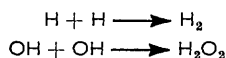


755. *Radiation Chemistry of Carbohydrates. Part XIV.* Mechanism of Degradation of D-Sorbitol during γ -Irradiation in Aqueous Solution.*

By G. O. PHILLIPS and K. W. DAVIES.

Paper chromatographic and radioisotopic methods have been used to examine the γ -radiation degradation of D-sorbitol in oxygen and *in vacuo* under a variety of conditions. Greater degradation occurs at pH 1.4 (initial $-G$ 4.8) than in neutral conditions (initial $-G$ 3.5). This increase is mainly due to an increase in hexose production. The disappearance of D-sorbitol is of first order in solute concentration. The effect of oxygen, variation in pH, solute concentration, and the addition of potassium iodide as a radical scavenger were examined. The results cannot be satisfactorily interpreted solely in terms of H atoms and OH radicals produced by the radiation action on water and point to possible contributions from direct-action type processes at solute concentrations as low as 10^{-2} moles/l.

WATER is decomposed under the influence of ionising radiations to give H, OH, H_2 , and H_2O_2 and solvated electrons. Hydrogen and hydrogen peroxide are thought to result from combination of like radicals in the spurs where the concentration of radicals is high:



By analogy with these reactions the back reaction $H + OH \longrightarrow H_2O$ has also been postulated. In dilute aqueous solutions, therefore, degradation has been attributed to the effects of such reactive species, and on this basis the yields of products would be expected to be independent of solute concentration. For a number of organic solutes such a dependence has not been observed,¹ and furthermore, the actual yields of products cannot be accounted for on the basis of accepted radical yields.² A similar behaviour was encountered during the γ -irradiation of aqueous monosaccharide³ and disaccharide⁴ solutions. Previously, aqueous hexitol solutions were suggested as a suitable dosimeter for ionising radiations, and the products of γ -irradiation *in vacuo* and in oxygen were examined.⁵ Since $-G(\text{D-sorbitol})$ in oxygen and *in vacuo* is greater than $G(\text{OH})$ at the pH's where the experiments were carried out, the results cannot be interpreted solely in terms of the commonly

* Part XIII, *J.*, 1964, 205.

¹ Maxwell, Peterson, and Sharpless, *Rad. Res.*, 1954, **1**, 530; Johnson, Scholes, and Weiss, *Nature*, 1956, **177**, 883; Donaldson and Miller, *Rad. Res.*, 1958, **9**, 487; Allan, Hayon, and Weiss, *J.*, 1959, **3913**; Hayon, *J. Phys. Chem.*, 1961, **65**, 1502.

² Barr and Schuler, *J. Phys. Chem.*, 1959, **63**, 808.

³ Phillips, *Rad. Res.*, 1963, **18**, 446; *Adv. Carbohydrate Chem.*, 1961, **16**, 13.

⁴ Phillips and Davies, Part XIII, *J.*, 1964, 205.

⁵ Phillips and Criddle, *J.*, 1961, 3756, 3763; 1963, 297.

proposed abstraction step invoked generally for alcohols: $\text{D-sorbitol} + \text{OH} \rightarrow \text{sugar radical} + \text{H}_2\text{O}$. A similarity between the degradation of D-sorbitol and aldohexoses is suggested by their identical initial rates of degradation ($-G$ 3.5 at solute concentrations of *ca.* $5 \times 10^{-2}\text{M}$). The mechanistic study reported here is, therefore, relevant to the general behaviour of sugars on γ -irradiation in aqueous solution.

EXPERIMENTAL

The ^{60}Co source and dosimetric and analytical techniques have been described in previous Papers in this Series. The dose rates employed varied between 0.75×10^{19} $\text{ev ml}^{-1} \text{hr}^{-1}$ in the small cells (45 ml.) and 0.84×10^{19} $\text{ev ml}^{-1} \text{hr}^{-1}$ in the large cell (300 ml.). Oxygenated conditions were achieved by continually passing oxygen through the cell during irradiations, and for irradiations *in vacuo*, the solutions were evacuated by the freeze-pump technique, or direct pumping of the solutions while shaking. Since no difference was observed between the two methods, the latter was generally adopted. Gas measurements were carried out in a glass gas burette calibrated to volumes of 1.034, 7.625, and 62.5 ml. A semi-automatic Toepler pump⁶ was used to fill the burette with the gas produced during irradiation. To measure hydrogen, the only gas produced initially, a cupric oxide combustion oven at 320° was used and water, the combustion product, was frozen in a cold trap.

RESULTS

Effect of Solute Concentration.—The concentration of D-sorbitol was varied from $5.24 \times 10^{-4}\text{M}$ to 1.048M , and solutions (300 or 45 ml.) were irradiated to doses of up to 4×10^{19} ev ml^{-1} . Excellent agreement was obtained with both cells.

