758. *Photo-degradation of Carbohydrates. Part II.*[1] *Primary Processes in the Direct Photolysis of Aqueous* D-*Sorbitol Solutions.*

By G. O. Phillips and P. Barber.

Irradiation of oxygenated D-sorbitol solutions with ultraviolet light of wavelengths greater than 2000 Å leads initially to the formation of D-glucose and L-gulose and smaller amounts of the corresponding hexonic acids. By the use of filter solutions it is shown that absorption of radiation in the spectral region 2300—2400 Å is responsible for most of the photo-degradation, although light of longer wavelengths may initiate reaction if given sufficient time. A study of the spectral output of the medium-pressure mercury lamp used supports this conclusion. Although the amount of light absorption is small, there is excitation of the non-bonding orbitals of the oxygen atoms to anti-bonding levels ($n \rightarrow \sigma^*$ transition) which induces dissociation. It is unlikely that the active wavelengths are sufficiently energetic to excite bonding orbitals from the ground state of the molecule or to induce direct ionisation.

After the product studies reported in the previous paper,[1] the primary processes which initiate photo-degradation of D-sorbitol will now be considered. Only qualitative information is available about the wavelengths of the ultraviolet radiations which are active in the direct photolysis of carbohydrates.[2] Laurent and Wertheim [3] found that introduction of a glass filter between a mercury lamp with strong emission lines at 2540, 2650, 2970, 3020, 3130, and 3650 Å and an aqueous D-glucose solution reduced the formation of an unidentified product which has an absorption band at 2650 Å. From the transmission characteristics of the glass it appears, therefore, that the most active part of the light has wavelengths below 2800 Å. Light of wavelength 2537 Å is generally assumed to be responsible for the photolysis of cellulose, although little consideration has been given to the mechanism of degradation.[4,5]

Rupture of the C–C or C–O bond in sugars requires an energy of 80—90 kcal. per mole. Removal of a hydrogen atom would require about 100 kcal. per mole. Light of wavelength 2537 Å is, therefore sufficiently energetic to initiate rupture of a sugar molecule. Another prerequisite, however, is that the radiation must be absorbed by the molecule, and since cellulose is usually considered transparent to ultraviolet light above 2000 Å, the latter condition cannot be assumed to be fulfilled. To overcome this apparent contradiction, it was postulated that the 1-acetal group is the weak chromophoric group responsible for absorption near 2650 Å.[5] Studies of the ultraviolet spectra of cellulose are as yet inconclusive.[6]

In addition to direct absorption of ultraviolet radiation by the sugar molecule in aqueous solution, photolysis of water to produce possible reactive species must be considered.[7]

D-Sorbitol was selected for the present mechanistic study because it cannot contain the proposed " acetal chromophore." The susceptibility of D-sorbitol to photons of *ca.* 5 ev is also of interest in view of the possibility that sub-excited electrons of equivalent energy may contribute to the γ-degradation of D-sorbitol in aqueous solution.[8]

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[1] Part I, Phillips and Criddle, preceding paper.

[2] Phillips, *Adv. Carbohydrate Chem.*, 1961, **16**, 13.

[3] Laurent and Wertheim, *Acta Chem. Scand.*, 1952, **6**, 678; Laurent, *J. Amer. Chem. Soc.*, 1956, **78**, 1875.

[4] Egerton, *J. Soc. Dyers Colourists*, 1949, **65**, 764; Launer and Wilson, *J. Amer. Chem. Soc.*, 1949, **71**, 958; Flynn, Wilson, and Morrow, *J. Res. Nat. Bur. Stand.*, 1958, **60**, 229.

[5] Beelik and Hamilton, *Das Papier*, 1959, **13**, 77; *J. Org. Chem.*, 1961, **26**, 5074.

[6] Treiber, *Svensk Papperstidn.*, 1955, **58**, 185; Schurz and Kienzl, *Monatsh.*, 1957, **88**, 78.

[7] Barrett and Baxendale, *Trans. Faraday Soc.*, 1960, **56**, 37.

[8] Phillips and Criddle, *J.*, 1961, 3756, 3763.

