Radiation Chemistry of Carbohydrates. Part 16.† Kinetics of $HO_2^{\bullet}$ Elimination from Peroxyl Radicals derived from Glucose and Polyhydric Alcohols

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Oxygenated aqueous solutions of H_2O_2 at pH 5.5 containing ethylene glycol, glycerol, *meso*-erythritol, D-xylitol, D-glucitol, *myo*-inositol, D-glucose, methyl α-D-glucoside, or bis-1-methylethyl ether as substrates were subjected to flash photolysis and the rise of conductivity measured as a function of time. Except for bis-1-methylethyl ether all substrates showed transient conductivity which decayed within several hundred ms. This transient conductivity is attributed to the formation of $HO_2^{\bullet}$ which dissociates into H^+ and $O_2^{\bullet -}$. The precursors of $HO_2^{\bullet}$ are α-hydroxy-peroxyl radicals derived from the various substrates. From the kinetic analysis it follows that the peroxyl radical of ethylene glycol shows one first-order elimination process (k 190 s^{-1}). Two first-order processes are observed with the mixture of the peroxyl radicals of glycerol, D-xylitol, *meso*-erythritol, D-glucitol (k *ca.* 200 and *ca.* 3 000 s^{-1}), *myo*-inositol (k 470 and k 2 700 s^{-1}), and methyl α-D-glucoside (k 480 and 2 000 s^{-1}). Three parallel first-order processes are shown by the peroxyl radicals of D-glucose (k 400, 2 700, and >70 000 s^{-1}). The simple assumption that the slow and fast elimination in the polyhydric alcohols is due to eliminations from the α, ω, and other positions is not sufficient to explain the results quantitatively. Neighbouring hydroxy-groups might influence the rate of elimination. The very fast component in D-glucose is ascribed to the peroxyl radical at C-1 of D-glucose. Peroxyl radicals at C-2, C-3, and C-4 are thought to eliminate at both a slow and a fast rate as do those of *myo*-inositol, that at C-5 not on the time scale of this experiment, whereas that at C-6 is expected to contribute to the slow elimination rate.

PEROXYL radicals derived from primary and secondary alcohols undergo a rapid $HO_2^{\bullet}$ elimination [1-4] according to reaction (1). The rate of this reaction depends on the nature of the flanking substituents R^1 and R^2. Parallel

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† Part 15, H. Zegota and C. von Sonntag, *Z. Naturforsch.*, 1977, **32b**, 1060.

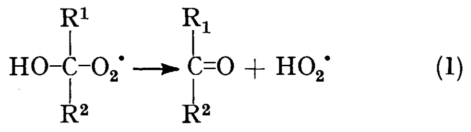
[1] Y. Ilan, J. Rabani and A. Henglein, *J. Phys. Chem.*, 1976, **80**, 1558.

[2] J. Rabani, D. Klug-Roth, and A. Henglein, *J. Phys. Chem.*, 1974, **78**, 2089.

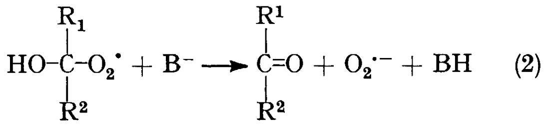
[3] E. Bothe, G. Behrens, and D. Schulte-Frohlinde, *Z. Naturforsch.*, 1977, **32b**, 886.

[4] M. N. Schuchmann, Doctoral thesis, Bochum, 1976.

to the monomolecular elimination there is a base (B^-) catalysed $O_2^{\bullet -}$ elimination (2). The rate of reaction (2) is somewhat below diffusion controlled in the case of OH^- and *ca.* 10^7 l mol^{-1} s^{-1} with phosphate as the base.



$$HO-\overset{R^1}{\underset{R^2}{C}}-O_2^\bullet \longrightarrow \overset{R_1}{\underset{R^2}{C}}=O + HO_2^\bullet \qquad (1)$$



$$HO-\overset{R_1}{\underset{R^2}{C}}-O_2^\bullet + B^- \longrightarrow \overset{R^1}{\underset{R^2}{C}}=O + O_2^{\bullet -} + BH \qquad (2)$$

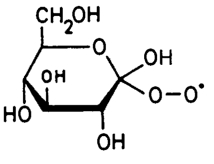
At high peroxyl radical concentrations reactions between two peroxyl radicals play a role, and the first-order processes can only be studied kinetically at low peroxyl radical concentrations. Under these conditions the conductivity technique is superior to the optical absorption technique, because the molar extinction coefficients of the intermediates are relatively small and of comparable magnitude at the accessible wavelength region. Above pH 4.75 (the pK value of $HO_2^\bullet$) the conductivity change caused by the ions H^+ and $O_2^{\bullet -}$ can be monitored readily. The substrate peroxyl radicals do not show conductivity below pH 7.

