Distinguishable Electron Traps in γ-Irradiated n-Propanol Glass

By F. S. DAINTON,* G. A. SALMON, and U. F. ZUCKER

(*University of Leeds, Cookridge High Energy Radiation Research Centre, Cookridge Hospital, Leeds* 16)

THE colour centres having λ_{max} 500 nm. which are formed on γ-irradiation of glassy alcohols at 77°K have been attributed[1–5] to trapped electrons, e_t^-, and may readily be destroyed by increasing the temperature from 77 to *ca.* 110°K or by illumination with visible light. We now report data which prove that γ-irradiated n-propanol glass contains trapped electrons which differ in trap depth and in response to heat and light.

The glasses were studied by low-temperature spectrophotometry with a specially adapted Unicam SP 700 recording spectrophotometer. The lowest attainable temperature of the cell compartment was 78°K. Photobleaching experiments were carried out *in situ*. Details of the experimental techniques will be described elsewhere.[6]

The γ-irradiated n-propanol glasses which contained 2% water v/v showed a broad intense optical absorption ($\lambda_{max} = 555$ nm.) which has been assigned[3] to e_t^-. Samples were warmed slowly (1 or 2° min.$^{-1}$) to some maximum temperature (T_{max}) maintained sufficiently long (5—10 min.) to allow a conveniently measurable amount of diminution of the absorption in the visible or i.r. region of the spectrum. They were then rapidly cooled and the spectrum was measured at 70°K. The changes in the absorption band attributed to e_t^- caused by successive treatments of this kind at progressively higher values of T_{max} are shown in Figure 1, which shows that diminution of absorption can be accompanied by some increase in absorption at a lower wavelength. Curve (a) of Figure 2 shows the total change in absorption which was caused by three cycles carried out at temperatures < 104°K and this is compared in curve (b) with the remaining absorption due to e_t^- as determined by subsequent complete decay at a temperature close to but $\ngtr 107$°K. During decay at $T_{max} > 104$°K the shape of the absorption remained unchanged from that shown by curve (b) in Figure 2.

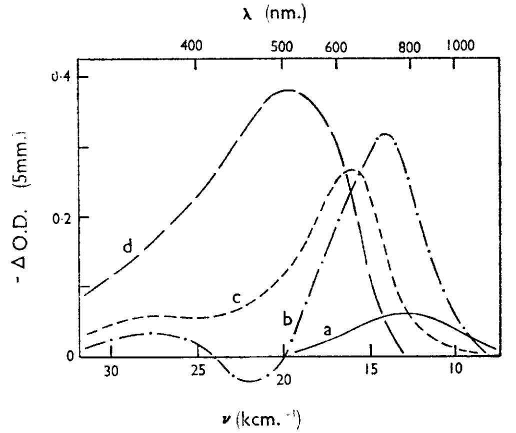

FIGURE 1. *Loss of absorption in γ-irradiated n-propanol glass held successively for* 5 *min. periods at* (a) 85, (b) 94, (c) 101, *and* (d) 104°K.

Photobleaching of γ-irradiated samples at 78°K with light of $\lambda > 835$ nm. resulted in only partial removal of the colour centres. Curve (a) of Figure 3 gives the absorption spectrum of these centres. Curve (b) of Figure 3 shows that part of the absorption of the colour centres which is unaffected by the near i.r. light but which could be subsequently removed with light of $\lambda > 610$ nm.

From experiments using monochromatic light, in conjunction with various solutes, we have shown[3,6] that photobleaching of e_t^- in n-propanol does not lead to the ejection of electrons from their traps, but rather to the unimolecular decomposition of the trapped electrons according to equation (1a) or (1b):

$$e_t^- \xrightarrow{h\nu} Et\dot{C}HO^- + H_2 \qquad (1a)$$

$$e_t^- \xrightarrow{h\nu} Et\dot{C}HOH + H_2 + EtCH_2O^- \qquad (1b)$$

Our results clearly indicate that the radiation-induced absorption band due to e_t^- is in fact composed of a large number of absorption bands of similar shape but different λ_{max}. The absence of any fine structure in the composite band rules out the presence of a small number of well defined groups of electrons with characteristic and distinctive absorption spectra.

The observed difference in the absorption spectra of trapped electrons must be attributed to differences in their trapping sites. These differences may arise from (*a*) substantial limitations on internal and external rotation of the propanol molecules during the electron trapping process,

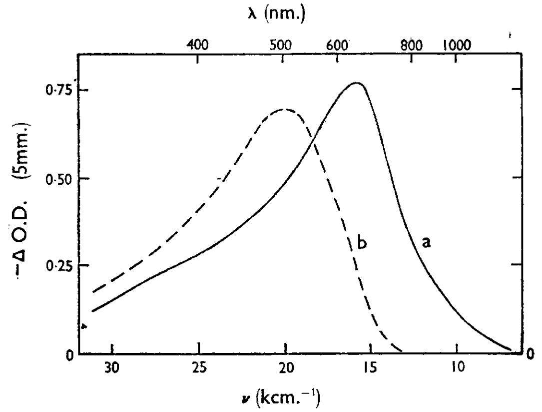

FIGURE 2. (a) *Loss of absorption caused by thermal treatment* < 104°K; (b) *spectrum of centres destroyed above* 104°K.

