Trapping of Radiation-induced Electrons in Cycloamylose Hydrates: Electron Spin Resonance Study

By J. Bardsley, P. J. Baugh, and G. O. Phillips*

(*Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT, *Lancs.*)

Summary Electrons produced by γ-irradiation are unexpectedly trapped in solid cycloamylose hydrates at 77 K.

Using electron spin resonance (e.s.r.) techniques trapped electrons have been observed in aqueous neutral ices, aqueous alkaline hydroxide ices, various organic solvents, alcohols,[1,2] and aqueous carbohydrate ices[1,3,4] at 77K. Here we report the formation and stabilization of electrons in solid cycloamylose hydrates[5] at 77K.

After irradiation of polycrystalline β-cycloamylose hydrate (14% w/w water) at 77K a purple colouration was observed. Subsequent e.s.r. analysis demonstrated the presence of carbohydrate radicals and a narrow line ($\Delta H = 12{\cdot}5 \pm 0{\cdot}5$ G; $g = 2{\cdot}0010 \pm 0{\cdot}0004$), which is completely removed on photobleaching with white light or on thermal annealing. This line has been assigned to the trapped electron, in view of the similarities in bleaching properties, e.s.r. power saturation, and line width, to e_t^- observed in other systems.[1–4]

Anhydrous β-cycloamylose exhibited no trapped electrons on irradiation at 77K. The e.s.r. line width of the species decreased to $\Delta H = 4{\cdot}4 \pm 0{\cdot}3$ G when observed in γ-irradiated β-cycloamylose containing D_2O instead of H_2O. This line width reduction on replacing H_2O by D_2O is consistent with the results obtained for aqueous carbohydrate systems[3,4] and indicates that, as in these systems, the protons of the surrounding water molecules contribute to the line width of the electron and form at least a partially 'water walled' trap.[6] Similar results are obtained using α- and γ-cycloamylose hydrates.

Recent structural work by Manor and Saenger[7] on α-cycloamylose hexahydrate, $(C_6H_{10}O_5)_6,6H_2O$, has demonstrated that two water molecules are included on the mean molecular axis of the cycloamylose ring. One of the water molecules is hydrogen bonded to the ring, whereas the second is in hydrophobic surroundings, being hydrogen bonded to the first water molecule only. The evidence points to the cycloamyloses existing as cage structures. It is possible that, in such a cage structure, the water molecules in hydrophobic surroundings could form a suitable site for trapping the electron at 77K. Thus, while it is most unusual for e_t^- to be observed in solid state organic systems of this type, the structural studies do point to a suitable association of water molecules within the matrix in the cycloamylose hydrates.

(*Received*, 8*th November* 1972; *Com.* 1879.)

1 B. G. Ershov and A. K. Pikaev, *Radiation Res. Rev.*, 1969, **2**, 1.
2 F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. Roy. Soc.*, 1969, **A 313**, 1.
3 P. J. Baugh, K. Kershaw, and G. O. Phillips, *J. Chem. Soc.* (*B*), 1970, 1482; J. Bardsley, unpublished results.
4 J. D. Zimbrick and L. S. Myers, jun., *J. Chem. Phys.*, 1971, **7**, 2899.
5 D. J. French, *Carbohydrate Chem.*, 1957, **12**, 189.
6 G. V. Buxton, F. S. Dainton, T. E. Lantz, and F. P. Sargent, *Trans. Faraday Soc.*, 1970, **66**, 2962.
7 P. C. Manor and W. Saenger, *Nature*, 1972, **237**, 393.