Here we present data on the peroxyl radicals from polyhydric alcohols including the cyclic inositol and from glucose. Bis-1-methylethyl ether and methyl α-D-glucoside have also been studied to help in the interpretation. The peroxyl radicals were generated by flash photolysis of oxygenated aqueous solutions of H_2O_2 (2×10^{-3}M) containing the solute (10^{-2}M). Under these conditions light is absorbed only by H_2O_2, and OH radicals are formed according to reaction (3). The OH

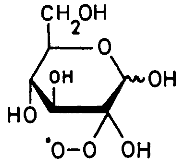
$$H_2O_2 \xrightarrow{h\nu} 2\cdot OH \qquad (3)$$

radicals abstract carbon bound hydrogen atoms from the substrate. The substrate radicals rapidly add oxygen forming in the case of D-glucose the peroxyl radicals (1)—(6).[4,5]

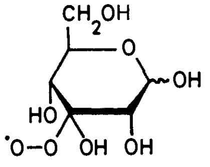
The fate of the glucose peroxyl radicals has been studied recently by extended product analysis.[4,5] The major products are compatible with reactions (1) and (2) as the main processes (*cf.* also products from the peroxyl radicals of ethylene glycol,[6] *scyllo*-inositol,[7] polyhydric alcohols,[8] and D-ribose [9]). In competition with these reactions (first-order in peroxyl radicals) there are processes which are second-order in peroxyl radicals and which eventually lead to fragmentation of the carbon skeleton. The yield of $HO_2^\bullet$ elimination of a certain radical depends on the ratio of the rate of $HO_2^\bullet$ elimination to the bimolecular decay (fragmentation). Assuming equal rate constants for the various second-order processes of the radicals (1)—(6), the probability of undergoing $HO_2^\bullet$ elimination will depend on the sum of the rates of reactions (1) and (2) (*i.e.* on $k_1 + k_2\cdot[OH^-]$)



(1)



(2)



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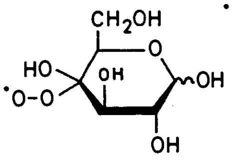

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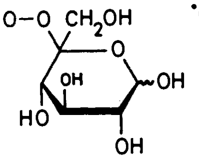
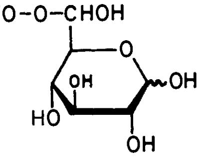


(5)



(6)

for the respective peroxyl radical. From experiments at different dose rates and using the above assumption it has been concluded that the rate constants of the first-order decay of the peroxyl radicals (1)—(6) follow the sequence $(1) \gg (2) \sim (3) \sim (4) > (6) \gg (5)$. The kinetic data from the present flash photolytic studies support this view.

RESULTS

Aqueous solutions (pH 5.5 and 6.0) containing 10^{-3}M-H_2O_2 and 10^{-2}M-substrates were photolysed with a 5 μs flash. Depending on the flash intensity the maximum concentrations of the conducting species were between 5×10^{-8} and 4×10^{-7}M. The build-up of conductivity was first-order for ethylene glycol (Figure 1) and a mixture of two first-order processes in the case of the other polyhydric

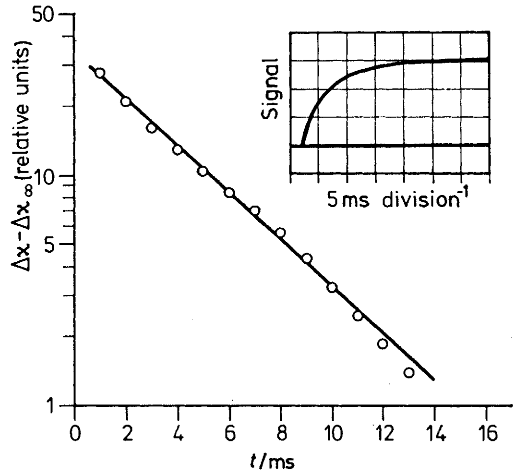


FIGURE 1 Kinetic analysis of the increase of conductivity ($\Delta\kappa$—$\Delta\kappa_\infty$) caused by the decay of peroxyl radicals derived from ethylene glycol. Data (open circles) are taken from the oscilloscope trace given in the inset. The lower trace in the inset is the base line

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[5] M. N. Schuchmann and C. von Sonntag, *J.C.S. Perkin II*, 1977, 1958.