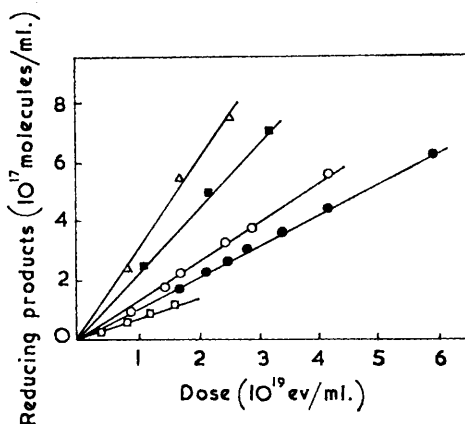


FIG. 1. Formation of reducing products during the γ -irradiation of D-sorbitol solutions in oxygen.

[D-Sorbitol]: \square $5.24 \times 10^{-4}\text{M}$; \bullet $5.24 \times 10^{-3}\text{M}$; \circ $5.24 \times 10^{-2}\text{M}$; \blacksquare $5.24 \times 10^{-1}\text{M}$; \triangle 1.048M .

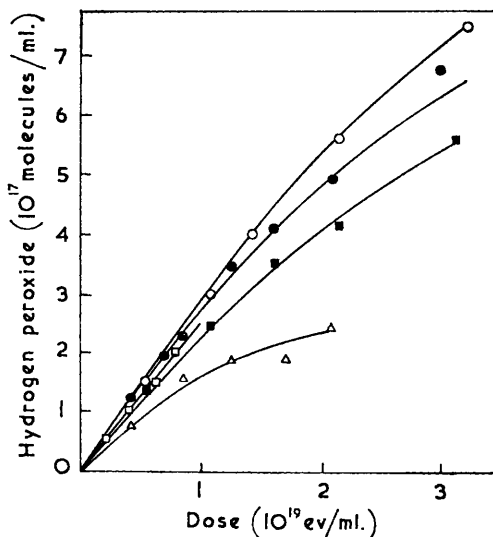


FIG. 2. Formation of hydrogen peroxide during the γ -irradiation of aqueous D-sorbitol solutions in oxygen.

[D-Sorbitol]: \circ $5.24 \times 10^{-4}\text{M}$; \bullet $5.24 \times 10^{-3}\text{M}$; \blacksquare $5.24 \times 10^{-2}\text{M}$; \square $5.25 \times 10^{-1}\text{M}$; \triangle 1.048M .

In oxygen. The dependence of the initial yields of reducing products on solute concentration for solutions, initially at pH 7, is shown in Fig. 1. Throughout this Paper initial G for reducing products is based on the hexose equivalent. During irradiations the pH falls to *ca.* 5. For the dose region studied, all yield-dose curves are linear. Initial formation of hydrogen peroxide at varying D-sorbitol concentration was measured and from the yield-dose curves, in

⁶ LeRoy, *Canad. J. Res.*, 1950, B, 28, 492.

Fig. 2, initial G values were obtained. The variation in initial G with concentration for these processes is in Fig. 3.

In vacuo. Gas analyses revealed that hydrogen is the only significant gaseous product at the low doses used. Reducing-power measurements were taken on the identical solutions used for gas analysis. The yield-dose curves of hydrogen and reducing products at increasing *D*-sorbitol concentrations are in Figs. 4 and 5; Fig. 3 illustrates the dependence of initial G values on *D*-sorbitol concentration.

FIG. 3. Variation of G values of products with *D*-sorbitol concentration.

In vacuo: \triangle Hydrogen
 \bullet Reducing products
In oxygen: \blacktriangle Hydrogen peroxide
 \circ Reducing products

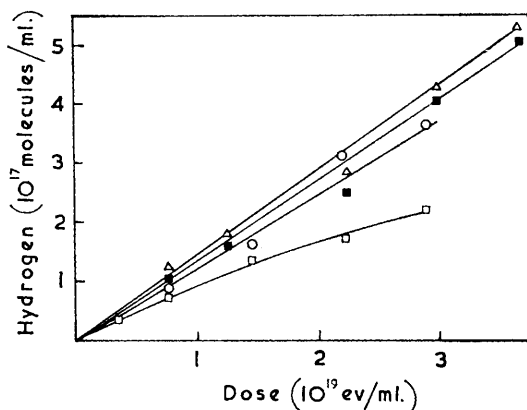
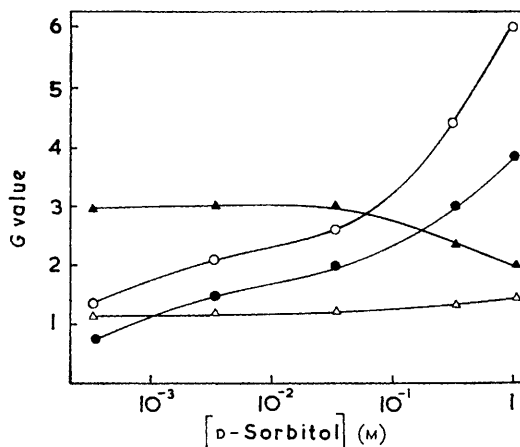