(*b*) non-equilibrium configuration frozen in to the glass during the rapid cooling necessary for its formation, or (*c*) a combination of both. The limitations in (*a*) will be greater for propanol than for lower alcohols because the energy available per rotational mode derived from the interactions between the electronic charge and the permanent and the induced dipoles will be least in this alcohol.

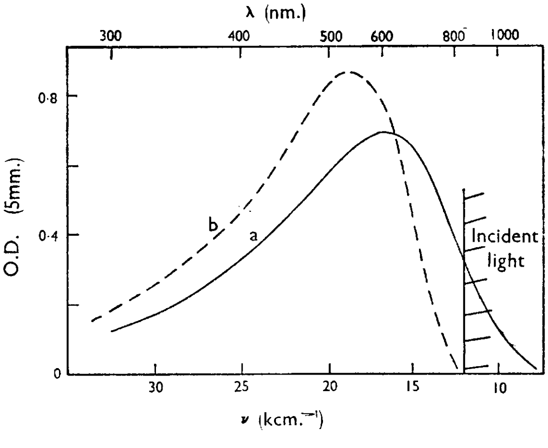

FIGURE 3. *Changes caused by illumination.* (a) *Spectrum of* e_t^- *removed by photobleaching with light of* $\lambda > 835$ *nm.*; (b) *spectrum of residual* e_t^- *which can be completely destroyed by illumination with light of* $\lambda > 610$ *nm.*

Trapped electrons will therefore be surrounded by propanol molecules in varying degrees of non-equilibrium configurations corresponding to potential wells of lower depth with associated larger λ_{max} for optical transitions to any common upper state. Slight warming of the glass permits rotational motion enabling the attainment of the equilibrium configuration and of a more homogeneous population of trapped electrons with a consequential shift of λ_{max} to the blue region of the spectrum, as illustrated in Figures 1 and 2. The selective photobleaching (see Figure 3) confirms the existence of trapped electrons of different λ_{max}.

As the temperature is raised further a permanent decay of the absorption supervenes, which at a constant temperature is a first-order process unaffected by the presence of 10^{-3}—10^{-2} M of electron scavenging solutes such as naphthalene, diphenyl, benzyl chloride, and sulphuric acid. Products such as the naphthalene and diphenyl anions or benzyl radicals are not formed under these conditions. We therefore suggest that the electrons are not released from their traps to be converted into mobile electrons but that the traps decompose to form hydrogen atoms as shown in equation (2).

$$\underset{\text{non-equilibrium}}{\overset{n}{\Sigma} e^-_{t,i}} \xrightarrow{kT} \underset{\text{equilibrium}}{n\, e^-_t} \xrightarrow{kT} \tfrac{1}{2}n\,(2\text{EtCH}_2\text{O}^- + \text{H}_2) \qquad (2)$$

In view of the unchanged hydroxypropyl-radical concentration observed by e.s.r. spectroscopy during this process, it is considered either that hydrogen atoms are not formed or that if formed they disappear by dimerisation rather than by abstraction of another hydrogen atom from a solvent molecule.

If reactions (1) and (2) correctly describe the photolytic and thermal destruction of e^-_t relation (3) must be satisfied:

$$G(e^-_t) = 2\{G(\text{H}_2)_p - G(\text{H}_2)_t\} \qquad (3)$$

where $G(\text{H}_2)_p$ and $G(\text{H}_2)_t$ are the radiation chemical yields of hydrogen gas determined respectively after photobleaching and after thermal bleaching of e^-_t. The initial values which have been determined are in good agreement with the proposed relationship (3):

$G(e^-_t) = 1{\cdot}7 \pm 0{\cdot}2$; $G(\text{H}_2)_p = 4{\cdot}4 \pm 0{\cdot}3$; $G(\text{H}_2)_t = 3{\cdot}5 \pm 0{\cdot}2$.

(*Received, July 5th,* 1968; *Com.* 897.)

[1] M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Amer. Chem. Soc.*, 1962, **84**, 4230.
[2] F. S. Dainton, G. A. Salmon, and J. Teply, *Proc. Roy. Soc.*, 1965, *A*, **286**, 27.
[3] F. S. Dainton, G. A. Salmon, P. Wardman, and U. F. Zucker, Proc. 2nd Tihany Sym. Radiation Chem., 1966, p. 247.
[4] R. A. Basson and K. J. van der Linde, *J. Chem. Soc.* (*A*), 1967, 1182.
[5] J. W. Fletcher and G. R. Freeman, *Canad. J. Chem.*, 1967, **45**, 635.
[6] F. S. Dainton, G. A. Salmon, and U. F. Zucker, to be published.