730. *Radiation Chemistry of Carbohydrates. Part VIII.*[1] *Action of γ-Radiation on Deaerated Solutions of* D-*Sorbitol.*

By G. O. Phillips and W. J. Criddle.

D-Glucose, L-gulose, D-arabinose, L-xylose, two-, three-, and four-carbon aldehydic fragments, and gluconic acid were identified and estimated by paper-chromatographic and radioactive-tracer methods in deaerated solutions of D-sorbitol after γ-irradiation. The gas released during irradiation is mainly hydrogen at low doses, but at higher doses carbon dioxide and carbon monoxide are also produced. After prolonged irradiation a polymer was isolated, and attempts have been made to elucidate the nature of the initial dimerisation which leads to polymer formation.

The following primary degradation processes have been distinguished from the yield–dose curves of the main products: (*a*) oxidation at the primary alcohol groups to give the corresponding hexoses, (*b*) scission of the molecule between $C_{(2)}$ and $C_{(3)}$ and between $C_{(4)}$ and $C_{(5)}$ to give two- and four-carbon aldehydic fragments, and (*c*) dimerisation of radicals of the type R·CH(OH)· produced by hydrogen abstraction at the primary alcohol groups. Hexonic acids, pentoses, and polymer are formed by secondary processes.

Changes in acidity, ultraviolet absorption spectra, and formation of hydrogen peroxide were also measured.

Previous papers in this series have considered the effect of ionising radiations on oxygenated solutions of carbohydrates. Throughout the investigations dilute solutions were used, and the energy of the radiation was absorbed almost exclusively by the water. Therefore chemical changes are initiated by the reactive species produced during primary radiolysis of the water. Ionisation and excitation of the water molecule through the agency of γ-radiation leads to the formation of hydrogen atoms and hydroxyl radicals.[2] In oxygen the initial step, $H_2O \rightsquigarrow H + OH$, is followed by $H + O_2 \longrightarrow HO_2$. Secondary reactions may also be initiated in oxygen as a result of peroxy-radical formation with sugar radicals formed by initial abstraction processes: $R\cdot + O_2 \longrightarrow RO_2\cdot$. Thus, in the absence of oxygen, chemical changes observed during irradiation of dilute carbohydrate solutions are initiated in the main by hydrogen atoms and hydroxyl radicals only, and may be expected to provide a simpler system for mechanistic studies. The nature of the chemical changes may therefore be considerably modified by presence of oxygen. This study of the effects of γ-radiation on evacuated D-sorbitol solutions, following out work on the corresponding oxygenating system,[1] is an attempt to evaluate the influence of oxygen on the chemical changes and mechanism of the degradation. In both investigations conditions have been maintained strictly oxygenated or evacuated throughout any particular irradiation. This factor is emphasised since investigations have been carried out utilising air-equilibrated solutions at doses which probably lead to oxygen depletion during the irradiation.[3] These conditions, therefore, provide neither an oxygenated nor an evacuated system and may be difficult to reproduce. As far as we are aware, no previous study of the effect of ionising radiation on evacuated D-sorbitol solutions has been reported.

Results and Experimental

The ^{60}Co source and experimental techniques are similar to those described previously.[4] The dose rates employed were 1·0 and 1·66 × 10^{17} ev min.$^{-1}$ ml.$^{-1}$ in the small cells (50 ml.) and 1·54 × 10^{17} ev min.$^{-1}$ ml.$^{-1}$ for the large cell (100 ml.). Before irradiation, the solutions were

[1] Part VII, preceding paper.
[2] Dainton, *Radiation Res.*, 1951, Suppl. 1, 1.
[3] Bothner-by and Balazs, *Radiation Res.*, 1957, **6**, 302.
[4] Phillips, Moody, and Mattok, *J.*, 1958, 3522.

evacuated by repeated pumping of the solutions directly and sealing the evacuated cells. The freeze-pump technique was also employed, but no differences were observed in the results of the two methods. To the large cell, a long curved arm was attached to which a number of sampling tubes were sealed. By using this modified cell it was possible to fill individual sampling tubes with irradiated solution at successively increasing doses without releasing the internal pressure of the cell and introducing oxygen. The individual sampling tubes containing irradiated solution were removed by sealing them under the vacuum.