FIG. 4. Formation of hydrogen during γ -irradiation of aqueous *D*-sorbitol solutions *in vacuo*.

[*D*-Sorbitol]: \square 5.24×10^{-4} M;
 \bullet 5.24×10^{-3} M;
 \triangle 5.24×10^{-2} M;
 \blacksquare 5.24×10^{-1} M;
 \triangle 1.048M.

Effect of pH.—The pH of *D*-sorbitol solutions was adjusted to 1.5 with sulphuric acid, and to 12.8 with sodium hydroxide. Untreated *D*-sorbitol solutions have pH 5–7. Acidic solutions were neutralised after irradiation before the measurement of reducing power.

D-Sorbitol in aqueous solution (5.24×10^{-1} M) was irradiated at pH 1.5 and 12.8 to doses of up to 3.65×10^{19} ev ml.⁻¹.

In oxygen, reducing products and hydrogen peroxide were measured and *in vacuo* reducing products and hydrogen. Yield-dose curves are shown in Figs. 6 and 7, and initial G values in Table 1.

Effect of Radical Scavengers.—The effect of adding sodium chloride and potassium iodide as

TABLE 1.

Effect of pH on the initial G of products formed during the irradiation of *D*-sorbitol solutions (5.24×10^{-2} M).

pH	(a) In oxygen			(b) <i>In vacuo</i>		
	1.5	5.7	12.8	Reducing products ...	2.0	0.9
Reducing products ...	2.0	2.6	1.0	Hydrogen	3.7	1.3
Hydrogen peroxide ...	3.5	3.0	3.0			

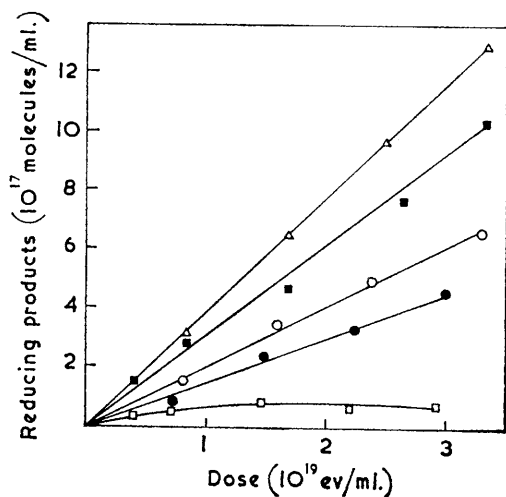


FIG. 5. Formation of reducing products during γ -irradiation of aqueous D-sorbitol solutions *in vacuo*.

[D-Sorbitol]: \square $5.24 \times 10^{-4}\text{M}$;
 \bullet $5.24 \times 10^{-3}\text{M}$;
 \circ $5.24 \times 10^{-2}\text{M}$;
 \blacksquare $5.24 \times 10^{-1}\text{M}$;
 \triangle 1.048M.

FIG. 6. Effect of pH on the formation of reducing products during γ -irradiation of aqueous D-sorbitol solutions *in vacuo* ($5.24 \times 10^{-2}\text{M}$).

In oxygen:

\square pH 1.5
 \triangle pH 12.8

In *vacuo*:

\circ pH 1.5
 \blacktriangle pH 12.8
 \bullet pH 1.5 (+ $1.048 \times 10^{-1}\text{M-NaCl}$)