[6] M. Ahmad, M. H. Awan, and D. Mohammad, *J. Chem. Soc.* (*B*), 1968, 946.

[7] A. Kirsch, C. von Sonntag, and D. Schulte-Frohlinde, *J.C.S. Perkin II*, 1975, 1334.

[8] K.-H. Stockhausen, *Atomenergie*, 1974, **24**, 51.

[9] C. von Sonntag and M. Dizdaroglu, *Carbohyd. Res.*, 1977, **58**, 21.

TABLE 1

First-order rate constants of HO_2^- eliminations of peroxyl radicals derived from various substrates

Substrate	k/s^{-1} pH 5.5, T 22 °C Slow	Fast	Within flash duration	Relative yields of the different reactions Slow	Fast	Within flash duration	Reference
Methanol	<10						3
Ethanol	50						3
Propan-2-ol	650						3
Ethylene glycol	190						This work
Glycerol	210	3 000		1	0.15		This work
meso-Erythritol	190	3 000		1	0.8		This work
D-Xylitol	220	2 800		1	0.9		This work
D-Glucitol	210	2 700		1	1.3		This work
myo-Inositol	470	2 600		1	0.8		This work
D-Glucose	400	2 600	$>70\ 000$	1	0.5	0.95	This work
Methyl α-D-glucoside	400	2 000		1	0.6		This work
Bis-1-methylethyl ether	<10						This work

alcohols (*e.g.* Figure 2). The rate constants and the ratio of the relative importance of the slow and the fast processes are listed in Table 1. No change in the half-lives has been observed on varying the light intensity eight-fold, except for a small second-order contribution at the highest intensities used.

The inset in Figure 3 shows the change of conductivity as a function of time for glucose as substrate. A very fast rise within the flash duration is observed. The rise time of this conductivity increase is too fast to determine the reaction rate. The latter is calculated to be faster than 70 000 s^{-1}. Following this jump a further increase is observed. A plot as given by Figure 3 indicates (at least) two parallel first-order reactions. Intensity studies have, again, shown that the complex curve in the inset in Figure 3 is due to parallel first-order reactions and not to second-order processes. At high intensities, however, second-order processes begin to play a role. Methyl α-D-glucoside showed the same behaviour as has been found for D-glucose except that the first fast jump was missing. Bis-1-methylethyl ether as substrate does not show any observable conducting intermediates during the time range of these experiments.

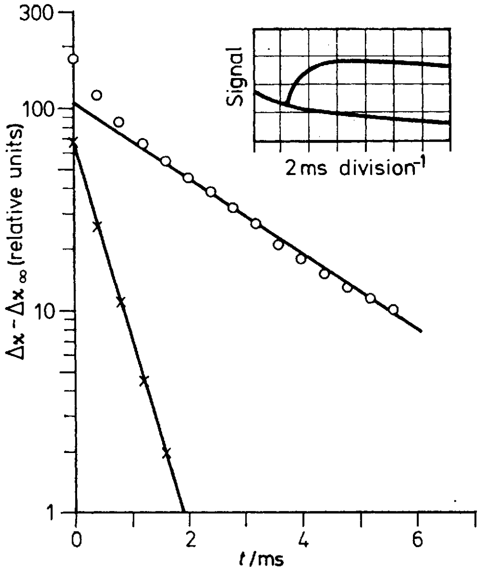

FIGURE 2 Kinetic analysis of the increase of conductivity ($\Delta\kappa$—$\Delta\kappa_\infty$) caused by the decay of peroxyl radicals derived from *myo*-inositol. The line through the circles represents the slow, that through the crosses the fast component

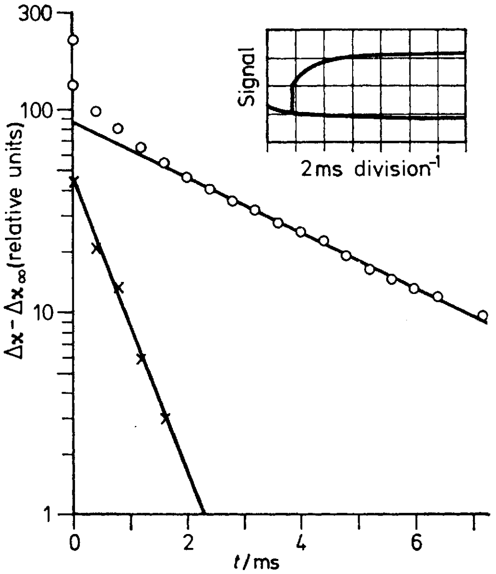

FIGURE 3 Kinetic analysis of the increase of conductivity ($\Delta\kappa$—$\Delta\kappa_\infty$) caused by the decay of peroxyl radicals derived from D-glucose. The difference between the two first experimental points represents the fast initial jump (not resolved kinetically)