RESULTS AND EXPERIMENTAL

Irradiations.—Initial experiments were carried out with unfiltered light from a Hanovia medium-pressure mercury lamp, as described in the preceding paper. Later, a larger and modified version of the apparatus described by Barrett and Baxendale [8] was used, so that filter solutions of varying path lengths could be interposed between the light source and irradiation vessel. Quartz vessels (500-ml. round-bottomed and 600-ml. flat-bottomed of 6·9 cm. outer diameter) have been used for irradiations. The vessels were held in distilled water in a metal tank and irradiated from below through a quartz window. The height of vessels could be accurately adjusted and filter solutions of the required path length introduced, as desired, in place of distilled water in the central compartment which housed the irradiation vessels. To prevent undue heating, this compartment was surrounded by a thermostat-controlled water-jacket. A shutter fitted to the quartz window enabled irradiation times down to a few seconds to be accurately achieved. Unless otherwise stated, all irradiations were carried out in oxygen.

Rate of Hexose Formation.—For the product studies by radioactive-isotopic and paper-chromatographic methods, described in the preceding paper, irradiation times of several hours were used. Greater accuracy can be obtained during the initial reaction by employing a reducing-power method [9] to measure hexose formation. As described in the preceding paper, oxygenated D-sorbitol ($5·5 \times 10^{-2}$M) solution (500 ml.) was irradiated at a distance of 1 cm. with unfiltered light, and during the irradiation aliquot parts (5 ml.) were withdrawn and the reducing powers were measured. D-Sorbitol is non-reducing. The rate of production of reducing products is shown in Fig. 1. After 1 hour's irradiation, $1·8 \times 10^{18}$ molecules hexose per ml. were produced; previous isotope-dilution methods indicated that $1·4 \times 10^{18}$ molecules of hexose per ml. were produced at this energy input. Since the ratio of the lamp output varied in the two experiments by 1 : 1·4, there is excellent agreement between the two methods. A previously undetected feature of the yield–dose curve is the initial sharp increase in hexose production. The form of the curve is unaltered when 8 mm. of quartz are interposed between the lamp and the irradiation vessel; the initial rate, however, is reduced by 60%. Spectrophotometric examination of the quartz showed that it transmits 57% at 2537 Å and 18% at 2000 Å. Since the rapid initial increase in rate of hexose formation does not allow initial rates to be measured with great accuracy, a measure of the overall change in reaction has been taken by measurement of the areas under the two curves. On this basis, introduction of 8 mm. of quartz in the light path reduces the overall reaction by 53%. The corresponding change in the rate of photolysis of hydrogen peroxide, estimated as described previously,[8] is 56%.

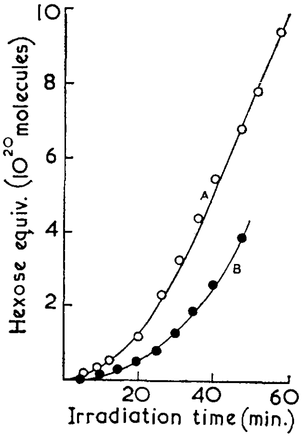

FIG. 1. Formation of reducing products during ultraviolet irradiation of aqueous D-sorbitol ($5·5 \times 10^{-2}$M) solutions (500 ml.) in oxygen.

A, Unfiltered light. B, 8 mm. quartz filter.

Interposing a Pyrex plate (4 mm.) between the lamp and the irradiation vessel cuts out all reaction up to 48 hours' irradiation. The Pyrex plate does not transmit light below 2940 Å.

In experiments described below, irradiations were carried out with the experimental arrangement described above. When a layer of x cm. of filter solution is interposed between

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[9] Somogyi, *J. Biol. Chem.*, 1952, **195**, 19.

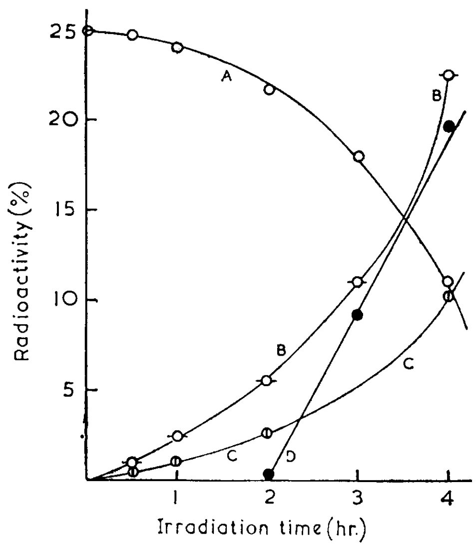

FIG. 2. Products of ultraviolet irradiation of a solution (100 ml.) of D-[^{14}C]sorbitol (13·75 mmoles; 2·32 μc/mmole) in oxygen at (*d* + 1) cm. of water, estimated by paper chromatography.

