Pulse Radiolysis and Election Spin Resonance Studies of the Dehydration of Radicals from 1,2-Diols and Related Compounds

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The complementary techniques of pulse-radiolysis and e.s.r. spectroscopy have been employed in a kinetic study of the dehydration of a variety of α,β-dihydroxyalkyl radicals $[^{\bullet}CR^1(OH)CR^2R^3OH]$ into the appropriate carbonyl-conjugated radicals $[^{\bullet}CR^2R^3C(O)R^1]$. The overall rates of proton-catalysed dehydration, as revealed by steady-state (e.s.r.) and time-resolved (pulse-radiolysis) experiments, indicate the importance of the electronic effects of substituents (contrast values of 1.2×10^9 and 9.8×10^8 dm^3 mol^{-1} s^{-1} for the radicals from cyclohexane-1,2-diol and butane-2,3-diol, respectively, with that for the radicals from erythritol of 4.2×10^6 dm^3 mol^{-1} s^{-1}). Time-resolved experiments allow information to be obtained about the generation of the protonated species $[^{\bullet}CR^1(OH)CR^2R^3OH_2{}^+]$ and for the loss of water from this intermediate.

For $^{\bullet}CR(OH)CMe_2OH$ (R = H and Me) evidence is obtained for a rapid uncatalysed dehydration reaction, (k 1—2 × 10^4 s^{-1}), which is believed to be assisted by the steric effect of the *gem*-dimethyl group as well as the polarity of the solvent. For the latter substrate, the reaction is characterized by a strongly negative activation entropy (−93 J mol^{-1} K^{-1}).

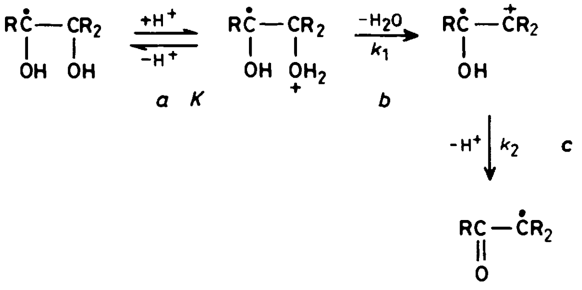
α,β-Dihydroxyalkyl radicals are shown to reduce methyl viologen with rate constants that depend strongly on the nature of the substituents; there is a correlation between the reducing power of the radical and its rate of dehydration.

The reactions of polyhydric alcohols with the hydroxyl radical in aqueous solution have been extensively studied (*e.g.* in radiolytic and biomimetic systems), mainly because of their suitability as models for more complicated carbohydrate substrates.[1]

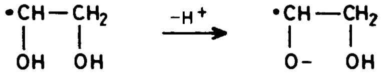
A particularly important finding, revealed by e.s.r. studies on ethane-1,2-diol at low pH,[2,3] and confirmed by product[1,4] and pulse-radiolysis studies,[5] is that the initial α,β-dihydroxyalkyl radical from this substrate undergoes an acid-catalysed dehydration reaction to give the carbonyl-conjugated radical $^{\bullet}CH_2CHO$. It has been suggested[5,6] on the basis of a wide range of experiments that this process occurs *via* a radical-cation (*e.g.*,[5] see Scheme 1). A related base-catalysed reaction has been shown to give the appropriate carbonyl-conjugated radical, *via* a radical-anion intermediate[5,7] [equation (1)], and rate constants for the loss of OH^- [equation (2)] have been determined.[7]

It has been suggested on the basis of qualitative e.s.r. experiments[8] that the presence of alkyl substituents can markedly increase the rate of the acid-catalysed reaction, and the limited kinetic information available is in accord with this (*cf.* second-order rate constants for dehydration of the radicals from ethane-1,2-diol[5] and butane-2,3-diol[9] of 9×10^6 dm^3 mol^{-1} s^{-1} and 1.3×10^8 dm^3 mol^{-1} s^{-1}, respectively). Alkyl substituents have also been shown[7] to increase the rate of loss of OH^- in their ionized counterparts [equation (2)].