Figure 4 gives an Arrhenius plot for the H^+ and $O_2^{\cdot -}$ formation from ethylene glycol, glycerol, and D-xylitol peroxyl radicals, and Figure 5 presents the same kind of plot for *myo*-inositol and D-glucose as substrates. Table 2

TABLE 2

Activation energies and pre-exponential factors of the slow and fast $HO_2^{\cdot}$ eliminations of peroxyl radicals derived from various substrates

Substrate	E_a/kJ mol^{-1} Slow	Fast	A/s^{-1} Slow	Fast
Ethanol	60		2×10^{12}	
Propan-2-ol	56		6×10^{12}	
Ethylene glycol	33		2×10^{8}	
Glycerol	41.5		5×10^{9}	
D-Xylitol	52	64.5	3.5×10^{11}	7×10^{14}
myo-Inositol	46	64.5	5×10^{10}	7×10^{14}
D-Glucose	46	64.5	5×10^{10}	7×10^{14}

lists the various activation energies and pre-exponential factors derived from these plots.

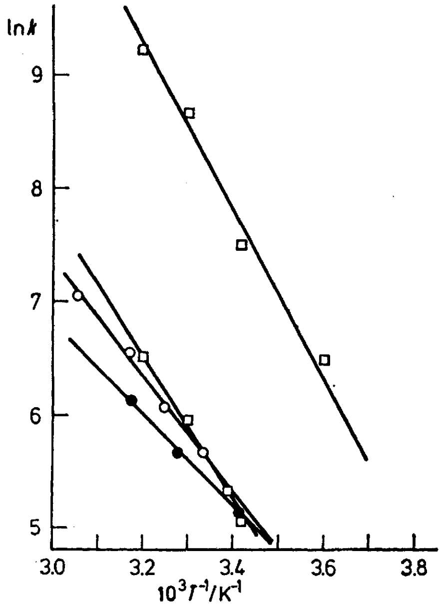

FIGURE 4 Arrhenius plots for the decay of peroxyl radicals derived from ethylene glycol, ●; glycerol, ○; and D-xylitol, □. The lower group of curves represents the slow component, the upper curve the fast component

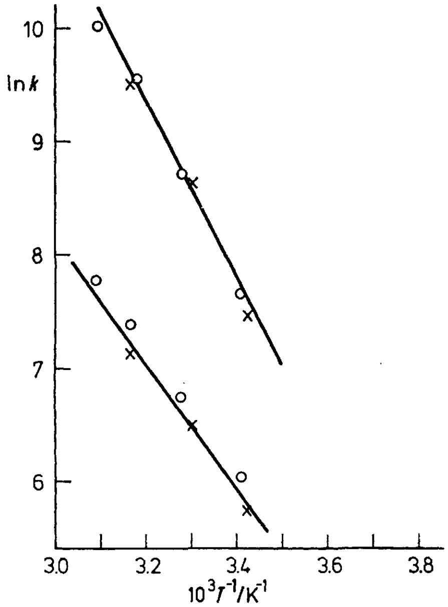

FIGURE 5 Arrhenius plots for the decay of peroxyl radicals derived from *myo*-inositol, ○; and D-glucose, +. The lower and upper solid lines represent the slow and fast processes, respectively

DISCUSSION

The reactions of peroxyl radicals from carbohydrates and polyhydric alcohols appear to be analogous to those of the simple alcohols [reactions (1) and (2)]. However, there is a marked difference in rates (Table 1). At pH 5.5 the contribution of a base catalysed reaction is negligible for the faster processes and only the uncatalysed $HO_2^{\bullet}$ elimination plays a role. For the slow reaction the base catalysed contribution is below 20%.

The elimination of $HO_2^{\bullet}$ from the peroxyl radical derived from ethylene glycol is similar to that from ethanol or propan-2-ol (Table 1). However, the higher polyhydric alcohols show a second, faster component the relative yields of which increases with chain length (Table 1). With the cyclic inositol also two components were observed.