A, Sorbitol (× ¼). B, Hexose.
C, Acid. D, Immobile product.

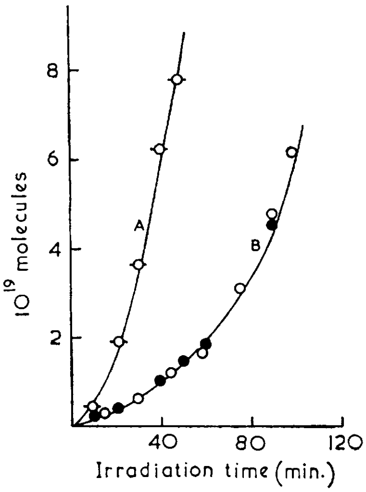

FIG. 3. Formation of products during ultraviolet irradiation of aqueous (100 ml.) D-sorbitol (13·75 mmoles) in oxygen at (*d* + 1) cm. of water.

A, Hexose. B (○), Acid. B (●), H_2O_2.

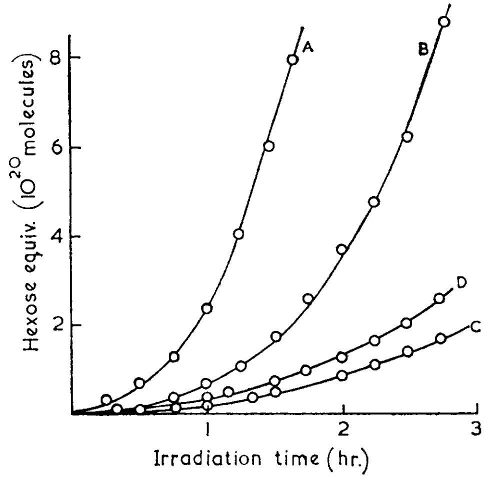

FIG. 4. Effect of increasing thickness of water and aqueous D-sorbitol as filters on the formation of reducing products.

(A—C) Water: A, *d* cm.; B, (*d* + 2) cm.; C, (*d* + 4) cm. D, (*d* + 1) cm. of aqueous 5 × 10^{-2}M-D-sorbitol.

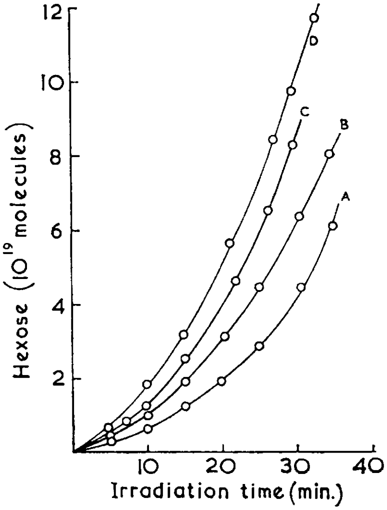

FIG. 5. Effect of D-sorbitol concentration on the formation of hexose.

A, 0·138M. B, 0·275M.
C, 0·413M. D, 0·55M.

the lamp and the irradiation vessel, the expression ($d + x$) cm. will be used, where d is the constant distance of the lamp from the quartz window (*ca.* 2 cm. of air).

Products at Low Energy Inputs.—Previously, the products of irradiation with unfiltered light were examined at high energy inputs where the initial sharp increase in reaction rate was not observed. For this reason, it was considered necessary to confirm that hexose formation is the main initial process during the early stages of the reaction and when a sufficiently thick water-filter is used to remove all light of 1850 Å which might induce photolysis of water. In a typical experiment, a solution (100 ml.) of D-[^{14}C]sorbitol (13·75 mmoles) of specific activity 2·32 μc/mmole was irradiated at ($d + 1$) cm. of water, and aliquot parts (0·1 ml.) were removed after successively increasing energy inputs and applied to filter paper strips (Whatman No. 1). The strips were irrigated in ethyl methyl ketone–saturated boric acid–glacial acetic acid (9 : 1 : 1) and dried, and the distribution of the radioactivity along the paper chromatogram was measured with an automatic radiochromatogram scanner.[10] Fig. 2 shows the yield–dose curves of total hexoses and hexonic acids in relation to the decrease in D-sorbitol concentration. In a duplicate experiment, acid, hexose, and hydrogen peroxide were estimated directly by titration (Fig. 3). After 1 hour's irradiation at ($d + 1$ cm.) of water, acid and hexose represent 4·4% decomposition in initial D-sorbitol, which may be compared with 4·7% decomposition when estimated by paper chromatography. Thus, subsequently in the investigation, the extent of photoreaction is measured by reducing-power methods at irradiation times where hexose formation in the main initial process.

