Radiation Chemistry of Carbohydrates. Part XIX.[1] Yields of Trapped Electrons and Radicals in γ-Irradiated, Frozen, Concentrated, Aqueous Solutions of Sugars

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Trapped electron (e_t^-) and sugar radical yields in aqueous carbohydrate matrices γ-irradiated at 77 K have been determined using photobleaching and electron scavenging methods. Maximum values of $Ge_t^- = 2{\cdot}2$ are found at 60% w/w solute and G(sugar radicals) = 2·3 at this solute concentration. Photobleaching results in reaction of the trapped electrons with the sugar to give almost an equivalent yield of sugar radicals and makes this method, therefore, unreliable for determining Ge_t^-. Conversion of radiation induced electrons into hydrogen atoms using H_2SO_4 doubles G(sugar radicals) at 60% w/w solute. From the variations in e_t^- and radical yields with carbohydrate concentration in acidic and neutral ices, an increase in the 'glassiness' of the ices can be monitored as the solute content is increased above *ca.* 40% w/w. An increase in the yield of e_t^- occurs here due to an increase in the number of suitable traps. Optical absorption spectra of e_t^- have been recorded at 77 K in frozen, aqueous D-glucose, D-fructose, and sucrose glasses; $\lambda_{max.}$ decreases linearly with increasing sugar concentration, giving by extrapolation $\lambda_{max.}$ (glassy ice) = 670—690 nm and $\lambda_{max.}$ (pure sugar glass) = 485, 505, and 516 nm for the three sugars.

IRRADIATION of organic and aqueous systems at 77 K leads to the formation of trapped species which can be observed by e.s.r. and optical spectroscopy. Trapped electrons (e_t^-) and other radical species have been identified in γ-irradiated aqueous alkaline ices,[2,3] glassy alcohols,[4-6] aqueous alcoholic glasses,[7] and aqueous carbohydrate ices [8-12] at 77 K. Electron and radical yields in γ-irradiated carbohydrate ices increase linearly

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with the carbohydrate content when the ices are predominantly polycrystalline in nature, that is up to 40% w/w carbohydrate.[11] A phase effect was subsequently observed above 40% w/w sugar,[12] based on yields of e_t^- obtained from photobleaching experiments, which is somewhat similar to the behaviour of alkaline ices.[13] Here we employ electron scavenging in addition to photobleaching methods to examine in more detail the influence of increasing the carbohydrate content of the ice and to determine whether these frozen systems really behave like alkaline ices or have properties more akin to aqueous alcoholic glasses irradiated at low temperatures.

EXPERIMENTAL

Materials and Sample Preparation.—Aqueous solutions of carbohydrates were prepared from AnalaR reagents and dissolved in either triply distilled H_2O or D_2O. Samples were prepared as ice cylinders at 77 K as previously described,[11,13] or by freezing droplets of solution from a capillary in liquid nitrogen. Frozen spheres of *ca.* 3 mm were employed. Sodium nitrite, ferric chloride, or sulphuric acid were added to the solutions in quantities sufficient to scavenge all the electrons

Irradiation and E.s.r. Analysis.—After irradiation the samples were stored in the dark in Pyrex tubes at 77 K. The radiation facilities and e.s.r. system employed have been described.[11] Dose was measured by Fricke dosimetry, using water instead of liquid nitrogen in the Dewar surrounding the sample tubes; the dose rate was $2{\cdot}2 \times 10^{17}$ eV g^{-1} min^{-1}.

E.s.r. spectra were recorded at the lowest possible microwave power levels (10^{-4} W). Photobleaching through the radiation port of the e.s.r. cavity was with white light from a tungsten bulb or filtered light (>540 nm) from a Hg high pressure point source. Absolute radical yields were determined by relating the double integration of the e.s.r. derivative absorption curves for the irradiated samples with e_t^- in irradiated 10M-NaOH ice, and adopting $Ge_t^- = 2{\cdot}1 \pm 0{\cdot}2$ [13b] for this system. The *G* values calculated refer to the dose absorbed by the frozen system as a whole.