TABLE 1. *Constituents present in* D-*sorbitol solutions irradiated* in vacuo.

(*a*) Butan-1-ol–acetic acid–water.

Autoradiographs	IV	V	VI	VII	VIII
R_F	0·18	0·21	0·24	0·28	0·43
Colour	Brown	Brown	Pink	Pink	Yellow
Constituent	Glucose + D-sorbitol	Gulose	Arabinose	Xylose	Tetroses

(*b*) Ethyl methyl ketone–saturated boric acid–acetic acid.

R_G	1·0	1·3	1·5	1·9	2·4
Colour	Brown	Brown	Pink	Pink	Yellow
Constituent	Glucose	Gulose	Arabinose	Xylose + D-sorbitol	Tetroses

FIG. 1. *Density of spots on autoradiograph, giving a measure of* ^{14}C *concentration along chromatograms.*

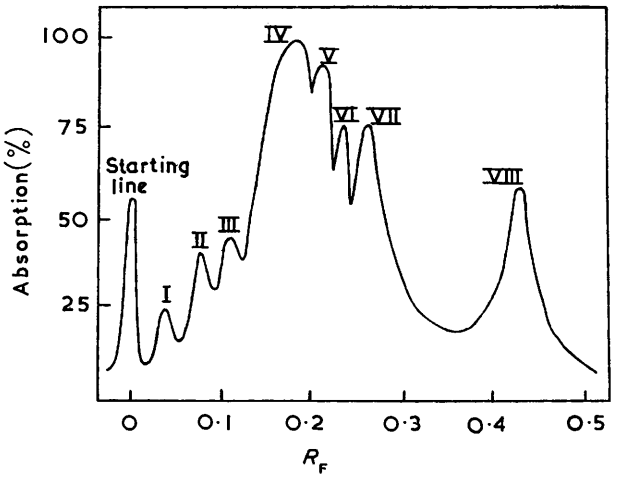
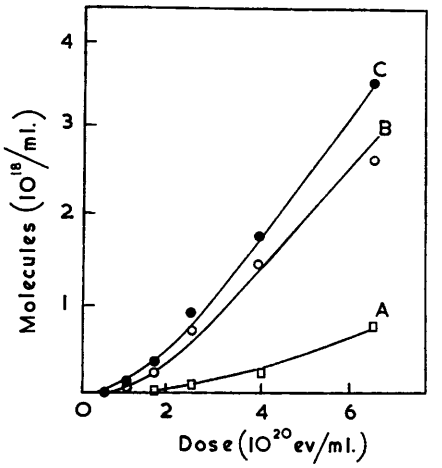


FIG. 2. *Acid formation during irradiation of deaerated solutions of* D-*sorbitol.*



A, *Volatile acid.* B, *Non-volatile acid.* C, *Total acid.*

Chromatographic Analysis of the Irradiated Solution.—A solution of D-sorbitol (5·49 millimoles) in water (100 ml.) was evacuated and irradiated to a total energy input of $7·2 \times 10^{22}$ ev and chromatographed in butan-1-ol acetic acid–water (4 : 1 : 5) and ethyl methyl ketone–saturated boric acid–acetic acid (9 : 1 : 1). The organic constituents detected in the irradiated solutions are shown in Table 1.

The presence of formic acid in the irradiated solution was detected as described in the previous paper. The distillate from the irradiated solution was treated with aqueous ammonia and ammonium formate and identified by paper chromatography with the irrigant 95% ethanol–concentrated aqueous ammonia (100 : 1).

A solution (100 ml.) of D-sorbitol (5·5 millimoles) containing *ca.* 25 μc of D-[^{14}C]sorbitol was irradiated to a total energy input of $8·4 \times 10^{22}$ ev. After chromatography in butan-1-ol–acetic acid–water, the autoradiograph was scanned with a Hilger photoelectric densitometer, and Fig. 1 shows the relative concentration of ^{14}C along the paper chromatogram. Constituents I, II, and III were not detected with *p*-anisidine, and are therefore non-reducing.

Acid Formation.—The formation of total acid, volatile acid, and non-volatile acid with

increasing dose is shown in Fig. 2. Volatile acid was estimated in the distillate after distillation of the irradiated solution at reduced pressure, and the non-volatile acid in the remainder. Titrations were carried out potentiometrically.

