Carbohydrate Research, 51 (1976) 269–271

Note

Ultraviolet (253.7-nm) photolysis of phenyl β-D-glucopyranosides in aqueous solution

W. GORDON FILBY, GLYN O. PHILLIPS, AND (THE LATE) MARTIN G. WEBBER
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Great Britain)
(Received February 26th, 1975; accepted for publication in revised form, March 10th, 1976)

γ-Irradiation of aromatic and aliphatic β-D-glucopyranosides has been extensively studied[1–8]. In the solid phase, scission of the glucosidic bond occurs, resulting in almost equivalent production of D-glucose, or other D-glucose derivatives, and phenolic compounds. Substitution of an aromatic for an aliphatic aglycon group results in a decrease in glucosidic bond scission.

In contrast, little work has been reported on the photolysis of aryl glucosides in aqueous solution. Heidt[9] studied the 253.7-nm photolysis of such glucosides in aqueous solution and concluded that the main reaction was a hydrolytic-type scission of the glucosidic bond, giving phenolic and sugar products in equivalent yields.

We now report additional physical and analytical data for the ultraviolet (253.7-nm) photolysis of phenyl β-D-glucopyranosides in aqueous solution, which pinpoints the difficulties in proposing a mechanism for glucosidic bond scission.

EXPERIMENTAL AND RESULTS

Phenyl β-D-glucopyranosides were obtained commercially (Koch–Light) or prepared by the methods of Helferich[10] and this laboratory[7,11]. The techniques for irradiating aqueous solutions of the glucosides ($2–3 \times 10^{-4}$M) have been described elsewhere[11]. The analytical determination of reducing products as D-glucose, phenolic compounds, and hydrogen peroxide have also been previously described[2,7,11].

Steady state photolysis. — The main emphasis was on the determination of quantum yields of products formed by homolytic scission of the glucosidic bond, *i.e.*, reducing sugar, phenolic compounds, and hydrogen peroxide. Irradiation temperature and substrate concentration had no noticeable effect on the quantum yields of these products when oxygenated solutions of the glucosides were irradiated in the range 20–65°. There was little effect on changing the nature of the saturating gas to nitrogen or nitrous oxide, although H_2O_2 yields were considerably diminished (see Table I). In addition, despite the considerable effect on singlet energies (calculated from emission spectra recorded on a self-compensating spectrofluorimeter) on changing the nature of the aglycon group, there was little trend in the product yields (see Table II), except for the *o*-cresyl derivative where anomalies may arise due to steric effects.

TABLE I

DEPENDENCE OF PRODUCT QUANTUM-YIELDS ON SATURATING GAS[a]

Gas	*Quantum yields*		
	Glucose	*Phenol*	*Hydrogen peroxide*
O_2	0.006	0.005	0.002
N_2	0.006	0.004	0.003
N_2O	0.005	0.006	0.0006

[a] Glucoside concentration, 2.27mM.

TABLE II

DEPENDENCE OF THE PRODUCT QUANTUM-YIELDS ON THE SUBSTITUENT IN PHENYL β-D-GLUCOPYRANOSIDES[a]

Substituent	*Product quantum yields* (ϕ)		
	Glucose	*Phenol*	*Hydrogen peroxide*
H	0.006	0.005	0.002
o-cresyl	0.008	0.004	0.001
m-cresyl	0.010	0.008	0.003
p-cresyl	0.008	0.008	0.002
p-chloro	[b]	0.01	0.003
p-methoxy	0.007	0.006	0.003

[a] Concentration of glucoside, 1–2.5mM. Saturating gas, oxygen. [b] Glucoside decomposed under analysis conditions.

DISCUSSION

The problems arising when proposing a valid mechanism for glucosidic bond-scission stem from (*a*) a lack of knowledge of the true identity of the products and (*b*) their invariant quantum-yields under different experimental conditions.