Optical Spectroscopy.—For low temperature optical spectroscopy we employed a Unicam SP 700 spectrophotometer with modifications as described by Dainton *et al.*[5] The unsilvered Dewars with Spectrosil optical windows, and the irradiation optical cells ($2{\cdot}5 \times 1{\cdot}5 \times 0{\cdot}5$ cm) constructed from Vitreosil rectangular quartz tubing were supplied by Thermal Syndicate. The system and temperature control method have been described.[5] Temperatures in the range 77—190 K could be maintained to within ±2·0° for several hours and were monitored using a copper–constantan thermocouple.

Carbohydrate solutions were frozen in the irradiation optical cell immersed in liquid nitrogen at 77 K and before irradiation the cell was rapidly transferred to the precooled optical Dewar in the cell compartment of the spectrometer. The spectrum was recorded initially to obtain a base line, which varied as cracking occurred in the frozen glass. Such cracking prevents truly quantitative results being obtained from the optical measurements. The optical cell was placed in the Dewar containing liquid nitrogen for irradiations, as for e.s.r. experiments and transferred to the optical Dewar for absorption spectral measurement. To obtain an approximate absorption spectrum of the electron, the background absorption spectrum of the cracked glass was subtracted from the spectrum of the same glass after irradiation.

RESULTS AND DISCUSSION

Changes in E.s.r. Spectra on Photobleaching and Scavenging.—Figure 1A shows the e.s.r. spectrum of irradiated frozen aqueous D-glucose solution (36% w/w) at 77 K. After removal of e_t^- by photobleaching Figure 1B is obtained, from which the e_t^- spectrum can be obtained by difference (Figure 1C). This spectrum is identical with comparable spectra of e_t^- obtained from other γ-irradiated aqueous glassy matrices at 77 K. On photobleaching no significant increase in sugar radical concentration can be observed from the e.s.r. spectra. However, we do find that e_t^- yields, inferred from electron scavenging data (Figure 1D) at low solute concentrations are higher than the yields of e_t^- determined by photobleaching (Table) suggesting that a reaction between the electron and solute occurs during this process. The ices are predominantly polycrystalline but contain regions of higher solute content [11] as a result of the rapid freezing process, to which a proportion of mobile electrons (e_m^-) may migrate and become trapped.

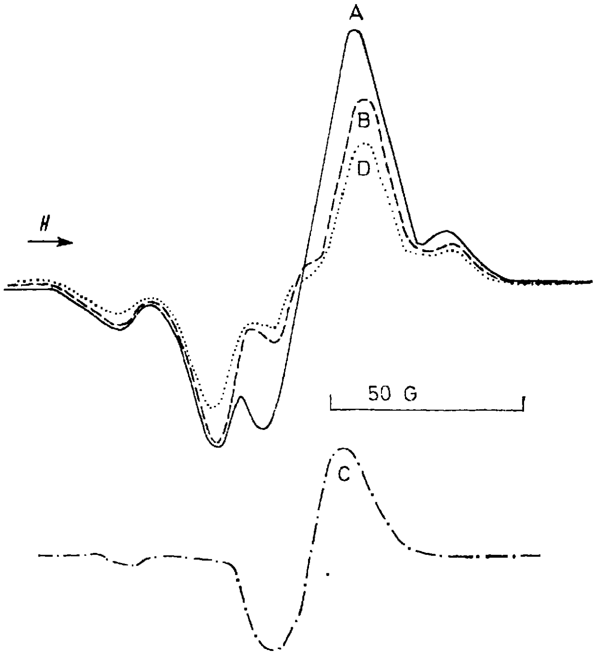

FIGURE 1 E.s.r. spectra of aqueous D-glucose ice (36% w/w) γ-irradiated at 77 K before and after photobleaching and in the presence of electron scavengers: A, before photobleaching; B, after photobleaching; C, e.s.r. spectrum of e_t^- obtained by subtracting B from A; D, in the presence of $NaNO_2$ or $FeCl_3$ (0·15M)

When a 60% w/w D-glucose, frozen, aqueous solution is similarly irradiated and then photobleached, there is

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[13] (*a*) T. Henriksen, *Radiation Res.*, 1964, **23**, 63; (*b*) H. Hase and L. Kevan, *J. Chem. Phys.*, 1969, **73**, 3290.

clearly a reaction between the electron excited by the light and the sugar, resulting in an increase in the concentration of sugar radicals (compare Figures 2A and B).