Absorption Spectra of Irradiated Solutions.—The ultraviolet absorption spectrum of a solution of D-sorbitol (5×10^{-2}M) before and after irradiation to an energy input of $7{\cdot}2 \times 10^{22}$ ev is shown in Fig. 3. It shows a characteristic absorption at 265 mμ, which is modified in position and intensity by the addition of acid and alkali.

TABLE 2. *Formation of hydrogen peroxide during the irradiation of evacuated* D-*sorbitol solutions.*

Dose (10^{19} ev ml.$^{-1}$)	0·4	1·0	1·5	2·0	2·5	3·4	4·4	5·0
H_2O_2 (10^{17} molecules ml.$^{-1}$) ...	0·25	0·4	0·55	0·9	1·0	1·25	1·7	1·9

Formation of Hydrogen Peroxide.—The rate of formation of hydrogen peroxide is shown in Table 2. Initial $G(H_2O_2)$ is 0·3—0·4.

FIG. 3. *Ultraviolet absorption spectra of*: (A) *unirradiated* D-*sorbitol*; (B) *polymer formed during irradiation in* H_2O; (C) *as* (B) *but with added* $KHCO_3$; (D) D-*sorbitol after energy input of* $7{\cdot}2 \times 10^{22}$ ev (100 ml.); (E) *as* (D) *but with added acid*; (F) *as* (D) *but with added* $KHCO_3$.

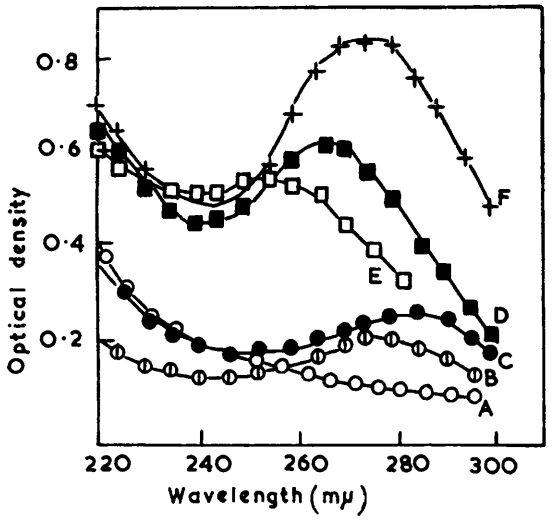
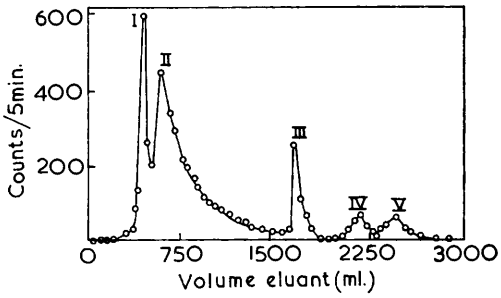


FIG. 4. *Separation of irradiation products on a charcoal–Celite column.*[5]



Gaseous Products.—Three solutions of D-sorbitol, each containing 1·37 millimoles in water (25 ml.), were deaerated in the small cells and irradiated to doses of 2·4, 4·8, and $7{\cdot}2 \times 10^{20}$ ev ml.$^{-1}$, severally. Each cell after irradiation was attached to a gas-line, and by using a break-seal the gases produced were expanded into an evacuated system of known volume. The quantity of gas produced was determined by direct pressure measurement at room temperature (21°). A known volume of gas was measured in a gas-burette and analysed. First, the gas was expanded through a system cooled in solid carbon dioxide–acetone, and the amount of water vapour present measured by the fall in pressure. All the measurements were corrected to constant temperature (21°). Expansion through a system cooled in liquid air gave a measure of the carbon dioxide formed. The hydrogen was converted into water, and carbon monoxide into carbon dioxide by passing the remaining gas over cupric oxide at 320°. Both these products were measured as described, providing a measure of the hydrogen and carbon monoxide content of the gas. A small amount of non-combustible gas remained, but was less than 2% of the total gas pressure of the original system. The results, shown in Table 3, indicate that the gas released during irradiation is mainly hydrogen. Carbon monoxide and carbon dioxide are formed in small amount only. On the basis of the results shown in Table 3 initial *G*(hydrogen) is *ca.* 1·0.