The fact that two different $HO_2^{\bullet}$ elimination rates are observed both for the open-chain polyhydric alcohols and for the cyclic inositol is not yet fully understood. In the case of inositol one might consider that peroxyl radicals have the peroxyl radical function in either the axial or equatorial position. These two types might have different elimination rates. In the open-chain polyhydric alcohols the peroxyl radicals in the inner part of the molecule (fast $HO_2^{\bullet}$ elimination) might eliminate faster than those at the α- and ω-positions [compare the elimination rate constants of the peroxyl radicals derived from isopropanol and ethanol (Table 1)]. If this is correct, the ratio of the yield of the fast and slow components should then correspond to the ratio of OH attack at the inner positions of the molecule and its α- and ω-positions. The latter ratio should be given by the ratio *G*(ketoses) : *G*(aldoses). Data on this ratio are available.[8] The comparison shows that the expected trend is observed but that the product ratio is generally higher than the ratios of the fast and slow processes in the present kinetic study. This shows that the above interpretation is not sufficient for the polyhydric alcohols. In addition one might assume that hydrogen bonding from neighbouring OH groups has an influence on the rate of elimination. Hydrogen bonding has been shown to be essential for $HO_2^{\bullet}$ elimination.[3]

In D-glucose, six different peroxyl radicals (1)—(6) are formed. Radicals (2)—(4) are of the same type as those derived from *myo*-inositol. One therefore would expect that these eliminate $HO_2^{\bullet}$ with two different rates which should be similar to those from *myo*-inositol. Indeed, Figure 5 shows that the activation energies and even the pre-exponential factors are identical for the two compounds. Radical (6) is expected to eliminate $HO_2^{\bullet}$ at a rate similar to that of the peroxyl radical of ethylene glycol. Since this rate is not much different from the slow component of radicals (2)—(4), it is likely that radical (6) contributes to the slow component.

Radical (5) is expected not to eliminate $HO_2^{\bullet}$ in an uncatalysed reaction,[5] since the rate constant for ring opening (from mutarotation) is too small to have a contribution from the open chain form. Similarly, on the time scale of our experiment, the peroxyl radical from bis-1-methylethyl ether does not eliminate $HO_2^{\bullet}$. Furthermore, it was observed [5] that radical (5) is more susceptible to second-order reactions than any of the other radicals as evidenced by the study of the dose rate dependence of products from (5).

The very fast jump of conductivity during the flash must be due to $HO_2^{\bullet}$ elimination from the peroxyl radical (1). This jump is fully eliminated if the OH group at C-1 is substituted by an OCH_3 group as in methyl α-D-glucoside. The other contributions, those of the radicals at C-2—C-4 andC -6 are the same both in methyl α-D-glucoside and in D-glucose (Table 1).

EXPERIMENTAL

The substrates and H_2O_2 (without stabilizers) were supplied by Merck and used without further purification except for glycerol which was refractionated under reduced pressure. Triply distilled water was redistilled three times under nitrogen from alkaline permanganate, from acidic dichromate, and finally from a quartz vessel. Perchloric acid was used to adjust the pH of the solution.

The photolysis flash was produced by the conventional flash photolysis set-up described earlier.[10] The flash (argon discharge) had a half-width of 5 μs and generated a photon density of $\leqslant 7 \times 10^{16}$ quanta cm^{-3}. An absorption filter (Schott WG 280) eliminated light below 280 nm. Under this condition light is only absorbed by H_2O_2 and not by the substrates.

Before, during, and after the flash the conductivity of the solution was measured with an apparatus, the main part of which is a double Wheatstone bridge operated with a direct current voltage of 95 V. Before each measurement the bridge was balanced and the pH value of the solution was calculated from the balance conditions. The output voltage from the bridge was displayed on a storage oscilloscope (Tectronix 6723) during each measurement both in the absence of the flash (base-line) and in its presence (signal-line). The base-line is mostly not horizontal due to polarisation and electrolysis effects. The difference between signal-line and base-line remains constant after the end of the reaction showing that the influences of polarisation and electrolysis are the same for the blank and the experiment. Data given in the figures were obtained from the differences of signals and blanks. The electrical rise time of the set up was 100—200 ns. The noise was smaller than the width of the oscilloscope trace.[3]

[7/926 *Received*, 30*th May*, 1977]

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[10] E. Bothe, Doctoral thesis, Bochum 1976.