Effect of Varying Thicknesses of Water.—D-Sorbitol solution (250 ml.; 5·5 × 10^{-2}M) was irradiated at d, ($d + 2$), and ($d + 4$) cm. of water, and Fig. 4 shows the rate of hexose formation at each level. As the vessel is moved further away from the lamp, there is a decrease in the light incident on the vessel because the beam is not collimated. The extent of attenuation due to geometry can be measured by the change in rate of photolysis of hydrogen peroxide (2 × 10^{-3}M) at 25° at d, (+ 2), and ($d + 4$) cm. The first-order rate constant for hydrogen peroxide photolysis shows a reasonably good correlation with the decrease in initial rate of hexose production (Table 1).

Effect of Increasing D-*Sorbitol Concentration.*—The initial rate of hexose formation increases with increasing D-sorbitol concentration during the irradiation of 0·138—0·55M-D-sorbitol solutions (300 ml.) at ($d + 1$) cm. water (Fig. 5). The path length of the irradiated solutions was 9 cm.

TABLE 1.

Effect of varying thicknesses of water on the photolysis of hydrogen peroxide and hexose production from 5 × 10^{-2}M-D-sorbitol solution (250 ml.).

Water-bath (cm.)	H_2O_2 (10^3 ksec.$^{-1}$)	Initial rate, hexose (10^{16} molecules/sec.)
d	3·2	3·9
$d + 2$	1·7	2·1
$d + 4$	0·54	0·64

Extinction Coefficient of Aqueous D-*Sorbitol.*—The effect of introducing 1 cm. of 5 × 10^{-2}M-D-sorbitol solution compared with the same thickness of water on the rate of hexose formation is shown in Fig. 4. Since it became apparent that D-sorbitol is the absorbing species during the photo-degradation, we examined the influence of D-sorbitol filter solutions of varying concentrations on the photolysis of hydrogen peroxide at ($d + 1$) cm. The filter solution was varied from 0 to 0·55M-D-sorbitol. At a water thickness of ($d + 1$) cm. there is complete transmission of the wavelengths responsible for the photolysis of hydrogen peroxide. If k_0 is the rate constant for the photolysis of hydrogen peroxide at ($d + 1$) cm. of water and k_s the rate constant at ($d + 1$) cm. of D-sorbitol solution of molar concentration C, then

$$\log k_s = -\varepsilon C + \log k_0$$

where ε is the extinction coefficient of D-sorbitol. Fig. 6 shows the plot of log k_s against D-sorbitol concentration. At the active wavelength (2537 Å) ε for D-sorbitol is 0·2.

Absorption Spectra of D-*Sorbitol Solutions.*—Owing to the general transparency of neutral sugar solutions in the visible and the ultraviolet region, little attention has been given to their

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[10] Phillips, Proc. Internat. Conference on Radioactive Isotopes, Copenhagen, 1960, p. 326.

detailed absorption spectra. We have carried out measurements on a Unicam S.P. 700 automatic recording spectrophotometer. The solutions are almost transparent up to 3000 Å. Thereafter, a continuum sets in extending into the vacuum-ultraviolet. After *ca.* 2100 Å the absorbancy rises sharply. Limitations imposed on the instrument by stray-light effects and the increased absorption of quartz [11] make it difficult to establish whether an absorption maximum falls in the near-ultraviolet (1800—2000 Å). To ensure the most favourable conditions, matched high-quality quartz (" Suprasil ") cells were used. Before use, the cells were cleaned for 24 hr. in a bath of concentrated sulphuric acid, phosphoric acid, potassium iodide, and chromium trioxide. During measurements, the instrument was continually flushed with nitrogen at a rate of not less than 100 l./hr.[11] Under these conditions D-sorbitol solutions ($5{\cdot}5 \times 10^{-2}$ to $5{\cdot}5 \times 10^{-1}$M) obey Beer's law in the region 2000—2537 Å, and Fig. 7 shows the molar extinction coefficient calculated for this region.