Polymer Formation.—When evacuated D-sorbitol solutions are irradiated to high doses, a polymer is formed. A typical experiment which led to this observation and enabled the polymer to be isolated is as follows: A solution of D-sorbitol (5·50 millimoles) in water (100 ml.) was evacuated and irradiated to a total energy input of $2·2 \times 10^{23}$ ev. The resulting yellow solution was dialysed for 6 days in a stream of water. Freeze-drying the solution remaining

TABLE 3. *Analysis of the gas formed during irradiation of evacuated* D-*sorbitol solutions.*

Volume of gas in cell 90·0 ml.

Dose	Pressure (mm. Hg)						H_2
(10^{20} ev ml.$^{-1}$)	Total	H_2	CO	CO_2	H_2O	Non-combustible	(10^{18} molecules ml.$^{-1}$)
2·4	22·8	19·0	1·8	—	1·8	0·2	2·2
4·8	30·8	25·5	2·2	—	2·0	0·3	3·4
7·2	45·0	36·9	2·5	3·1	2·1	0·4	4·4

after dialysis afforded a light fibrous solid, which is exceptionally soluble and is acidic in water. Chromatography in butan-1-ol–acetic acid–water showed that one component was present, which did not move and could readily be detected with alkaline silver nitrate. The ultraviolet absorption spectrum of the polymer in aqueous solution is shown in Fig. 3. Addition of alkali only slightly modifies the spectrum. For an energy input of $2·2 \times 10^{23}$ ev, the polymer accounted for *ca.* 25% of the initial D-sorbitol.

Dimer Formation.—D-Sorbitol (1·37 millimoles) in water (25 ml.) containing *ca.* 6—7 μc of D-[^{14}C]sorbitol was evacuated, sealed, and irradiated to a dose of $7·2 \times 10^{20}$ ev ml.$^{-1}$. The mono- and di-saccharide constituents in the irradiated solution were separated by chromatography on a charcoal–Celite column.[5] The eluate was monitored for radioactivity, and in this way individual sugar fractions which separated on the column were conveniently detected. A small amount of suction was applied to increase the rate of flow through the column. After elution with water (1·5 l.), the column was eluted with ethanol (1·0 l.), and constant volumes (30 ml.) were collected. Thin layers of each fraction were counted directly by using a thin-window Geiger–Müller tube. After a small correction had been applied for the relative absorption of β-particles by 5% aqueous ethanol and water, the separation shown in Fig. 4 was obtained, indicating five components. Examination of the fractions by paper chromatography showed that fractions I, II, and III contained the major part of the monosaccharide products, while IV and V contained a neutral disaccharide as indicated by chromatography in acidic and basic irrigants (R_F 0·09). By counting paper chromatograms directly we estimate that ~50% of the activity represented by peaks IV and V is due to the disaccharide. Thus, if it is assumed that the total activity in the eluate, represented by the area under the curve in Fig. 4, is proportional to the initial D-sorbitol concentration, an approximate value (0·03 millimole) for the concentration of the disaccharide may be obtained. This value is tentative, and further investigations are in progress to measure accurately the disaccharide concentration.

Estimation of Products by the Isotope Dilution Method.—The main products, D-glucose, D-gluconic acid, D-glucuronic acid, D-arabinose, L-xylose, D-xylose, three-carbon and two-carbon aldehydic fragments, oxalic acid, and unchanged D-sorbitol were estimated by application of isotope dilution analysis directly to the untreated irradiated solutions as described in the previous paper. Table 4 shows the yields of products at two energy inputs ($6·4 \times 10^{22}$ and $2·2 \times 10^{23}$ ev) for evacuated D-sorbitol solutions (100 ml.).