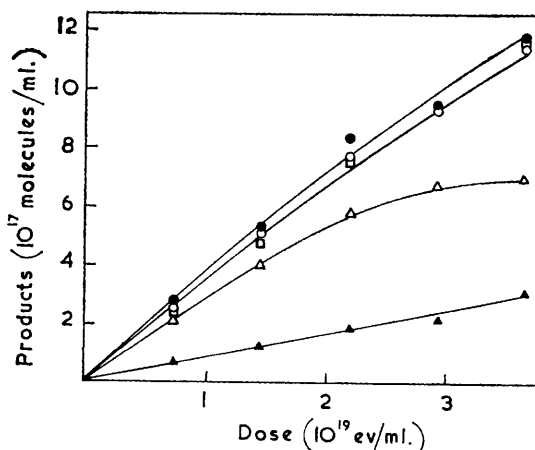
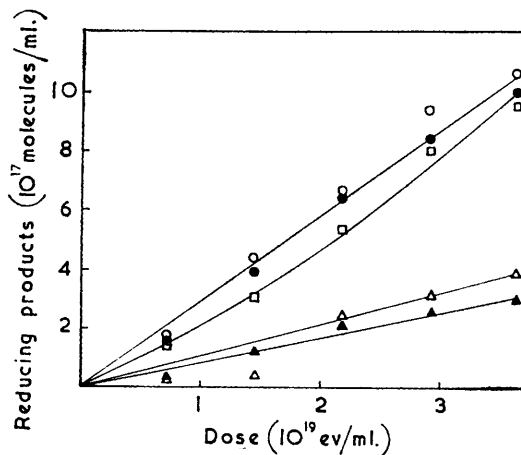


FIG. 7. Effect of pH during the γ -irradiation of aqueous D-sorbitol solutions ($5.24 \times 10^{-2}\text{M}$).

Hydrogen peroxide in oxygen:

\square pH 1.5
 \triangle pH 12.8

Hydrogen *in vacuo*:

\circ pH 1.5
 \blacktriangle pH 12.8
 \bullet pH 1.5 (+ $1.048 \times 10^{-1}\text{M-NaCl}$)

scavengers was examined. The concentration of D-sorbitol was maintained at $5.24 \times 10^{-2}M$ and the concentration of scavenger ion varied.

(a) Sodium chloride at concentrations of 5.24×10^{-2} – $5.24 \times 10^{-1}M$ was added to aqueous D-sorbitol solutions ($5.24 \times 10^{-2}M$) at pH 7, and irradiated *in vacuo* to doses of up to 4.62×10^{19} ev ml.⁻¹. The influence of pH on the formation of products was examined in the presence of sodium chloride. Table 2 summarises the results in terms of the initial *G* values of products, which were in each case calculated from linear yield-dose curves.

(b) Potassium iodide was added to aqueous D-sorbitol solutions ($5.24 \times 10^{-2}M$) and irradiated to doses of 3.65×10^{19} ev ml.⁻¹ in oxygen and *in vacuo*. The initial yields of products calculated from linear yield-dose curves are shown in Table 3. At concentrations higher than $5.24 \times 10^{-2}M$,

TABLE 2.
Effect of sodium chloride on the initial *G* of products formed during the irradiation of aqueous D-sorbitol solutions ($5.24 \times 10^{-2}M$) *in vacuo*.

pH	5–7	5–7	5–7	5–7	1.5	1.5
NaCl ($10^{-2}M$)	0	5.2	10.5	52.4	0	10.5
Reducing products	2.0	2.0	2.0	1.8	3.0	3.0
Hydrogen	1.3				3.7	3.7

potassium iodide interferes with the spectrophotometric estimation of hydrogen peroxide by the titanium sulphate method.

Rate of Formation of Products.—Using paper chromatographic and radioactive tracer methods we could measure the rate of formation of individual products and the $-G$ for D-sorbitol under various conditions of pH and added radical scavengers. A cell was constructed (vol. 25 ml.) which could be used in oxygen or *in vacuo*. The experimental procedure is the same throughout this section. In a typical experiment D-sorbitol solution ($5.24 \times 10^{-2}M$, 25 ml.) containing

TABLE 3.
Effect of potassium iodide on the initial *G* of products formed during irradiation of aqueous D-sorbitol solutions at pH 7.

	Oxygen		<i>In vacuo</i>	
Potassium iodide ($10^{-3}M$)	5.24	52.4	5.24	52.4
Reducing products	1.5	0.2	1.5	0.2
Hydrogen peroxide	1.1			
Hydrogen			1.2	0.7