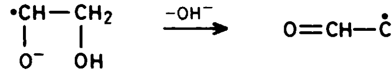
Current interest in the radiation chemistry of DNA[10] and, in particular, the mechanism of ring-opening of the 2-deoxyribose moiety[11] (with the demonstration that some of the proposed reactions are acid-catalysed) led us to attempt to extend and rationalize the effect of structure and substituents on the acid-catalysed loss of water from α,β-dihydroxy-substituted radicals; the two complementary techniques of e.s.r. spectroscopy and pulse-radiolysis have been employed, the former to provide details of structural identification and steady-state analysis and the latter to allow time-resolved studies to be undertaken.



Scheme 1.



$$\underset{OH}{^{\bullet}CH}-\underset{OH}{CH_2} \xrightarrow{-H^+} \underset{O^-}{^{\bullet}CH}-\underset{OH}{CH_2} \qquad (1)$$



$$\underset{O^-}{^{\bullet}CH}-\underset{OH}{CH_2} \xrightarrow{-OH^-} O{=}CH-\dot{C}H_2 \qquad (2)$$

Results

(*a*) *E.s.r. Flow-system Studies.*—An overall kinetic analysis was first attempted *via* the development of a kinetic scheme for the Ti^{III}–H_2O_2 flow system.[12] Thus, it has been shown[13,14] that under certain conditions a pseudo-steady state exists in the cavity of the e.s.r. spectrometer in rapid-flow experiments and hence that kinetic analysis of the system is possible. The overall reaction scheme may be represented by the equations (3)—(7), where SH is the substrate whose reaction with $^{\bullet}OH$ yields n different radicals ($S^{1\bullet} \rightarrow S^{n\bullet}$), one of which ($S^{1\bullet}$) can undergo acid-catalysed conversion into $Y^{\bullet}$.

$$\mathrm{Ti^{III}} + \mathrm{H_2O_2} \xrightarrow{k_3} \mathrm{Ti^{IV}} + \mathrm{HO^-} + \mathrm{HO^\bullet} \quad (3)$$

$$\mathrm{HO^\bullet} + \mathrm{SH} \xrightarrow{k_4} \mathrm{S^{1\bullet}} + \mathrm{S^{2\bullet}} + \cdots \mathrm{S^{n\bullet}} \quad (4)$$

$$\left.\begin{array}{ll} 2\mathrm{S^{i\bullet}} \xrightarrow{k_5} & (5) \\ \mathrm{S^{i\bullet}} + \mathrm{S^{j\bullet}} \xrightarrow{k_6} & (6) \end{array}\right\} \text{molecular products}$$

$$\mathrm{S^{1\bullet}} + \mathrm{H^+} \xrightarrow[-\mathrm{H_2O}]{k_d} \mathrm{Y^\bullet} \quad (7)$$

Application of the steady-state principle to $[\mathrm{S^{1\bullet}}]$ yields equation (8), if k_4 is assumed to be very rapid.

$$\frac{d[\mathrm{S^{1\bullet}}]}{dt} = rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t - k_d[\mathrm{S^{1\bullet}}][\mathrm{H^+}] - 2k_5[\mathrm{S^{1\bullet}}]^2 - k_6[\mathrm{S^{1\bullet}}]\left(\sum_{i=2}^{n}[\mathrm{S^{i\bullet}}] + [\mathrm{Y^\bullet}]\right) = 0 \quad (8)$$

In this expression $[\mathrm{X}]_t$ refers to the concentrations at a time t after mixing and r is the fraction of •OH radicals which react to give $\mathrm{S^{1\bullet}}$ (rather than any other species). On the assumption that all the radicals terminate at comparable rates (which is reasonable for radicals of similar structure and molecular weight), r may be obtained from the concentration of $\mathrm{S^{1\bullet}}$ (relative to the other radicals present) under conditions where no acid-catalysed reaction takes place. If the total concentration is defined as $[\mathrm{S^\bullet}]_\mathrm{T}$, equation (8) simplifies to equation (9), which on rearrangement gives (10).

$$rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t = k_d[\mathrm{S^{1\bullet}}][\mathrm{H^+}] + k_6[\mathrm{S^{1\bullet}}][\mathrm{S^\bullet}]_T \quad (9)$$

$$\frac{1}{[\mathrm{S^{1\bullet}}]} = \frac{k_d[\mathrm{H^+}]}{rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t} + \frac{k_6[\mathrm{S^\bullet}]_\mathrm{T}}{rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t} \quad (10)$$