G Values for trapped radicals and electrons in aqueous D-glucose ices γ-irradiated at 77 K

Solute concentrations (% w/w)	$G(\cdot R'OH$ [a] $+ e_t^-)$ Unphotobleached	$G(\cdot R'OH)$ Photobleached	$G(\cdot R'OH)$ Scavenged		Ge_t^- [b]
			$NaNO_2$ $FeCl_3$	H_2SO_4	
20	1·4	1·3	0·9	1·3	0·5 (0·4)
36	2·2	2·1	1·5	2·1	0·7 (0·6)
45	2·9	2·6	1·8	2·9	1·1 (1·1)
50	3·6	3·4	2·2	3·5	1·4 (1·3)
60	4·5	4·5	2·3	4·5	2·2 (2·2)
70	4·5	4·2	2·4	4·5	2·1 (2·1)
80	4·5	4·2	2·5	4·5	2·0 (2·0)

[a] For predominantly polycrystalline 'ice' *i.e.* at low solute concentrations there is a contribution from OH to the G value (see Figure 3). [b] Ge_t^- obtained by subtraction of $G(\cdot R'OH)$ for $NaNO_2$ or $FeCl_3$ scavenged, from $G(\cdot R'OH + e_t^-)$ for unphotobleached sample; in parentheses Ge_m^- obtained similarly for H_2SO_4 and $NaNO_2$ scavenged samples indicating the proportion of e_t^- reacting to give an excess of sugar radicals.

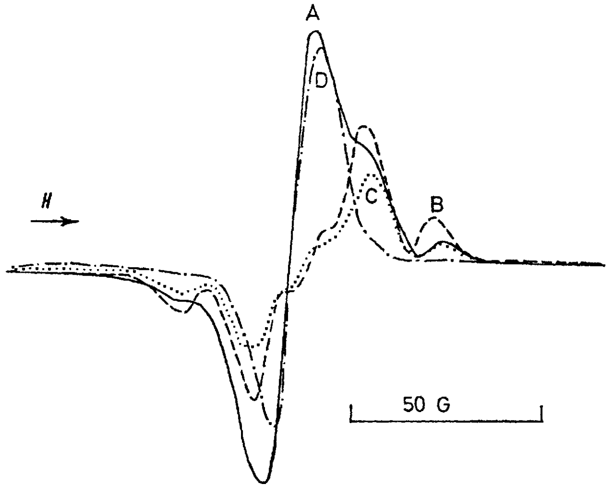

FIGURE 2 E.s.r. spectra of aqueous D-glucose ice (60% w/w) γ-irradiated at 77 K before and after photobleaching and observed in the presence of electron scavengers: A, before photobleaching; B, after photobleaching; C, in the presence of $NaNO_2$ (0·16M) or $FeCl_3$ (0·15M); D, e.s.r. spectrum of e_t^- obtained by subtracting C from A