[¹⁴C]D-sorbitol (20 μc) was irradiated to doses ranging from 0 to 18.0×10^{19} ev ml.⁻¹ at a dose rate of 1.25×10^{17} ev min.⁻¹ ml.⁻¹. Samples (*ca.* 0.25 ml.) were removed at successively increasing doses and aliquot portions (0.05 ml.) were applied to filter paper strips 50 cm. long and 2.75 cm. wide. After irrigation in methyl ethyl ketone-acetic acid-saturated boric acid (9 : 1 : 1) the papers were scanned using an automatic radiochromatogram scanner which was connected to a lead castle housing two Geiger-Müller end window tubes so that both the top and underside of the paper were scanned simultaneously. Thus the formation of products and the rate of degradation of D-sorbitol were measured. Before use all the labelled [¹⁴C]D-sorbitol was purified by two-dimensional paper chromatography and subsequent elution of the [¹⁴C]D-sorbitol spot. This procedure eliminated the considerable quantities of self-decomposition products present. A typical histogram for [¹⁴C]D-sorbitol irradiated *in vacuo* at pH 7 to a dose of 10.5×10^{19} ev ml.⁻¹ is shown in Fig. 8. Dimer (I), D-glucose (II), L-gulose (III), D-sorbitol (IV), and lower-carbon fragments (V) are detectable. At high doses it is possible to detect pentoses also. It is important, therefore, to estimate the products formed at low doses to obtain reliable initial *G* values. The procedure adopted has been described.⁵ Yield-dose curves for the products and D-sorbitol degradation during the irradiation of D-sorbitol solutions ($5.24 \times 10^{-2}M$) *in vacuo* at pH 7 and 1.5 are shown in Figs. 9 and 10. Thereafter, when radical scavengers were added to the reaction, the results are in Table 4, from which yield-dose curves can be obtained and initial *G* values calculated. In the experiments with potassium iodide, hexoses are the only products formed in sufficient quantity to be estimated by the paper chromatographic method. Ultraviolet absorption spectra of irradiated solutions at pH 1.5 containing potassium iodide showed absorption maxima at 290 and 355 mμ, which correspond with spectra of iodine and potassium iodide mixtures in water. The irradiations at pH 7 where potassium iodide was added showed a single absorption maximum at 265 mμ.

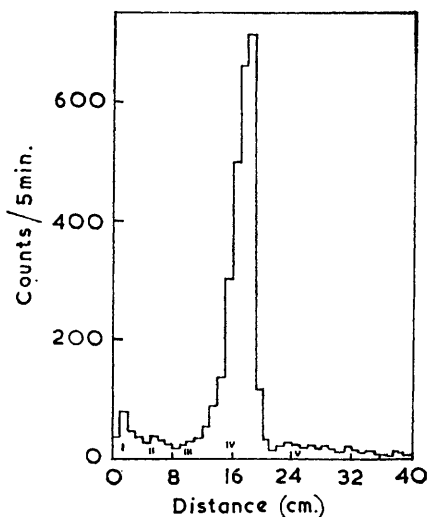


FIG. 8. Typical histogram after γ -irradiation of aqueous $[^{14}\text{C}]$ -D-sorbitol ($5.24 \times 10^{-2}\text{M}$; $20\mu\text{c}$) *in vacuo* at pH 5—7. Dose 10.5×10^{19} ev/ml. I Dimer; II D-Glucose; III L-Gulose; IV D-Sorbitol.

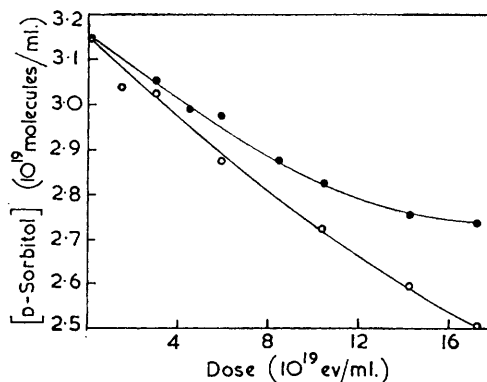


FIG. 9. Effect of pH on the degradation of D-sorbitol on γ -irradiation in aqueous solution ($5.24 \times 10^{-2}\text{M}$) *in vacuo*. ● pH 5—7. ○ pH 1.5.

TABLE 4.

Effect of potassium iodide on the degradation of D-sorbitol ($5.24 \times 10^{-2}\text{M}$) during γ -irradiation.