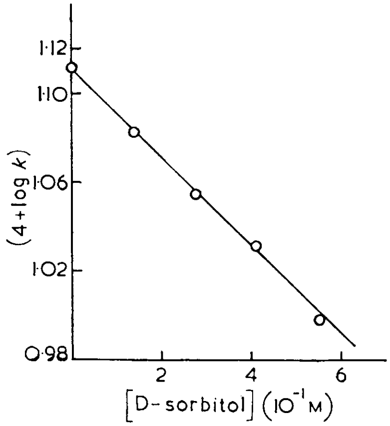

FIG. 6. Effect of D-sorbitol filters on the rate of photolysis of hydrogen peroxide (2×10^{-3}M).

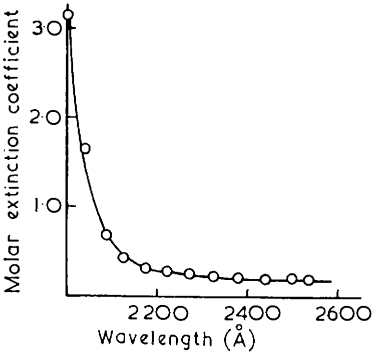

FIG. 7. Absorption spectrum of D-sorbitol in water.

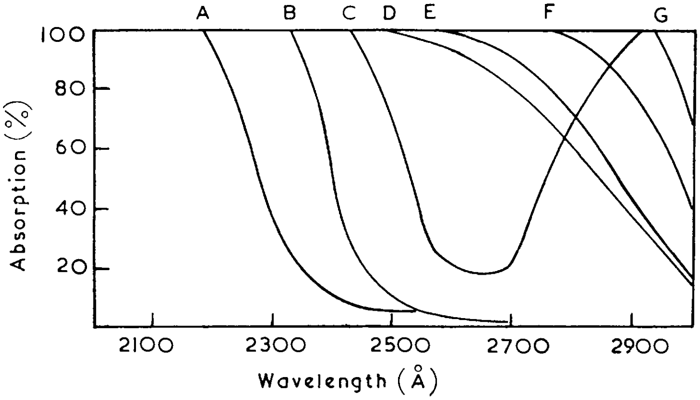

FIG. 8. Absorption spectrum of filter solutions.
A, 0·1M-NaOAc. B, 2M-NaOAc. C, 0·0008M-Dye X. D, 0·02M-$CuSO_4$. E, 0·03M-$CuSO_4$. F, 0·06M-$CuSO_4$. G, Pyrex glass.

The Active Wavelengths for Photo-degradation.—To ascertain the part of the spectral output of the lamp which is active in photolysis, filter solutions were interposed between the lamp and $5{\cdot}5 \times 10^{-2}$M-D-sorbitol solution (300 ml.) at ($d + 1$) cm., and the rate of photolysis compared with ($d + 1$) cm. of water. The following filter solutions were used: 2 and 3×10^{-2}M-copper

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[11] Johnson, *Spectrovision*, 1960, No. 8, 1; No. 9, 9.

sulphate, 0·1 and 2M-sodium acetate, 8 × 10^{-4}M-5,7-dimethyl-1,4-diazacyclohepta-4,6-diene iodide (dye X).[12] The absorption spectra of the filter solutions did not change significantly during irradiations and are shown in Fig. 8. Table 2 shows the effect of introducing the filter solutions on the rate of hexose formation, and Table 3 summarises the results in terms of initial rates and overall reaction up to 35 min. irradiation time.

Quantum Yields.—In the region 2300—2537 Å the molar extinction coefficient of D-sorbitol is 0·2. By using the quantum yield of 1·0 for the photolysis of 2 × 10^{-3}M-hydrogen peroxide solution at 25°, it is possible to measure the output of the lamp in this region. It has been assumed that the quantum yield remained constant at 1·0 over the range 2300—2537 Å. From the initial rate of hexose formation, in experiments where the geometry and path length are standardised, the initial quantum yield has been estimated (Table 4).

TABLE 2.

Effect of introducing filter solutions at (d + 1) cm. on the formation of hexose (given in 10^{19} molecules) during irradiation of aqueous 0·05M-D-sorbitol (300 ml.).