Due to this behaviour, first observed here, for sugar ices, it follows that simply observing the decrease in overall radical yield on photobleaching cannot provide a reliable value for Ge_t^-. As an alternative we have examined the influence of adding an electron scavenger, $NaNO_2$ (<0·16M) to the system prior to irradiation. The trapped electron resonance is thus absent from the e.s.r. spectrum (Figure 2C) and the resulting sugar radical concentration is much lower than for the irradiated system with no scavenger present and which has been photobleached (Figure 2B). There is a slight change in the appearance of the e.s.r. spectrum due to a small contribution from the centre line ($M_I = 0$) of the $NO_2\cdot$ radical triplet, produced by the direct effect of radiation on the nitrite ion,* which is superimposed on the spectrum of the sugar radicals. A correction has been made in all calculations of radical yields when $NaNO_2$ is present to allow for this absorption. To check on the validity of the results obtained for ices containing $NaNO_2$ a second electron scavenger, $FeCl_3$ was employed. The e.s.r. spectra (Figures 1D and 2C) and radical yields obtained were extremely similar for irradiated ices containing this scavenger. Thus it can be assumed that when the mobile electrons are scavenged either by Fe^{3+} or NO_2^- the ensuing reaction * in no way effects the yield of sugar radicals. Figure 2D gives the e_t^- spectrum obtained by subtraction of the spectra shown in Figures 2A and C. Frozen aqueous D-fructose and sucrose solutions behave similarly to D-glucose and show an enhancement of the sugar radical yield after photobleaching and a reduction in the presence of $NaNO_2$ or $FeCl_3$.

E.s.r. Line Widths of e_t^-.—In frozen D-glucose solutions (20—36% w/w) e_t^- and sugar radical yields are a maximum at a dose of $2{\cdot}15 \times 10^{20}$ eV g^{-1} and photobleaching causes no significant increase in carbohydrate radical concentration. Here, therefore, it is reasonable to use the peak-to-peak separation directly from the e.s.r. spectrum of e_t^- (Figure 1C) to determine the line width. The line width of e_t^- measured in this way is independent of the nature of the carbohydrate, D-glucose, D-fructose, or sucrose, in the frozen matrix and is the same in frozen H_2O; $\Delta H = 12{\cdot}9 \pm 0{\cdot}5$ G ($g = 2{\cdot}0014 \pm 0{\cdot}0004$) compared with $4{\cdot}5 \pm 0{\cdot}2$ G for D_2O solutions. It would, therefore, appear that the electron trapping site is predominantly 'water walled.' Based on $\Delta H = 13{\cdot}5 \pm 0{\cdot}5$ G and $6{\cdot}3 \pm 0{\cdot}3$ G for e_t^- in H_2O and D_2O respectively, we previously found a coupling to protons of $a_H/g_e\beta_e = 5{\cdot}26 \pm 0{\cdot}3$ G,[11] assuming interaction with four water molecules and the smaller line widths reported here make little difference to this value.

When there is an enhancement of the carbohydrate radical spectrum after photobleaching, the e_t^- spectrum obtained by difference may not represent the true line width. Under these circumstances the line width can be

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* The direct and indirect effects of ionizing radiations on the nitrite ion in frozen aqueous solutions may be summarized in reactions (i) and (ii) The reaction of e_m^- with nitrite ion leads

$$NO_2^- \rightarrow NO_2\cdot + e_m^- \qquad \text{(i)}$$

$$e_m^- + NO_2^- \rightarrow [NO_2^{2-}] \longrightarrow NO + O^{2-} \qquad \text{(ii)}$$

to the formation of a radical anion considered from e.s.r. observations to be characterised also by a triplet (L. Kevan, P. N. Moorthy, and J. J. Weiss, *J. Amer. Chem. Soc.*, 1964, **86**, 771). No definite details of its stability in frozen aqueous systems have been reported; however, it is probable that it dissociates to give nitric oxide and the oxide ion as suggested for aqueous solution at room temperature. From the results obtained here, by comparison with ferric chloride and H_2SO_4 as electron scavengers, it appears that this species is unstable and thus would contribute little to the e.s.r. spectra observed. Furthermore, nitric oxide apparently exhibits a detectable e.s.r. absorption in the solution or the solid phase only under exceptional circumstances.

more reliably obtained from the difference spectrum after the addition of $NaNO_2$ or $FeCl_3$ (Figure 2D). We find that the e_t^- spectra obtained in this way for frozen aqueous 40—80% w/w D-glucose solutions after a dose of $1{\cdot}32 \times 10^{19}$ eV g^{-1} have an identical line width to those of e_t^- in the 20—36% w/w D-glucose frozen matrices ($12{\cdot}9 \pm 0{\cdot}5$ G). Thus the e_t^- line widths are independent of sugar concentration.