(a) [KI] $5.24 \times 10^{-2}\text{M}$, pH 7, <i>in vacuo</i> .										
Dose (10^{19} ev/ml.)	0	1.5	3.0	4.5	6.0	8.25	10.5	14.25	18.0	
Hexose (10^{17} molecules/ml.)	0	0.76	2.00	4.2	3.9	6.0	8.5	10.2	14.4	
D-Sorbitol (10^{19} molecules/ml.)	3.156	3.148	3.122		3.100	3.083	3.068	3.043	3.013	
(b) [KI] $5.24 \times 10^{-2}\text{M}$, pH 1.5, <i>in vacuo</i> .										
Dose (10^{19} ev/ml.)	0	1.5	3.0	4.5	6.0	8.25	10.5			
Hexose (10^{17} molecules/ml.)	0	1.0	3.8	5.0	6.2		10.0			
D-Sorbitol (10^{19} molecules/ml.)	3.156	3.140	3.115	3.095	3.080	3.05	3.055			
(c) [KI] $5.24 \times 10^{-2}\text{M}$, pH 7, in oxygen.										
Dose (10^{19} ev/ml.)	0	3.0	6.0	10.5	14.25	18.0				
Hexose (10^{17} molecules/ml.)	0	2.1	5.2	6.4	10.2	12.4				
D-Sorbitol (10^{19} molecules/ml.)	3.156	3.145	3.100	3.080	3.055	3.035				
(d) [KI] $5.24 \times 10^{-2}\text{M}$, pH 1.5 in oxygen.										
Dose (10^{19} ev/ml.)	0	1.5	4.5	6.0	8.25	10.5	14.25	18.0		
Hexose (10^{17} molecules/ml.)	0	1.0	3.0	3.8	4.4	5.8	8.8	9.3		
D-Sorbitol (10^{19} molecules/ml.)	3.156	3.14	3.12	3.11		3.07	3.02	3.01		
(e) [KI] $1.048 \times 10^{-1}\text{M}$, pH 7, in oxygen.										
Dose (10^{19} ev/ml.)	0	1.5	3.0	4.5	6.0	8.25	10.5	14.25	18.0	
D-Sorbitol (10^{19} molecules/ml.)	3.156	3.150	3.146	3.131	3.156	3.151	3.141	3.141	3.146	

TABLE 5.

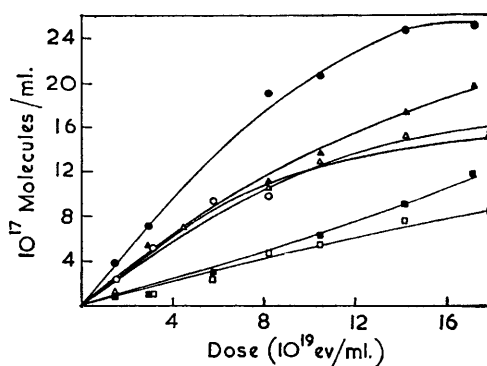
G values for degradation of D-sorbitol ($5.24 \times 10^{-2}\text{M}$) and the products formed in the presence and absence of inorganic salts at pH 7 and 1.5.

Condition	Vac.	Vac.	Vac.	Vac.	Oxygen	Oxygen
pH	7	1.5	7	1.5	7	1.5
KI (10^{-2}M)	—	—	5.24	5.24	5.24	5.24
—G(D-Sorbitol)	3.6	4.8	0.8	1.3	0.7	0.9
G(dimer)	0.5	0.6	—	—	—	—
G(hexose)	1.4	2.4	0.8	1.1	0.7	0.7
G(tetrose)	1.2	1.5	—	—	—	—
G(hydrogen)	1.3	3.7	0.7	—	—	—

Table 5 summarises the results in terms of the initial $-G$ values for D-sorbitol and initial G values of the main products.

FIG. 10. Effect of pH on the formation of products during γ -irradiation of aqueous D-sorbitol solutions ($5.24 \times 10^{-2}M$) *in vacuo*.

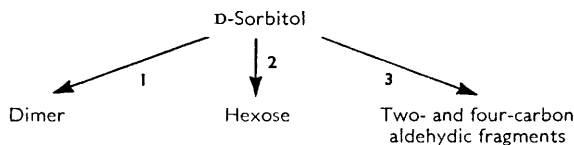
pH.....	1.5	5-7
Dimer	●	□
Hexose	○	○
Tetrose	▲	△



DISCUSSION

The course of the γ -radiation degradation of D-sorbitol has previously been examined under both oxygenated and evacuated conditions.⁵ The paper chromatographic method for measuring rates of product formation adopted here gives identical results with those previously obtained by isotope dilution methods. For example, during irradiation of D-sorbitol solutions *in vacuo* at pH 7, the paper chromatographic method gives $-G(\text{D-sorbitol})$ 3.6 and initial $G(\text{hexose})$ 1.4 compared with corresponding values of 3.5 and 1.4 obtained by isotope dilution.⁵ We therefore generally adopted the less tedious paper-chromatographic method, and when taken in conjunction with measurements of the initial rates of production of reducing products, hydrogen peroxide, and hydrogen, it is possible to examine the course of the radiation degradation of D-sorbitol over a wide variety of conditions.

