to those present at any later stage is always in the range 0·97 ± 0·08. Moreover if a solute is present the photobleaching of any e_t^- causes *little if any augmentation* of the yield of product. Consequently the predominant photochemical process must be the trap decomposition reaction (10) and not, as is the case in triethylamine,[10]

$$e_t^- + h\nu \longrightarrow H_2 + \dot{C}H_2O^- \ (\longrightarrow \dot{C}H_2OH + MeO^-) \qquad (10)$$

3-methylpentane,[11] 2-methyltetrahydrofuran,[12] and neutral[18,19] or alkaline ice,[13,14] one of photodetachment from the trap. Therefore the quantum yield of the bleaching process in alcohols should, in contrast to other matrices, be constant, as has been observed.[3,15]

(vii) If equations (8) and (10) correctly represent the thermal and photobleaching processes respectively and if (a) the diffusing H atoms emerging from reaction (8) combine with one another and (b) the $\dot{C}H_2OH$ radicals do not disproportionate at these low temperatures, equations (11) and (12) should be valid where the subscripts p and t denote photo- and thermal bleaching respectively. The product yields

$$G(CH_2O)_p = G(CH_2O)_t = 0 \qquad (11)$$

$$G(e_t^-) = 2\{G(H_2)_p - G(H_2)_t\} = 2\{G(CH_2OH)_{2\,p} - G(CH_2OH)_{2\,t}\} \qquad (12)$$

from γ-radiolysis of methanol glass after photo- or thermal bleaching of e_t^- have been given elsewhere.[3] They show good material balance and also show that equation (11) is almost true, and hence that $G(e_t^-)$ is *ca.* 2·4. By using the nitroform anion formed in reaction (1) as an index of $G(e_t^-)$ when sufficient tetranitromethane is present to make the contribution of the trapped electron to the optical density at 526 nm. negligible, we find $G(e_t^-) = 2·7 \pm 0·3$ in fair agreement with the value already quoted. Furthermore, experiments with considerably more than sufficient N_2O or tetranitromethane present to prevent any electron trapping show that $G(H_2)$ cannot be reduced below 1·7. The measured $G(H_2)$ from thermally bleached pure methanol glass should be the sum of this quantity and half $G(e_t^-)$, *i.e.* 3·0 which is to be compared with the observed value of 3·2.

Thus, methanol *resembles* n-propanol in that (a) visible light decomposes the trapped electrons forming H_2, and (b) a smaller number of electrons escape reaction with $R\overset{+}{O}H_2$ in the liquid phase than in the glass, *i.e.* $G(e_t^-) > G(e_s^-)$. Both alcohols differ from triethylamine, 3-methylpentane, 2-methyltetrahydrofuran, and alkaline ice where light causes a photodetachment of the electron from the trap. Methanol *differs* from *n*-propanol in that the trapped electrons do not so easily decompose the medium so that on warming some of the electrons become mobile and can migrate to and react with any added reactive solute. If no solute is present they react with $\overset{+}{\mathrm{MeOH}_2}$. In aqueous alkaline glasses where the electron is even more stable, both heat and light will release the electron as such from the trap and in the absence of other solutes it recombines with OH or O^- [16] (or in certain circumstances with e_t^-)[17] so that $G(H_2)_{t,p} \approx 0$.

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