Radical and Trapped Electron Yields.—Where the ices are predominantly polycrystalline (up to 40% w/w) it was previously demonstrated that radical yields are linear with carbohydrate concentration and show good agreement on extrapolation with sugar radical yields in γ-irradiated, polycrystalline D-glucose and sucrose.[11]

Here e_t^- and sugar radical yields have been measured over 20—80% w/w D-glucose and are based on the yield of trapped electrons in γ-irradiated 10M-sodium hydroxide ($Ge_t^- = 2{\cdot}1 \pm 0{\cdot}2$). Figure 3A shows the variation in total radical yield (e_t^- + sugar radicals) with D-glucose concentration and the corresponding G values are given in the Table. The total radical yield is linear up to *ca.* 40% w/w solute with the gradient of the curve increasing from this concentration to 60% w/w; saturation then occurs up to the 80% w/w solute limit due primarily to a saturation in the yield of e_t^-. Extending the two initial sections of the curve linearly as indicated in Figure 3A gives an intersection which indicates that a transition in the yield occurs at *ca.* 40% w/w solute [evident also from the curve for the e_t^- yield (Figure 3D)]. It is worth noting here that this is the concentration at which the ices become transparent enough for optical absorption spectra of e_t^- to be observed (see Figure 4B).

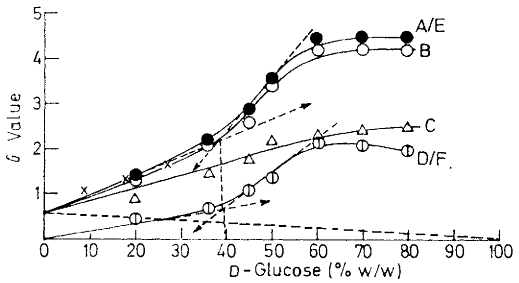

FIGURE 3 Variations in G(radical) with solute concentration for aqueous D-glucose ices γ-irradiated at 77 K: A, G(total radicals), ×, ref. 11; B, G(residual radicals) after photobleaching; C, G(radicals) in the presence of $NaNO_2$; D, $G(e_t^-)$; E, G (radicals) in the presence of H_2SO_4; F, G(excess sugar radicals). The two initial sections of curves A/E and D/F are extended linearly as indicated to illustrate intersection at *ca.* 40% w/w solute

The total radical yields obtained for 20—80% w/w D-glucose ices (Figure 3) containing electron scavengers, $NaNO_2$ or $FeCl_3$, are summarised in the Table. At low solute concentrations the ·OH radical contributes considerably to the total yield of radicals. On a direct action basis G(OH) would be expected to follow the broken line illustrated in Figure 3 and a correction can be made to the G value curves for radicals (Figures 3B and C) to allow for ·OH contribution.

At low solute concentrations the reactions (1) and (2) describing the direct action effect satisfactorily account

$$\mathrm{ROH}^* \longrightarrow \cdot\mathrm{R'OH} + \mathrm{H}\cdot \qquad (1)$$

$$\mathrm{H_2O}^* \longrightarrow \cdot\mathrm{OH} + \mathrm{H}\cdot \qquad (2)$$

for the formation of radicals. We do not wish to speculate extensively on the role of the positive ions, $ROH^{+\cdot}$ and $H_2O^{+\cdot}$, in view of their little known chemistry. However, since a high proportion of electrons are trapped at high solute concentrations the positive ions formed must undergo alternative reactions to recombination with geminate electrons. The yields of $ROH^{+\cdot}$ and $H_2O^{+\cdot}$ will depend on the weight fraction, ionization energies of each component, and their local environments. Reactions (3)—(5) of the positive ions could account for the sugar

$$\mathrm{ROH}^{+\cdot}\ (+\ \mathrm{H_2O}) \longrightarrow \cdot\mathrm{R'OH} + \mathrm{H^+(H_3O^+)} \qquad (3)$$