Time (min.) ...	5	10	15	20	25	30	35	40	45	50	55
Water	0·11	0·35	0·62	1·02	1·62	2·25	2·85	3·95	5·25	6·52	7·52
0·1M-NaOAc ...		0·25	0·30	0·42	0·95	1·25	1·60	2·15	2·95	3·60	4·25
2M-NaOAc ...		—	0·15	0·30	0·51	0·75	0·95	1·26	1·75	2·12	2·25
0·02M-CuSO$_4$...					0·25	0·45		0·70		0·98	1·15
0·03M-CuSO$_4$...							0·15		0·22	0·25	0·28
0·0008M-Dye X						0·28	0·31	0·48	0·58		0·81
0·06M-CuSO$_4$...											No reaction

TABLE 3.

Effect of filter solutions on initial rate of hexose formation and overall reaction.

	Sodium acetate		Dye X	Copper sulphate		
	0·1M	2M	0·0008M	0·02M	0·03M	0·06M
Reduction (%) in:						
overall reaction rate	33	60	95	92	98	100
initial rate	56	80	91	89	98	100

TABLE 4.

Initial quantum yield for hexose production during photo-degradation of D-sorbitol (path length, l, = 9 cm.

Height (cm.)	D-Sorbitol (10^{-1}M)	No. of quanta incident ml.$^{-1}$ sec.$^{-1}$ (× 10^{18})	No. of quanta absorbed ml.$^{-1}$ sec.$^{-1}$ (× 10^{16})	Initial rate of hexose formation (10^{14} molecules ml.$^{-1}$ sec.$^{-1}$)	Initial quantum yield (× 10^2)
(d + 1)	2·75	0·66	0·44	0·91	2·0
(d + 2)	2·75	0·55	0·37	0·77	2·1
(d + 3)	2·75	0·41	0·24	0·57	2·4
(d + 1)	0·138	0·66	0·29	0·41	1·4
(d + 1)	2·75	0·66	0·46	0·60	1·3
(d + 1)	4·13	0·66	0·56	0·76	1·3

From the absorption spectrum of hydrogen peroxide, it is clear that wavelengths not absorbed by D-sorbitol solutions may contribute to the photolysis of hydrogen peroxide solution. This proportion may be estimated by comparison of the photolysis of 2 × 10^{-3}M-hydrogen peroxide at (d + 1) cm. of 3 × 10^{-2}M-copper sulphate and (d + 1) cm. of water. It was shown that it was necessary to apply a correction amounting to 10% in our actinometry.

Spectral Output of Lamp.—No details could be supplied by the makers about the spectral output of the lamp. Consequently, an investigation was initiated into the nature of the output by using a normal-incidence, concave grating vacuum-spectrograph at the Nuclear Physics Division, Atomic Energy Research Establishment, Harwell. The quartz window of the spectrograph was 5 mm. thick and the lamp was situated 2 cm. from the window, so that conditions were identical with those in our irradiations. Ilford Q1 and Q2 plates suitable for the vacuum-ultraviolet region were used and the spectrograph showed a dispersion of 16·7 Å per mm. across the photographic plate.

[12] Kasha, *J. Opt. Soc. Amer.*, 1948, **38**, 929.

After elimination of ghost lines,[13] Table 5 gives the observed lines and reported lines to which they may correspond.

TABLE 5.

Spectral lines (Å) of a Hanovia 220 w medium-pressure mercury lamp.

Obs.	1966	2255	2282	2300	2320	2340	2344	2350	2375	2378	2399	2456	2456	2482
Lit.[14]	1973	2259		2302	2323	2340	2345	2352	2374	2378 2380	2399·4 2399·7	2447	2464	2482·0 2482·7

Obs.	2536R	2595	2604	2628	2643	2656	2679	2702	2758	2765	2779	2797	2808	2826
Lit.[14]	2536R	2593	2603	2625	2642·5 2642·6 2642·8	2655 2654 2652	2675	2698·8 2699·5	2753	2760	—	2799	2803	2820

TABLE 6.

Formation of reducing products during the irradiation of 0·275M-D-sorbitol solution with 2537 Å radiation.

Time (hr.)	0	19	24	48	90	112	115	122
Hexose (10^{19} molecules)	0	1·3	1·5	5·0	9·1	15·8	16·3	17·4

Photolysis of D-*Sorbitol Solutions* in vacuo.—A $5{\cdot}5 \times 10^{-2}$M-solution of D-sorbitol (300 ml.) was evacuated and irradiated with light from the Hanovia 220 w lamp at $(d + 1)$ cm. water. Samples were removed without introducing air to the system, as described previously.[8] The rate of formation of reducing material, expressed as hexose equivalent is shown in Table 7.