Provided the value of $rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t$ is known, the rate constant for dehydration (k_d) should be obtained from the gradient of a plot of $1/[\mathrm{S^{1\bullet}}]$ against $[\mathrm{H^+}]$ [and the termination rate constants k_6 (k_5) obtained from the intercept]. However, several possible limitations on this scheme must be considered. Firstly in order to ensure that $[\mathrm{S^\bullet}]_\mathrm{T}$ remains constant, experiments must be carried out at pH values where the extent of rearrangement to $\mathrm{Y^\bullet}$ is small (because $\mathrm{Ti^{III}}$ is known to remove carbonyl-conjugated radicals by reduction[15]). Secondly, under certain circumstances both hydrogen peroxide and $\mathrm{Ti^{IV}}$–EDTA complexes can oxidize simple hydroxyl-conjugated radicals,[16,17] though conditions employed in these experiments ensure that only the former can be of any significance (since $[\mathrm{H_2O_2}] \gg [\mathrm{Ti^{IV}}]$). The rate of oxidation by $\mathrm{H_2O_2}$ is independent of pH in the range employed in these experiments[16] and the above equation may be modified to include the appropriate term; this gives equation (11) (in which k_{ox} is the rate constant for oxidation) from which it follows that k_d can still be derived from a plot of $1/[\mathrm{S^{1\bullet}}]$ *versus* $[\mathrm{H^+}]$.

$$\frac{1}{[\mathrm{S^{1\bullet}}]} = \frac{k_d[\mathrm{H^+}]}{rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t} + \frac{k_6[\mathrm{S^\bullet}]_\mathrm{T}}{rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t} + \frac{k_{ox}}{rk_3[\mathrm{Ti^{III}}]_t} \quad (11)$$

In a series of e.s.r. experiments with 1,2-diols and related compounds in which $[\mathrm{H_2O_2}]_t$ and $[\mathrm{Ti^{III}}]_t$ were held constant (with $[\mathrm{H_2O_2}]_0 = 0.011$ mol dm^{-3} and $[\mathrm{Ti^{III}}]_0 = 0.0027$ mol dm^{-3}, both after mixing, and with a constant flow-rate with a dead-time of 50 ms), steady-state values of $[\mathrm{S^{1\bullet}}]$ (the concentrations of the appropriate α,β-dihydroxy-substituted radicals) were obtained as a function of $[\mathrm{H^+}]$ (see Experimental section). It was found that equation (11) holds well, within the limits of experimental error, for regions where $[\mathrm{S^\bullet}]_\mathrm{T}$ is not affected significantly by radical reduction. $[\mathrm{S^{1\bullet}}]^{-1}$ was found to depend linearly on $[\mathrm{H^+}]$; analysis according to equations (10) or (11), *i.e.* in which the slope is equated to $k_d/rk_3[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t$, allows values of k_d to be determined [since the denominator terms are known: k_3 has been estimated[18] as 2 700 dm^3 mol^{-1} s^{-1}, $[\mathrm{H_2O_2}]_t \simeq [\mathrm{H_2O_2}]_0$ (as peroxide is in excess), and $[\mathrm{Ti^{III}}]_t$ is calculable from the exponential decay of this species with time].* The values of k_d found by this method for the dehydration of α,β-dihydroxyalkyl radicals from butane-2,3-diol, propane-1,2-diol [both •CH(OH)CHMeOH and •CMe(OH)CH$_2$OH)], ethane-1,2-diol, and glycerol [both •CH(OH)CH(OH)CH$_2$OH and •C(OH)(CH$_2$OH)$_2$] are collected together in Table 1. This Table also includes an estimate of the dehydration rate constant for •CH(OH)CH(OH)CH(OH)CH$_2$OH (from erythritol: detailed analysis was prevented by the complex, overlapping nature of the spectra), and, for comparison, the rate constant for reaction of two different types of α,β-dihydroxy-substituted radical from myoinositol (one of which is distinguished by possessing an axial β-OH group, *cf.* ref. 12). For 2-methylpropane-1,2-diol and 2-methylbutane-2,3-diol, flow experiments were precluded by the limited quantity of material available: photolytic e.s.r. experiments are described in the next section.