$$\mathrm{H_2O}^{+\cdot} + \mathrm{ROH(H_2O)} \longrightarrow \cdot\mathrm{OH} + \mathrm{ROH_2^+(H_3O^+)} \qquad (4)$$

$$\cdot\mathrm{OH} + \mathrm{ROH} \longrightarrow \mathrm{H_2O} + \cdot\mathrm{R'OH} \qquad (5)$$

radicals formed in the high solute ices. Homolytic ion-molecule reactions involving the sugar are less likely since $ROH^{+\cdot}$ will be almost totally surrounded by water molecules even at 60% w/w solute concentrations. The G values for sugar radicals can be equated with the G values for ROH^* (direct action), $ROH^{+\cdot}$, and $H_2O^{+\cdot}$ by equation (6). On this basis at 60% w/w solute since

$$G(\text{sugar radicals}) = G_{\mathrm{ROH}^*} + G_{\mathrm{ROH}^{+\cdot}} + G_{\mathrm{H_2O}^{+\cdot}} \qquad (6)$$

G(sugar radical) $\simeq Ge_t^-$ the direct action contribution (defined by G_{ROH^*}) to the G value may be minimal while at low solute concentration it may predominate.[13a]

In order to explain the enhancement of the sugar radical yield during photobleaching (Figure 3B) the following reactions must be considered. The photo-excited electron reacts either with a sugar molecule (ROH_t) in the trap (t) wall during trap decomposition [reaction (8a/b)] or with a protonated species (ROH_2^+ or H_3O^+) in the bulk matrix after mobilisation from the trap [reaction (9)] to produce sugar radicals represented

$$\mathrm{e_t^-} \xrightarrow{h\nu} (\mathrm{e_t^-})^* + \mathrm{e_m^-} \qquad (7)$$

$$(\mathrm{e_t^-})^* + \mathrm{ROH_t} \longrightarrow \cdot\mathrm{R'O^-} + \mathrm{H_2} \qquad (8a)$$

$$\searrow \mathrm{RO^-} + \mathrm{H}\cdot \xrightarrow{\mathrm{ROH_t}} \cdot\mathrm{R'OH} + \mathrm{H_2} \qquad (8b)$$

$$\mathrm{e_m^-} + \mathrm{ROH_2^+(H_3O^+)} \longrightarrow \mathrm{H}\cdot \xrightarrow{\mathrm{ROH}} \cdot\mathrm{R'OH} + \mathrm{H_2} \qquad (9)$$

by $\cdot R'O^-$ and ·R'OH. Similar behaviour was found for methanol [4,5] and n-propanol [5] which was interpreted in terms of a reaction predominating between the photo-excited trapped electron and the solute in the trap wall.

In view of an apparent lack of reactivity of the photoexcited electron towards an electron scavenger present in the matrix photodetachment [reaction (9)] was considered less likely.[4] In contrast it should be noted that no significant reaction occurs between the hydrated electron (e_{aq}^-) and sugars in aqueous solution according to pulse radiolysis observations.[14]

We have not been able to conduct any selective wavelength photobleaching experiments here but it is worth mentioning that the sugar radical yield is enhanced on photobleaching either with white light or filtered light (>540 nm), and the increase almost equals the original e_t^- concentration. However, Steen and Moan[15] have shown using this technique that for irradiated ethylene glycol–water glasses (50% w/w) with an electron scavenger present, the photoexcited electron reacts mainly with the solute in the trap and does not become photodetached to any great extent except when short wavelength light is employed. Therefore, from our results, it can be concluded that γ-irradiated, frozen, aqueous sugar solutions, particularly containing higher solute concentrations, behave similarly when photobleached to glassy alcohols and alcohol-water mixtures.

Because of the radicals produced by interaction of the electron with the sugar during photobleaching, the total radical yield remains essentially unchanged (Figure 3B; Table). It is not, therefore, valid to measure absolute Ge_t^- by this method. Moreover, different power saturation effects of the species present lead to an apparent difference in Ge_t^- at various microwave powers. Nevertheless, Zimbrick and Myers[11] have used the photobleaching method to determine Ge_t^- over a range of sugar concentrations and appear to have taken no account of this effect. Predictably, therefore, the maximum yields of e_t^- which they find are lower than we have determined here using electron scavenging experiments.