TABLE 7.

Formation of reducing products during the irradiation of $5{\cdot}5 \times 10^{-2}$M-D-sorbitol solutions *in vacuo*.

Time (hr.)	18	24	44
Hexose equivalent (10^{19} molecules)	11·5	18·5	20·2

DISCUSSION

When oxygenated D-sorbitol solutions are irradiated with unfiltered light from a medium-pressure lamp, or with filtered light (6 mm. quartz and 1 cm. water), the main initial process is hexose formation $R{\cdot}CH_2{\cdot}OH \longrightarrow R{\cdot}CHO$. Formation of hexonic acids occurs at a lower initial rate $R{\cdot}CH_2{\cdot}OH \longrightarrow R{\cdot}CO_2H$. Measurement of reducing power provides a sensitive method of following initial hexose production at energy inputs where the subsequent secondary processes are insignificant. By this method it is seen that there is an initial marked increase in rate of hexose formation with increasing energy input, and this is a characteristic of irradiations with filtered and unfiltered light (Figs. 1 and 5).

Initially two lines of evidence suggested that the chemical effects of ultraviolet light on aqueous D-sorbitol were due to hydrogen atoms and hydroxyl radicals. First, hexose formation was observed, which parallels the effect of γ-radiation of oxygenated D-sorbitol solutions, where the changes are due to reactive species formed during radiolysis of water. Secondly, Barrett and Baxendale[7] found that chemical changes accompanying ultraviolet irradiation of aqueous methanol were due to hydrogen atoms and hydroxyl radicals. Here, the dominant process was photolysis of water by 1849 Å radiation:

$$H_2O \xrightarrow{h\nu} H{\cdot} + {\cdot}OH$$

followed by

$$\begin{aligned} H{\cdot} + CH_3{\cdot}OH &\longrightarrow {\cdot}CH_2{\cdot}OH + H_2 \\ {\cdot}OH + CH_3{\cdot}OH &\longrightarrow {\cdot}CH_2{\cdot}OH + H_2O \\ 2{\cdot}CH_2{\cdot}OH &\longrightarrow (CH_2{\cdot}OH)_2 \end{aligned}$$

The primary radical may alternatively decompose to give formaldehyde.

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[13] Burton, personal communication.

[14] Massachusetts Institute of Technology Wavelength Tables, John Wiley, New York, 1939.

Our results cannot, however, be interpreted on this basis and indicate that direct photolysis of D-sorbitol occurs without the participation of photolytic products from water. For example, introduction of quartz (8 mm.) between the unfiltered light and the irradiation vessel reduced the initial rate of hexose formation by 60% and the overall reaction after 35 minutes' irradiation by 53%. Since quartz transmits 57% of the light at 2537 Å and 18% at 2000 Å, it appears that wavelengths between these limits are responsible for the photo-degradation. The behaviour is similar to that of hydrogen peroxide, whose rate of photolysis is reduced by 56% on interposition of the quartz. Photolysis of hydrogen peroxide is mainly due to light of 2537 Å, while light of 1849 Å is the most active mercury line for photolysis of water.

Barrett and Baxendale[7] calculate the decadic coefficient of water at 1849 Å to be 1·2. No significant amount of this radiation would, therefore, be transmitted through 1 cm. of water and 3 mm. of quartz, as in our experimental arrangement. Fig. 4 shows that hexose is produced when the light passes through 1, 2, and 4 cm. of water. Furthermore, water must be transparent to the radiation responsible for the photo-degradation, for the decrease in initial rate of hexose formation can be accounted for entirely by the geometrical losses of light caused by moving the vessel further from the source (Table 1). The amount of degradation increases as the concentration of D-sorbitol is increased (Fig. 5), indicating that there is direct absorption of light by the sugar.