Rate of Formation of Products.—A solution of D-sorbitol (5·49 millimoles) in water (100 ml.) containing *ca.* 25 μc of D-[^{14}C]sorbitol was evacuated and irradiated in the large cell which had been modified to enable small samples to be withdrawn at successively increasing doses without release of the pressure. Accurately known amounts (0·5 ml.) of the irradiated solution were chromatographed in two irrigants after increasing doses, and the radioactivities of the spots were measured. In butan-1-ol–acetic acid–water it was possible to isolate gulose, arabinose, xylose, and tetroses as discrete spots; in ethyl methyl ketone–saturated boric acid–acetic acid gulose, glucose, arabinose, and the tetroses ran independently. Thus, by using the two irrigants, it was possible to obtain yield–dose curves for glucose, gulose, arabinose, xylose, and the tetroses. By difference the rate of disappearance of D-sorbitol was also measured and the results are shown in Fig. 5. At high doses, it is probable that some 2-oxo-D-*arabino*-aldohexose (glucosone)

[5] Whistler and Durso, *Amer. Chem. Soc.*, 1950, **72**, 677.

and 2-oxo-L-*xylo*-aldohexose are formed by secondary degradation of D-glucose and L-gulose respectively. These products run identically with the corresponding hexoses in butan-1-ol–acetic acid–water and would therefore lead to rather high values for glucose and gulose at high doses. The initial yields from paper chromatography, however, should not be affected. The rate of polymer formation was estimated by measuring the radioactivity which remained on the starting line at increasing doses (Fig. 5).

In order that accurate initial *G* values could be evaluated, and the accuracy of the paper-chromatographic method of obtaining yield–dose curves verified, D-glucose, D-gluconic acid,

TABLE 4. *Products when aqueous* D-*sorbitol is irradiated with γ-radiation* in vacuo.

(a) *Initial* D-*sorbitol* 5·40 *millimoles. Energy input* 6·4 × 10^{22} ev (vol. 100 ml.).

Product	D-Sorbitol	D-Glucose *c*	D-Glucose *d*	D-Gluconic acid	D-Glucuronic acid	D-Arabinose
Carrier (millimoles)	1·00	1·10	1·00	1·02	1·00	1·00
Spec. activity (μc/millimole)	0·32	0·032	0·051	0·025	—	0·018
Yield (millimole) ...	2·00	0·21	0·30	0·14	—	0·12

Product	L-Xylose	D-Xylose	Three-carbon fragments	Two-carbon fragments	Oxalic acid
Carrier (millimoles)	0·95	1·03	0·90	2·00	2·00
Spec. activity (μc/millimole)	0·020	—	0·005	0·015	0·003
Yield (millimole) ...	0·13	—	0·05	0·50	0·14

Tetroses estimated from paper chromatography 0·37 millimole. Formic acid determined as volatile acid by titration 0·13 millimole.

(b) *Initial* D-*sorbitol* 5·52 millimoles. *Energy input* 2·2 × 10^{23} ev (vol. 100 ml.).

Product	D-Sorbitol	D-Glucose	D-Gluconic acid	D-Glucuronic acid	D-Arabinose
Carrier (millimoles)	1·20	1·00 [c]	0·98	1·00	1·10
Spec. activity (μc/millimole)	0·039	0·024	0·047	—	0·020
Yield (millimole) ...	0·25	0·13	0·26	—	0·14

Product	L-Xylose	Three-carbon fragment	Two-carbon fragment	Oxalic acid
Carrier (millimoles)	1·08	1·00	2·00	2·00
Spec. activity (μc/millimole)	0·021	0·009	0·004	0·004
Yield (millimole) ...	0·14	0·10	0·13	0·13

Tetroses estimated from paper chromatography 0·25 millimole. Polymer (% of initial D-sorbitol by weight) (*a*) 4·6, (*b*) 25·5.

[c] As penta-*O*-acetate. [d] As glucosazone.

D-arabinose, and two-carbon aldehydic fragments were determined by isotope dilution analysis at four doses, 0·5, 1·0, 1·6, and 2·5 × 10^{20} ev ml.$^{-1}$. The yield–dose curves obtained are shown in Fig. 6; the rate of disappearance of D-sorbitol was also measured.