From the difference in G(total radicals), *i.e.* e_t^- + sugar radicals, in the absence of an electron scavenger and G(sugar radicals) determined when an electron scavenger is present ($NaNO_2$ or $FeCl_3$), an estimate of Ge_t^- can be obtained for these irradiated ices over the range of D-glucose concentrations, 20—80% w/w (Figure 3). A maximum yield of e_t^- ($G = 2{\cdot}2$) is found at 60% w/w D-glucose, which decreases slightly to $G = 2{\cdot}0$ at 80% w/w solute. This maximum yield of e_t^- at 60% w/w solute is comparable to the yields of e_t^- found in sodium hydroxide ice[16] and methanol glass.[5] However, it is higher than the values found by Pikaev and his coworkers.[8] ($Ge_t^- = 1{\cdot}5$ for 5M-D-glucose ice) and Zimbrick and Myers[12] ($Ge_t^- = 1{\cdot}8$ for various 3·5—4M-sugar ices) based on photobleaching results. The small decrease in yield we find from 60—80% w/w solute concentration is probably due to a decrease in the number of suitable traps at the higher concentrations.

When H_2SO_4 is added in concentrations sufficient to totally scavenge the electron (<0·8M), the total yield of sugar radicals is identical with the initial e_t^- + sugar radical yields in neutral ices (Figure 3E); a correction was made to allow for the e.s.r. absorption attributable to the paramagnetic species produced by the direct action of radiation on H_2SO_4 in the ice. No change in the e.s.r. spectrum is detectable under these conditions from the spectrum of the sugar radicals evident for neutral ices which had been photobleached to remove e_t^-. There is little doubt, therefore, that the new radicals formed when H_2SO_4 is added are derived from the sugar and not from the H_2SO_4. The yields of these species are accounted for by the mechanism (10)—(12) where ROH_2^+ represents

$$e_m^- + H^+ \longrightarrow H\cdot \qquad (10)$$

$$e_m^- + ROH_2^+ \longrightarrow [ROH_2\cdot] \qquad (11)$$

$$H\cdot + ROH \longrightarrow \cdot R'OH + H_2 \qquad (12)$$

the protonated sugar molecule. The total G(sugar radicals) when H_2SO_4 is added is 4·5 at 60% w/w solute identical to the yield of e_t^- + sugar radicals for neutral ice and thus it is apparent that $Ge_t^- = G$('excess' sugar radicals). The hydrogen atoms produced are thus sufficiently mobile and reactive enough at 77 K to abstract hydrogen atoms from solute molecules in the ice. For γ-irradiated 6M-H_2SO_4 glasses containing propan-2-ol it has been demonstrated[17] that hydrogen atoms produced by reaction (10) react at diffusion controlled rates at 90 K. However, it is not unreasonable to consider that the hydrogen atoms are formed and react at sites suitable for trapping the electron when H_2SO_4 is absent. The increase in G(sugar radicals) with D-glucose concentration during γ-irradiation of these acidic ices (*ca.* 0·8M-H_2SO_4) shows the same trend (see Table) as that found for $G(e_t^-$ + sugar radicals) in neutral sugar ices thus also demonstrating that an increase in 'glassiness' occurs at higher solute concentrations. It is interesting to note that the trapped hydrogen atom (H_t) yield increases with the sulphuric acid content of an aqueous glass[18] and is a maximum for *ca.* 8M-H_2SO_4 glasses. The high yield of H_t was attributed to a greater mobility of electron in the glass compared to a polycrystalline matrix. It is possible to draw an analogy between this system and the one we have investigated here. The yield of 'excess' sugar radicals increases with the increasing 'glassiness' of the matrix (Figure 3F) and exhibits a maximum at 60% w/w solute indicating that this is the concentration at which the hydrogen atom yield is maximal. Even at low solute concentrations the total sugar radical yield is still somewhat larger than when $NaNO_2$ is present indicating that hydrogen atoms react with solute molecules to a small extent here also.