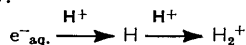
Greater degradation of D-sorbitol occurs at pH 1.5 ($-G$ 4.8) than under neutral conditions ($-G$ 3.6). In acid and neutral solution the disappearance of D-sorbitol is of the first order as may be seen by the linear relationship between $\log[\text{D-sorbitol}]$ and dose and is typical of aqueous sugars on γ -irradiation. This behaviour has previously been considered to arise from competition of the reaction products with the solute for reactive species produced by radiation action.³ The results described here indicate that similar products are formed at pH 1.5 and in neutral conditions, and *in vacuo* the reaction may be represented as annexed:



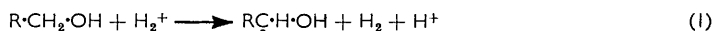
Yield-dose curves for dimer formation, hexose, and four-carbon fragments indicate that reactions (1), (2), and (3) are initial processes; initial G values for each process are shown in Table 5. The greater decomposition at pH 1.5 than at pH 7 may be accounted for almost entirely by an increased production of hexose. Reducing-power measurements confirm this observation (Table 1) and show that, as the pH is increased to 12.8, the yield of hexose is further reduced. This latter behaviour points to the participation of OH radicals in the decomposition at pH 7, a process which may be reduced at pH ~ 12 due to ionisation of the radical $\text{OH} \rightarrow \text{O}^- + \text{H}^+$.

The hydrogen yield is appreciably higher in acid (G 3.7) than in neutral solution (G 1.28) and decreases further as the pH is increased to 12.8 (G 0.8). Such a pH dependence is consistent with the hydrogen atom playing an active part in the decomposition of

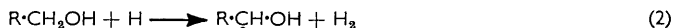
D-sorbitol *in vacuo*. It has been suggested⁷ that the hydrogen atom may exist in three forms which are related as follows:



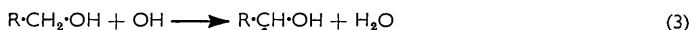
In acid solution, therefore, a possible reaction is



The predicted hydrogen yield at pH 1.5 would, on this basis, be $G_{\text{H}} + G_{\text{H}_2}$ at this pH,² namely 3.95, compared with the experimental value of 3.7. Identical stoichiometry would result from the reaction



For neutral and alkaline solutions, the values given by Allan and Scholes⁸ are generally considered to be reasonably accurate, namely G_{H} 0.6 and $G_{\text{electrons}}$ 2.3. On this basis and reaction (2) the yield of hydrogen at pH 5.7 should approximate to 1.05 which is in fair agreement with the experimental value of 1.25. In neutral solutions, therefore, degradation of D-sorbitol may result from reaction 2 and



To account for the observed $-G(\text{D-sorbitol})$, further reactions which do not lead to the production of hydrogen must be invoked. There are indications that such reactions may be of the direct-action type, which normally would not be expected to be significant at concentrations of *ca.* $5 \times 10^{-2}\text{M}$. Capture of electrons having energies below 5 eV may lead to direct excitation of the D-sorbitol molecule as occurs during photochemical studies on aqueous D-sorbitol solutions.⁹ Here, photons of energies below 5 eV initiate direct photolytic degradation. Sub-excitation electrons of equivalent energies could behave similarly. Evidence that direct capture of solvated electrons by D-sorbitol or other radiolysis products does not occur to any significant extent has recently been obtained using the pulse radiolysis technique.¹⁰

Although reactions are considered here only in terms of the primary alcohol group, it must be pointed out that similar abstraction reactions can also occur elsewhere in the molecule to yield two- and four-carbon fragments.

A limitation in the above postulated mechanism arises at pH 1.5 when reaction of all H atoms and OH radicals would result in $-G(\text{D-sorbitol})$ 6.55 on the currently accepted values of G_{H} and G_{OH} .² However, *in vacuo*, disproportionations of the type



could reduce the experimentally observed $-G$.

As the concentration of D-sorbitol is increased from $5.24 \times 10^{-4}\text{M}$, the initial G for reducing products increases from 0.8 to 3.8. The hydrogen yield, however, under similar circumstances increases only from 1.2 to 1.45. This small increase may be due to the scavenging of more H atoms from the back reaction $\text{H} + \text{OH} \longrightarrow \text{H}_2\text{O}$ at higher concentrations. The effect of concentrations noted also points to the participation of direct action effects. No region was observed where the product yields are independent of solution concentration (Fig. 3).

When iodide ions are present an easy exchange¹¹ occurs with OH radicals:



⁷ Hochenadel, *Rad. Res.*, 1962, **17**, 286; Collinson, Dainton, Smith, and Tazuke, *Proc. Chem. Soc.*, 1962, 140; Matheson, *Ann. Rev. Phys. Chem.*, 1962, **13**, 77; Dainton and Peterson, *Proc. Roy. Soc.*, 1962, *A*, **267**, 443.

⁸ Allen and Scholes, *Nature*, 1960, **187**, 218.

⁹ Phillips and Barber, *J.*, 1963, 3990.

¹⁰ Ebert, Davies, Keene, and Phillips (unpublished results).

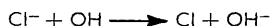
¹¹ Platzman and Hart, "Mechanisms in Radiobiology," ed. M. Errera and A. Forsberg, Academic Press, New York, 1961, Vol. 1, p. 93.