However, a number of experimental observations can be explained. The absence of a quenching effect by oxygen on the product quantum-yields suggests that the primary reactive species is a singlet state probably initially formed in an upper excited level, as the radiation energy is ~4.9 eV.mol^{-1} whereas the singlet energy determined by fluorescence is in the range 3.9–4.25 eV.mol^{-1}. The detection of H_2O_2 as a primary product in N_2- or N_2O-saturated solution implies that water molecules may be decomposed during the initial photo-reaction processes.

The formation of H_2O_2, which is to be expected when oxygen is present, requires an initial reaction involving sugar-peroxy radicals which lead ultimately to hydroperoxy radicals ($2HO_2\cdot \rightarrow O_2+H_2O_2$) or H_2O_2 production directly.

The observation of phenoxyl-type radicals by flash photolysis* suggests that scission of the glucosidic bond occurs with the oxygen atom preferentially attached to the aromatic aglycon group. It is difficult to envisage that the reducing sugar formed *via* reaction of D-glucopyranosyl radicals produced simultaneously is D-glucose if the subsequent radical reactions are similar to those proposed recently to account for the formation of keto and deoxy sugars and sugar lactones in γ-irradiated, aqueous solutions of cellobiose[12] and D-glucose[13]. The formation of the parent phenol is also difficult to explain, unless an aryl glucosidic radical is initially formed which undergoes a hydrolytic-type scission[12].

Since the product quantum-yields are extremely small, a major proportion of the scission reactions must result in geminate radical recombination. Shizuka[14] has estimated that the recombination efficiency of the phenyl acetates photolysed in cyclohexane is $\sim$0.9. Carbohydrates in aqueous solution are strongly associated with the solvent[15] and considerable caging of the radicals could result. Such an effect could account for the low quantum-yields and the lack of dependence on the aglycon substituent. The subsequent reactions, which are predominantly free radical in nature, are less prone to the influence of such substituents than ionic reactions[14].

REFERENCES

1 G. O. Phillips, F. S. Blouin, and J. C. Arthur, Jr., *J. Radiation Res.*. 23 (1964) 527–536.
2 G. O. Phillips, W. G. Filby, J. S. Moore, and J. V. Davies, *Carbohydr. Res.*, 16 (1971) 89–103.
3 G. O. Phillips, W. G. Filby, J. S. Moore, and J. V. Davies, *Carbohydr. Res.*, 16 (1971) 105–111.
4 G. O. Phillips, W. G. Filby, and W. L. Mead, *Carbohydr. Res.*, 18 (1971) 165–172.
5 N. K. Kochetkov, *Zh. Obshch. Khim.*, 35 (1965) 2246–2251.
6 N. K. Kochetkov, *Zh. Obshch. Khim.*, 35 (1964) 897–900.
7 J. S. Moore and G. O. Phillips, *Carbohydr. Res.*, 16 (1971) 79–81.
8 P. J. Baugh, K. Kershaw, G. O. Phillips, and M. G. Webber, *Carbohydr. Res.*, 31 (1973) 199–209.
9 I. J. Heidt, *J. Franklin Inst.*, 234 (1942) 473–486.
10 B. Helferich, *Z. Chem.*, 226 (1934) 276.
11 J. S. Moore, Ph.D. Thesis, University of Wales, 1966; W. G. Filby, Ph.D. Thesis, University of Salford, 1970.
12 M. Dizdaroglu and C. von Sonntag, *Z. Naturforsch. B*, 28 (1973) 635–646.
13 M. Dizdaroglu, D. Henneberg, G. Schomburg, and C. von Sonntag, *Z. Naturforsch. B*, 30 (1975) 416–425.
14 H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *Bull. Chem. Soc. Jap.*, 42 (1969) 1831–1836.
15 W. A. Pryor, *Free Radicals*, McGraw-Hill, New York, 1966.

---

*From a brief series of flash-photolytic and low-temperature e.s.r. experiments, absorptions were assigned to the phenoxyl (PhO·; λ_{max} 310–320 nm) and hydroxymethyl radicals ($\cdot CH_2OH$; a_H 1.9–2.0 mTesla), respectively.