Thus γ-irradiated neutral and acidic sugar ices exhibit

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[18] R. Livingston and A. J. Weinberger, *J. Chem. Phys.*, 1960, **33**, 499.

similar patterns of behaviour when the solute content is increased both manifesting the change in physical state of the matrix.

Optical Absorption of e_t^-.—The optical absorption of e_t^- in the visible region was examined for frozen sugar solutions above 40% w/w solute, for which clear but cracked glasses are formed. The optical absorption maximum of e_t^- observed in these glasses shifts to shorter wavelengths on increasing the carbohydrate concentration and is also linearly dependent on solute in the range 40—80% w/w as illustrated in Figure 4.

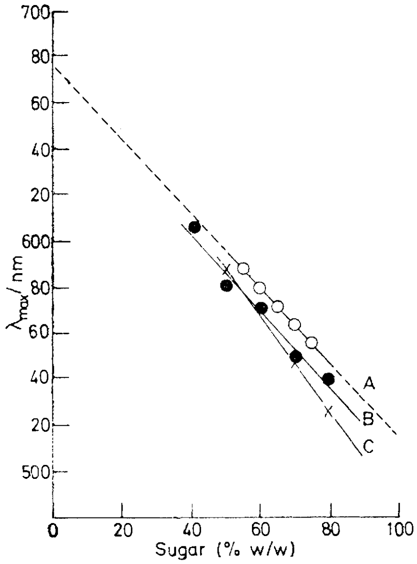

FIGURE 4 Effect of solute concentration on the optical absorption of e_t^- in aqueous carbohydrate ices γ-irradiated at 77 K: A, sucrose, broken line illustrates extrapolation to obtain $\lambda_{max.}$ value at 0 and 100% w/w solute; B, D-glucose; C, D-fructose

Extrapolation to 100% w/w solute gives $\lambda_{max.}$ values of 485, 505, and 516 nm for D-glucose, D-fructose, and sucrose. These values are of theoretical interest only since Pikaev and his co-workers [19] have reported that no trapped electrons are observed in pure glassy sugars irradiated at 77 K. However, they are comparable to $\lambda_{max.}$ observed for other systems where the water content can be varied from 0—100% w/w, and in which e_t^- optical absorption can be observed for 100% w/w solute.[7,20]

Extrapolation to 100% w/w H_2O gives $\lambda_{max.}$ values for glassy ice of 670—690 nm for D-glucose, D-fructose, and sucrose which are somewhat higher than $\lambda_{max.}$ observed for pulse [21] and γ-irradiated [22] crystalline ice.

The thermal decay of e_t^- was followed by recording initially a temperature profile of the decay in the temperature range 77—190 K. From this curve the temperatures at maximum slope of the profile, *i.e.* 140—150 K for D-glucose and D-fructose and 130—150 K for sucrose were selected to study the thermal decay. The e_t^- thermal decay characteristics are similar to those observed for e_t^- in NaOH ice.[23] For D-glucose in the region where e_t^- decay is maximal (149 K) second-order kinetics were observed.

The optical results support the e.s.r. data in that an increase in 'glassiness' occurs above *ca.* 40% w/w D-glucose. No optical absorption can be recorded below this concentration due to the opaque nature of these matrices which normally is indicative of a polycrystalline state. The shift in $\lambda_{max.}$ to shorter wavelengths at higher solute concentrations, however, which indicates a deeper trap, *i.e.* the molecular dipoles oriented more strongly towards the electron, is not completely compatible with the e.s.r. data. No increase in the electron line width is observable with increasing sugar content of the ice which might be expected to be of the order of 1—2 G in view of the trend shown in other systems.[24] Thus if hydroxylic protons on sugar molecules do contribute to the e_t^- line width at higher solute concentration they do not interact more strongly with the electron than protons from water molecules.

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