In an independent series of experiments, the initial rate for formation of glycollaldehyde was measured so that a distinction could be drawn between total two-carbon aldehydic fragments and glycollaldehyde originating only by scission of the two carbon atoms at each end of the molecule. For isotope dilution estimations the 2,4-dinitrophenylhydrazone was prepared, which is a specific derivative for glycollaldehyde. A typical estimation is as follows: A solution of D-sorbitol (1·37 millimoles) in water (30 ml.) was evacuated and irradiated to a dose of 0·5 × 10^{20} ev ml.$^{-1}$. The irradiated solution (5 ml.) with specific activity 4·2 μc of D-[^{14}C]sorbitol per millimole was treated with carrier glycollaldehyde (0·5 millimole) and a saturated solution of 2,4-dinitrophenylhydrazine (10 ml.) in 2% sulphuric acid.[6] The solid which separated was recrystallised eight times from ethyl acetate, to give the pure derivative, m. p. 155°, constant spec. activity 0·011 μc millimole. This corresponded to 0·024 millimole of glycollaldehyde.

From the yield–dose curves initial *G* values for the primary products may be quoted.

[6] Collatz and Neuberg, *Biochem. Z.*, 1932, **255**, 27.

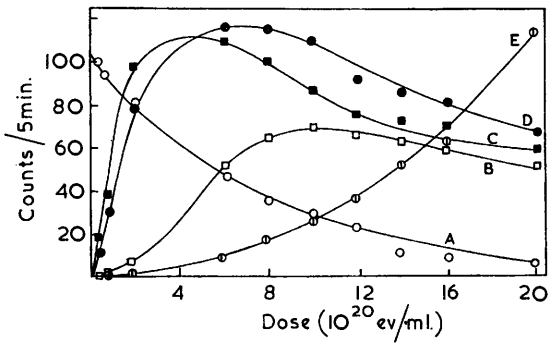
Initial G values calculated from isotope dilution measurements are as follows: $-G$(D-sorbitol) 3·5; G(individual hexoses) 0·7; G(glycollaldehyde) 1·0; G(two-carbon aldehydic fragments) 1·3.

Discussion

During γ-irradiation of evacuated D-sorbitol solutions there is preferential attack at the primary alcohol groups, and in this respect evacuated solutions resemble oxygenated D-sorbitol. Glucose, gulose, xylose, arabinose, and tetrose fragments were detected by paper chromatography in D-sorbitol solutions irradiated *in vacuo*. Isotope dilution confirmed, as in oxygen, that the isomers present are D-glucose, D-arabinose, and L-gulose. Thus, on configurational grounds, it is probable that gulose is present as the L-isomer, and that the tetroses are D-erythrose and L-threose. Isotope dilution analysis revealed the accompanying formation of two-carbon aldehydic fragments and, by utilising a derivative for glycollaldehyde, a distinction may be drawn between this product and other two-carbon fragments present. The results indicate that glycollaldehyde comprises 77% of the two-carbon fragments formed initially.

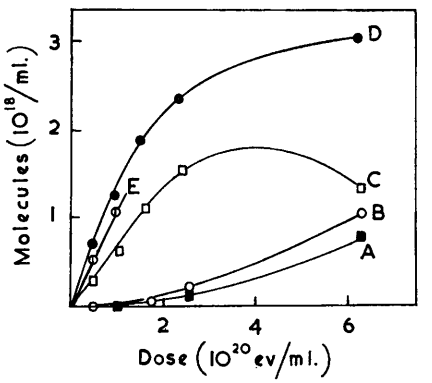
Primary and secondary processes may be identified by reference to the yield–dose curves of the main products. Hexose formation is a primary process (Figs. 5 and 6). Initial

FIG. 5. *Formation of products during irradiation of deaerated solutions of* D-*sorbitol, determined by paper chromatography.*



(A) D-*Sorbitol* ($\times 10^{-1}$). (B) *Pentoses.* (C) *Tetroses.* (D) *Hexoses.* (E) *Polymer* ($\times 0{\cdot}2$).

FIG. 6. *Formation of products, as for* Fig. 5, *but determined by isotope dilution analysis.*

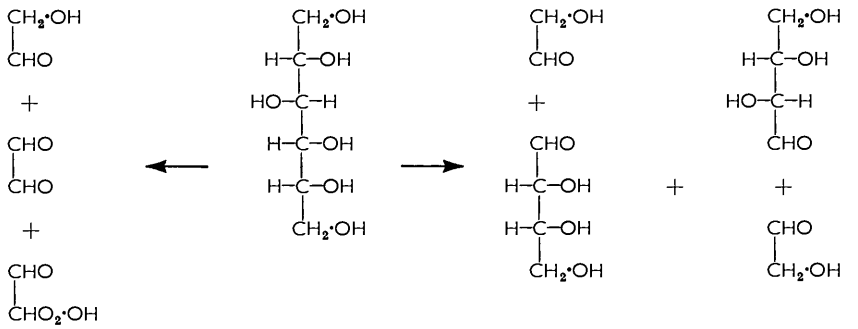


(A) D-*Arabinose.* (B) D-*Gluconic acid.* (C) D-*Glucose.* (D) *Two-carbon aldehydic fragments.* (E) *Glycollaldehyde.*