(*b*) *Pulse-radiolysis Studies*.—(i) *Direct observation*. Pulse radiolysis of N$_2$O-saturated aqueous solutions containing substrate (at 0.1 mol dm^{-3}, a concentration sufficient to ensure complete scavenging of OH• as well as H•) at pH 6 led to the detection of weak optical absorptions in the region 210—350 nm, which (except for 2-methylpropane-1,2-diol and 2-methylbutane-2,3-diol; see Figure 1 and also later) did not alter appreciably in the time-scale 0—100 μs. These absorptions are assigned[5] to the initially formed 1,2-dihydroxyalkyl radicals ($\mathrm{S^{1\bullet}}$).

At low pH values these absorptions were found in most cases to be rapidly replaced by a second, much stronger absorption which had a maximum in the region 200—240 nm (see Figures 1 and 2 and Table 2). The rate of replacement of the initial absorption with the second (which we assign to the carbonyl-conjugated radical, Y•, produced on dehydration) was found to be pH- and substrate-dependent.

Extinction coefficients for the latter species were determined at pH 1—3 (see Table 2) by measuring the maximum optical density at $\lambda_{\text{max.}}$ (or at 220 nm if no maximum was observed), assuming $G = G(\mathrm{OH}) + G(\mathrm{H}) = 6.6$ molecules/100 eV (0.68 μmol J^{-1}). For the calculation of ε the fractional yields of 2-alkanoyl radicals produced from the parent glycols were either taken from a previous study[7] on the base-catalysed loss of OH$^-$ from the same radicals, or determined by scavenging the initial 1,2-dihydroxyalkyl radicals at pH 6—7 using *p*-benzoquinone and measuring the optical density at 430 nm, where *p*-benzosemiquinone has a maximum. The fractional yields [expressed in terms of $G(\cdot\mathrm{CRR^1OH})/G(\mathrm{OH + H})$] are also shown in Table 2. [For calibration an N$_2$O-saturated solution containing 0.1 mol dm^{-3} formate and 0.2 mmol dm^{-3} *p*-benzoquinone at pH 6 was used; in this system, G(benzosemiquinone) = $G(\mathrm{OH}) + G(\mathrm{H})$ = 0.68 μmol J^{-1}.]

Though the build-up of the appropriate carbonyl radical could be monitored for 2-deoxyribose, with glucose and ribose

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* For all of the radicals studied here, the intercept on the ordinate was found to be approximately as calculated from the second term only in equation (11), utilizing k_6 (*i.e.* the cross-termination rate constant) as *ca.* 10^9 dm^3 mol^{-1} s^{-1} (as expected for small, uncharged radicals). This suggests that the third term is negligible and that oxidation is less important ($k_{ox} \ll 10^5$ dm^3 mol^{-1} s^{-1}) than for simple α-hydroxyalkyl radicals (possibly because of the $-I$ effect of the β-OH group).

Table 1. Rate constants for the acid-catalysed dehydration of radicals from 1,2-diols and related compounds

	Results from pulse radiolysis experiments^{a}					
			k_d/dm^3 mol^{-1} s^{-1}			
Parent compd.	k_1/s^{-1}	K/mol dm^{-3}	$\frac{k_1}{K}$	MV^{2+} method	$k_{obs}/[H^+]$	Results from e.s.r.^{a} k_d/dm^3 mol^{-1} s^{-1}
Cyclohexane-1,2-diol	1.8×10^6	1.5×10^{-3}	1.2×10^9	9.9×10^8	1.3×10^9	
2-Methylbutane-2,3-diol	1.8×10^6	7.4×10^{-4}	2.4×10^9		1.7×10^9	
Butane-2,3-diol	2.8×10^6	2.6×10^{-3}	9.8×10^8	1.2×10^9	9.7×10^8	1×10^9
2-Methylpropane-1,2-diol	2.7×10^6	3.7×10^{-3}	7.1×10^8		7.0×10^8	
Butane-1,2-diol	8.5×10^5	5.3×10^{-3}	1.6×10^8		1.5×10^8	
Propane-1,2-diol	7.1×10^5	5.6×10^{-3}	1.3×10^8		9×10^7	$4.1 \times 10^{8\,b}$ $1.8 \times 10^{8\,c}$
Ethane-1,2-diol	7.5×10^5 $(8.6 \times 10^5)^{g}$	4.6×10^{-2} $(1.8 \times 10^{-1})^{h}$	1.6×10^7 $(4.8 \times 10^6)^{h}$	1.9×10^7	1.1×10^7	2.4×10^7
Glycerol	6.5×10^5	1.3×10^{-1}	5.0×10^6	5.8×10^6	3.5×10^6	$1.0 \times 10^{7\,d}$ $4.6 \times 10^{6\,e}$
Erythritol	3.5×10^5	8.0×10^{-2}	4.2×10^6	2.4×10^6	2.9×10^6	$\sim 6 \times 10^6$
Myoinositol	2.4×10^5 4.8×10^5	3.2×10^{-1} 2.35	7.6×10^5 2.0×10^5		5.7×10^5 1.0×10^5	$7.0 \times 10^{5\,f}$ $5.7 \times 10^{4\,g}$
2-Methoxyethanol^{i}	1.0×10^5	4.7×10^{-2}	2.2×10^6		4.9×10^5	
2-Hydroxymethylfuran^{j}	4.8×10^5	8.4×10^{-2}	5.6×10^6		2.8×10^6	
2-Deoxyribose	7.6×10^5	4.0×10^{-2}	2.0×10^7		1.5×10^7	