For aqueous D-sorbitol solutions ($5.24 \times 10^{-2}\text{M}$) an equimolar concentration of potassium iodide reduces $-G(\text{D-sorbitol})$ from its original value 3.6 to 0.8 at pH 7 and from 4.8 to 1.3 at pH 1.5. These observations are confirmed by reducing-power measurements since initial $G(\text{reducing products})$ falls from 2 in the absence, to 0.2 in the presence, of $5.24 \times 10^{-2}\text{M}$ -potassium iodide; $5.24 \times 10^{-3}\text{M}$ -potassium iodide reduces the initial G to 1.5. Simultaneously there is a small fall in initial $G(\text{hydrogen})$ from 1.25 to 0.7 at pH 7 with $5.24 \times 10^{-2}\text{M}$ -potassium iodide, while $5.24 \times 10^{-3}\text{M}$ -potassium iodide exerts little or no influence on $G(\text{hydrogen})$.

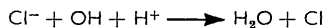
The results indicate competition between D-sorbitol and iodide for hydroxyl radicals. Hummel and Allen¹² showed that OH radicals react faster with ethanol than with bromide ions. It is not, therefore, possible to conclude absolutely that the non-scavengable contributions ($-G$ 0.8 at pH 7 and 1.3 at 1.5) are entirely due to processes which are distinct from those initiated by free-radical attack. However, it is probable that such processes contribute significantly to the radiation decomposition and that such reactions are inhibited also by the presence of potassium iodide, since the decreases in $-G(\text{D-sorbitol})$ at pH 7 and 1.5 on addition of equimolar potassium iodide are greater than G_{OH} at these pH's. When the concentration of potassium iodide is doubled relative to D-sorbitol, the degradation is reduced to undetectable proportions. It is possible, therefore, that direct-action processes are mainly responsible for the non-scavengable reaction at equimolar iodide-sugar mixtures.

The reduction in hydrogen yield at pH 7 by potassium iodide is also dependent on iodide concentration. Reactions have been postulated in photochemical studies which may be responsible for this behaviour.¹³⁻¹⁵

A noteworthy observation is the absence of any significant effect of chloride ions on the yields of products. In neutral solution this behaviour could be predicted since the neutral reaction



is endothermic. However, the reaction



is exothermic,¹⁶ but is clearly less favourable than reaction of the OH radical with D-sorbitol.

A mechanism for the γ -radiation degradation of D-sorbitol solutions in oxygen has been advanced previously.⁵ As for irradiations *in vacuo*, $-G(\text{D-sorbitol})$ is greater than G_{OH} . D-Sorbitol may compete effectively with oxygen for hydrogen atoms as in the case of ethanol solutions.¹² Alternatively, direct-action effects may participate as suggested previously.⁵ At $5.24 \times 10^{-2}\text{M}$ -D-sorbitol, $G(\text{H}_2\text{O}_2)$ at pH 1.5 and 7 is consistent with the previously suggested mechanism of hexose formation⁵ and equal to $G_{\text{H}_2\text{O}_2} + 0.5 G_{\text{OH}}$. The hexose yield (G 2.4) also agrees with G_{OH} as required by the mechanism. The increase in yields of products with increasing D-sorbitol concentration is accompanied by a decrease in yield of hydrogen peroxide. This behaviour is also consistent with the competition reaction of solute and H for O_2 as outlined above. Another possibility is that D-sorbitol at high concentration may scavenge OH radicals from the spur, which might otherwise lead to the production of molecular hydrogen peroxide.

Summarising, it is clear that simple radical mechanisms do not satisfactorily account for all the features of the γ -radiation degradation of D-sorbitol in aqueous solutions which are reported here. The results indicate that there may be significant contributions from direct

¹² Hummel and Allen, *Rad. Res.*, 1962, **17**, 310.

¹³ Grossweiner and Matheson, *J. Phys. Chem.*, 1957, **61**, 1089; Edgecombe and Norrish, *Proc. Roy. Soc.*, 1959, *A*, **253**, 154.

¹⁴ Hayon, *J. Phys. Chem.*, 1961, **65**, 1937.

¹⁵ Jostner, Levine, Ottolenghi, and Stein, *J. Phys. Chem.*, 1961, **65**, 1232.

¹⁶ Allen, "Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand Co. Ltd., Princeton, New Jersey, 1961, p. 63.

action type processes, even in solution of $5 \times 10^{-2}\text{M}$, and which increase in importance at higher solute concentrations. The species which might account for this behaviour may be electrons having energies below the first excitation level of water

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UNIVERSITY COLLEGE, CATHAYS PARK, CARDIFF.

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