By the use of filter solutions, the limits of wavelength necessary for photolysis can be narrowed. The results may be interpreted by reference to the absorption spectra shown in Fig. 8. The reductions in hexose production by 0·1M- (33—56%) and 2M-sodium acetate (60—80%) indicate that the active wavelength is in the spectral region 2300—2400 Å. Dye X and 0·02M-copper sulphate reduce the amount of reaction by about 90%, which indicates that, although the major portion of the active light is below *ca.* 2460 Å, on prolonged irradiation sufficient absorption of light of higher wavelength occurs, and that it is sufficiently energetic to initiate reaction. The complete inhibition of reaction by Pyrex glass sets an upper limit of 2940 Å to the active light, which can be further reduced to 2778 Å by the absence of reaction observed with a 0·06M-copper sulphate filter. Thus, the most effective spectral region, as indicated by the filter experiments, is *ca.* 2300—2400 Å, with increased effectiveness the lower the wavelength. Photolysis by light of higher wavelengths is not precluded, and it has been demonstrated, by using a lamp which emits only 2537 Å radiation, that such light is effective (Table 6). The overall contribution from light of wavelength greater than 2537 Å to the photolysis is, however, small.

Our investigation of the spectral output of the medium-pressure mercury lamp supports this conclusion. It is significant that with identical thicknesses of quartz on the window of the spectrograph as in our experiments no 1849 Å line was observed. To ensure the most favourable conditions of observation, the spectral output of a new lamp was compared with that of one which had been operating for *ca.* 350 hr. No difference was found in the number and position of the lines from the two lamps, and light of λ 1849 Å was, in each case, absent.

Our study reveals that eleven spectral lines, none of which was a ghost, were observed in this region. We have been unable to measure quantitatively the contribution of these lines to the total output of the lamp, but there are indications that they may, together, contribute a total energy of the same order as the 2537 Å resonance line for a medium-pressure lamp.[15]

As a rule, it is possible to elucidate the general absorption requirements of a photochemical system by reference to the ultraviolet absorption spectrum. Owing to the general transparency of neutral sugars in the visible and the near-ultraviolet region, little attention has been given to their detailed absorption spectrum.[2] For cyclic sugars

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[15] Pitts, *J. Chem. Educ.*, 1954, **34**, 112.

containing a potentially reducing aldehyde group, the general view expressed in the literature is that no selective absorption at *ca.* 2800 Å occurs—this would be characteristic of a free aldehyde group.[16] As far as we are aware, no quantitative study of the absorption spectrum of D-sorbitol has been reported. The present measurements indicate a small, yet significant, absorption in the region 2000—2537 Å (Fig. 6). An indirect measurement of the molar extinction coefficient of D-sorbitol at 2537 Å was obtained by studying the influence of D-sorbitol filter solutions on the rate of photolysis of hydrogen peroxide. Here, light of 2537 Å is primarily responsible. Absorption of light by D-sorbitol was observed, and the molar extinction (0·2) obtained is in agreement with the value directly measured spectrophotometrically.

Thus, the two requirements for photochemical reaction to occur are fulfilled. Light of 2300—2537 Å, corresponding to an energy of 124—113 kcal./mole, is absorbed by the D-sorbitol molecule, and it is sufficiently energetic to rupture a C–C bond or a C–O bond (80—90 kcal./mole) or remove a hydrogen atom (100 kcal./mole).

The initial quantum yield for hexose formation is low and indicates that, at the wavelengths absorbed, the fragments possess insufficient energy to escape from the solvent cage. The increase in the rate of hexose formation with time of irradiation may be related to the formation of the species which absorbs at 265 mμ.[1] Since hydrogen peroxide is also formed it is possible that the enhanced rate may also be due to photolysis of hydrogen peroxide to give hydroxyl radicals which may react with D-sorbitol.

The absorption spectrum and photo-dissociation of D-sorbitol may be attributed to excitation of the non-bonding electrons on the oxygen atom. Saturated hydrocarbons, for example, absorb in the far-ultraviolet region,[17] and the shift in absorption towards the visible region for D-sorbitol, as for aliphatic alcohols, is due to the presence of electrons associated with the oxygen atom. For alcohols, absorption becomes significant at about 1961 Å, and, in view of the width of the band, the maxima for a series of aliphatic alcohols fall in the narrow range 1835—1808 Å.[18] For D-sorbitol the absorption band is moved towards the visible region, compared with aliphatic alcohols. This behaviour may be due to the introduction of further oxygen atoms. Introduction of a second oxygen atom into cyclic ethers, for example, moves the maxima towards the visible region.[19] The primary process for D-sorbitol is, therefore, excitation of non-bonding orbitals on the oxygen atom to anti-bonding orbitals ($n \rightarrow \sigma^*$) transition). It is unlikely that the active wavelength is sufficiently energetic to excite bonding orbitals from the ground state of the molecule ($\sigma \rightarrow \sigma^*$ transition) to anti-bonding levels or to induce direct ionisation.

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