[a] The errors in the rate and equilibrium constants measured by pulse radiolysis are estimated as ±10%; for the e.s.r. experiments, the errors in k are believed to be ±30%. [b] $\dot{}$CMe(OH)CH$_2$OH. [c] $\dot{}$CH(OH)CHMeOH. [d] $\dot{}$C(OH)(CH$_2$OH)$_2$. [e] $\dot{}$CH(OH)$\dot{C}$H(OH)CH$_2$OH. [f] Isomer with β-OH axial (see ref. 12). [g] Isomer with β-OH equatorial (see ref. 12). [h] From ref. 5. [i] For reaction of $MeOCH_2\dot{C}HOH$ to $\dot{}CH_2CHO$. [j] For reaction of $\overline{\mathrm{OCH_2CH_2CH_2C}}\mathrm{H\dot{C}HOH}$ to $HOCH_2CH_2CH_2\dot{C}HCHO$.

Table 2. Optical absorption data for carbonyl-conjugated radicals $R_2\dot{C}$–C(O)R^{a} and yield and rate data for reaction of α,β-dihydroxyalkyl radicals with *p*-benzoquinone

Precursor	$\lambda_{max.}$/nm	$\lambda_{obs.}$/nm^{b}	$G(\dot{}CRR'OH)/G(OH + H)^{c}$	Extinction coefficient^{d} ε/m^2 mol^{-1}	$k(\dot{C}RR'OH$ + *p*-benzoquinone)^{a} /dm^3 mol^{-1} s^{-1}
Cyclohexane-1,2-diol	235	240	0.39^{e}	730	
2-Methylbutane-2,3-diol	220	240	0.76	710	1.9×10^9
Butane-2,3-diol	230	240	0.71^{e}	660	
2-Methylpropane-1,2-diol	235	240	0.81	840	2.0×10^9
Butane-1,2-diol	215	230	0.63	890	2.5×10^9
Propane-1,2-diol	220	230	0.80^{e}	490	
Ethane-1,2-diol	$\leqslant 210$	220	1.00^{e}	440	
Glycerol	$\leqslant 210$	230	1.00^{e}	540	
Erythritol	$\leqslant 210$	220	1.00^{f}	580	
Myoinositol	$\leqslant 210$	220	1.00^{e}	380	
2-Deoxyribose	$\leqslant 210$	240	0.93^{g}	400	1.6×10^9

[a] Individual isomeric radicals from substrates could not be distinguished. The errors in the rate constants are estimated to be ±10%. [b] Employed for kinetic studies. [c] Determined using *p*-benzoquinone (see text). [d] At $\lambda_{max.}$ measured at pH 1—3. [e] From ref. 7. [f] Assumed. [g] This number represents all radicals formed from this substrate that are able to reduce *p*-benzoquinone.

only the (pseudo-first-order) decay of the primary radicals was seen (though dehydration and production of carbonyl-conjugated radicals from these species has been established by e.s.r. experiments[19]). With these compounds $\lambda_{max.}$ for the carbonyl-conjugated radicals is presumably <210 nm (and/or $\varepsilon_{max.}$ <200 m^2 mol^{-1}). No meaningful kinetic analysis proved possible in these cases.