G(D-glucose) is 0·7, and since both hexoses are formed at identical rates (Fig. 5) initial G(L-gulose) is also 0·7. For the rate of disappearance of D-sorbitol, initial G is 3·5, which is equal to initial $-G$(D-sorbitol) in oxygen.. As in oxygen, pentose formation *in vacuo* is a secondary process (Figs. 5 and 6), the rate of formation increasing appreciably only when appreciable hexose concentrations are present. Similarly, gluconic acid and glucosone arise by secondary processes (Fig. 5). The rate of acid formation at low doses is negligible (Fig. 2) and, *in vacuo*, therefore, it appears that the direct conversion $R{\cdot}CH_2{\cdot}OH \longrightarrow R{\cdot}CO_2H$, encountered in oxygen, does not take place to any appreciable extent.

Chain scission appears to be more significant during irradiations *in vacuo* than in oxygen. Two- and four-carbon aldehydic fragments are formed by primary processes (Figs. 5 and 6). From paper-chromatogram measurements initial G(tetrose) is 0·9; isotope dilution analysis gives initial G(two-carbon aldehydic fragments) 1·3 and for glycollaldehyde, also a primary product, initial G 1·0. The dominating primary scission occurs, therefore, between $C_{(2)}$ and $C_{(3)}$ and between $C_{(4)}$ and $C_{(5)}$, with accompanying formation of D-erythrose and L-threose. The somewhat higher yield of two-carbon fragments in relation to glycollaldehyde may be an indication that a small amount of

symmetrical scission to give three two-carbon fragments also occurs. These scission processes are as illustrated.



There is appreciable evidence from investigations in allied fields [7] that hydroxyl radicals formed during primary radiolysis of water may initiate reaction at primary alcohol groups through primary abstraction processes of the type: $OH + R{\cdot}CH_2{\cdot}OH \longrightarrow R{\cdot}CH(OH){\cdot} + H_2O$. *In vacuo*, hydrogen atoms may be expected to react with equal facility, $H + R{\cdot}CH_2{\cdot}OH \longrightarrow R{\cdot}CH(OH){\cdot} + H_2$. Such abstraction processes are consistent with our results for the irradiation of D-sorbitol solutions in oxygen and *in vacuo*. The gas released during irradiations *in vacuo* is almost exclusively hydrogen, and it is only at high doses that smaller amounts of carbon dioxide and carbon monoxide are produced, probably as a result of secondary decarboxylation. Hydrogen is formed by a primary process with initial $G \sim 1$ (Table 3). Since truly primary reactions, in terms of the initial radicals formed, are now being considered, it is important that a clear distinction be drawn between the initial products detectable by our methods and the primary radicals which give rise to these products. For example, hexoses, the primary products detected during the irradiation of D-sorbitol solutions *in vacuo* and in oxygen may arise from the primary radicals $R{\cdot}CH(OH){\cdot}$ by reactions of the type annexed.

In vacuo $R{\cdot}CH(OH){\cdot} + OH \longrightarrow R{\cdot}CH(OH)_2 \longrightarrow R{\cdot}CHO$

In oxygen $R{\cdot}CH(OH){\cdot} + O_2 \longrightarrow R{\cdot}CH(OH){\cdot}O_2{\cdot}$

$H + O_2 \longrightarrow HO_2$

$R{\cdot}CH(OH){\cdot}O{\cdot} + HO_2 \longrightarrow R{\cdot}CHO + H_2O_2 + O_2$

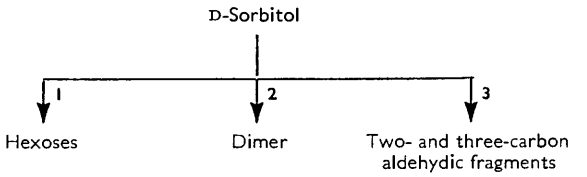
Therefore, in view of the similarity in the primary abstraction processes, an interpretation for the difference in the products formed during irradiation of D-sorbitol solutions in oxygen and *in vacuo* must be sought in terms of the subsequent fate of $R{\cdot}CH(OH){\cdot}$ radicals under both conditions. It is significant that the yield of individual hexoses is lower *in vacuo* (initial G 0·7) than in oxygen (initial G 1·1). A fate must, therefore, await the $R{\cdot}CH(OH){\cdot}$ radicals in the absence of oxygen other than that leading to hexose. We consider that these radicals may also dimerise to form a disaccharide, a reaction comparable with glycol formation during the irradiation of alcohols in the absence of oxygen: [8] $2R{\cdot}CH(OH){\cdot} \longrightarrow [R{\cdot}CH(OH)-]_2$.

It was to establish whether this process occurs that dimers were sought in the irradiated solution. Paper chromatography revealed a neutral component in the same position as a disaccharide, and this dimer can be separated from the irradiated solution by chromatography on a charcoal–Celite column.[5] Our estimation of dimer concentration is too inaccurate to allow an initial G value to be quoted. Nevertheless, on the basis of

[7] Garrison, *Ann. Rev. Phys. Chem.*, 1957, **8**, 129; Jayson, Scholes, and Weiss, *J.*, 1957, 1358.
[8] Swallow, *Biochem. J.*, 1953, **54**, 253; Baxendale, *Trans. Faraday Soc.*, 1960, **56**, 37.

the single estimation, it appears that the dimer is present in amounts comparable to those of the hexoses. After high doses a polymer was recovered from the irradiated solution, and the yield–dose curve (Fig. 5) shows that it is formed only slowly at low doses. Consequently, experiments to separate the dimer were conducted at doses unlikely to yield significant amounts of polymer. If dimerisation is regarded as the initial step in polymer formation, then further polymerisation probably arises by the random coupling of sugar radicals formed by the action of hydroxyl radicals and hydrogen atoms on organic constituents. When only pure solute is present, the initial coupling process is not complicated and leads only to the dimer. However, as the constituents in the irradiated solution increase in number and complexity, so will the structure of the polymer. Barker, Grant, Stacey, and Ward [9] have already observed that acidic polymers formed on prolonged irradiation of maltose, glucose, glucono-1,4-lactone, lactic acid, glycollic acid, and amino-acid solutions *in vacuo*. Further, the polymers show considerable similarity. It is also significant that in no instance has a polymer been isolated in oxygen. This is consistent with the previously mentioned secondary combination of oxygen with initially formed sugar radicals to form intermediate peroxy-radicals.

After the primary abstractions by hydroxyl radicals and hydrogen atoms, three initial degradation processes are indicated by our results for the irradiation of D-sorbitol solutions *in vacuo:*



Reactions 1 and 3 account for initial G 2·7, which may be compared with $-G$(D-sorbitol) 3·5. There is some evidence that dimerisation may account for the remaining degradative processes. If, as is probable, the difference between total G(hexose) *in vacuo* (1·4) and in oxygen (2·2) is the result of dimerisation, then the entire degradation of D-sorbitol may be accounted for in terms of reactions 1, 2, and 3.

The secondary reactions are many. From the results of our investigation on the irradiation of hexose solutions *in vacuo* it is evident that most of the secondary products arising during D-sorbitol irradiations *in vacuo* are formed by secondary degradation of the initially formed hexoses, D-glucose and L-gulose. These secondary products include pentoses, hexonic acid, osones, and the constituents responsible for the characteristic absorption at 265 mμ. Oxalic acid probably arises by oxidation of two-carbon fragments. Evidence for the increasing complexity of the system at higher energy inputs may be seen in Table 1. At energy input $6{\cdot}4 \times 10^{20}$ ev, the total of products estimated accounts for 70% of the initial D-sorbitol irradiated, but only 53% could be accounted for in terms of the same products after an energy imput of $2{\cdot}2 \times 10^{23}$ ev. Further investigations are proceeding into the mechanism of the degradation.

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[9] Barker, Grant, Stacey, and Ward, *J.*, 1959, 2648.