The fast build-up of the carbonyl-conjugated secondary radicals observable in the region 210—240 nm was shown by curve-fitting to be first order, and the rate constant k_{obs} was found to increase with increasing [H$^+$]. At low concentrations of [H$^+$] the k_{obs} values increased linearly with [H$^+$], and at higher [H$^+$] increase with [H$^+$] in the k_{obs} values became progressively less, though a plateau was not reached. This indicates that, at high [H$^+$], reactions other than simple protonation of the dihydroxyalkyl radical become rate-determining and we suggest that other protonation equilibria may be involved (see later). The bimolecular rate constants obtained from the initial slopes of the plots of k_{obs} *versus* [H$^+$] are presented in Table 1.

These rate constants approach the diffusion-controlled limit (10^{10} dm^3 mol^{-1} s^{-1}) for those compounds that contain electron-donating alkyl substituents, whereas for compounds with electron-withdrawing hydroxymethyl groups, the values are in the range 10^5—10^6 dm^3 mol^{-1} s^{-1}.

In the case of myoinositol a build-up of optical density was seen between pH 1—3 with a rate constant (k_{obs}) of 5.7×10^5 dm^3 mol^{-1} s^{-1}. At [H$^+$] $\geqslant$ 0.5 mol dm^{-3} a second component in the build-up became visible: from the dependence of its rate of formation on [H$^+$] the bimolecular rate constant for this process (presumably the *slower* dehydration of an isomeric radical) was determined as 1.0×10^5 dm^3 mol^{-1} s^{-1}.

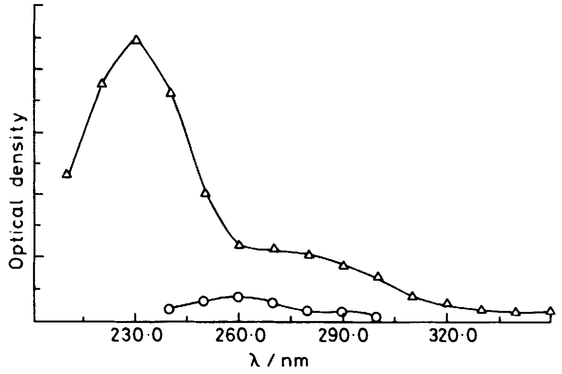


Figure 1. Optical density (arbitrary units) of absorptions detected during pulse-radiolysis (0.4 μs pulse) of solutions of 2-methylpropane-1,2-diol (0.1 mol dm^{-3}) saturated with N_2O at pH 6: ○ observed at 2—6 μs after pulse, and assigned to the initial α,β-dihydroxyalkyl radical $\cdot CH(OH)CMe_2OH$, △ observed 60—80 μs after pulse, and assigned to the dehydrated radical $\cdot CMe_2CHO$

The findings presented were used to test the applicability of the mechanism proposed by Henglein and co-workers[5] for ethane-1,2-diol (see Scheme 1). Thus if it is assumed that equilibrium [reaction *a*] is rapidly attained, that no significant radical termination occurs, and that k_2 [deprotonation, reaction *c*] is much larger than k_1 [for loss of water, step *b*], then kinetic analysis[5] gives equation (12) in which $\tau_{1/2}$ is the half-life of the build-up of $\cdot Y$ and $K = [H^+][\cdot CR(OH)CR_2(OH)]/[\cdot CR(OH)CR_2(OH_2)^+]$.

$$\tau_{1/2} = \frac{\ln 2}{k_1} + \frac{K \ln 2}{k_1}\,\frac{1}{[H^+]} \qquad (12)$$

On the basis of equation (12) a plot of $\tau_{1/2}$ *versus* $[H^+]^{-1}$ should give a straight line (so that values of k_1 can then be determined from the intercept and K obtained from the gradient). This behaviour was found to hold with all the diols studied (see *e.g.* Figure 3), provided that points obtained at relatively high $[H^+]$ were used: significant deviation from linearity was observed at low $[H^+]$, which could be due to distortion of the build-up by *bimolecular* decay of the initial radicals (and which would lead to smaller $\tau_{1/2}$ values than predicted; see also later).

Table 1 contains values of k_1 and K determined from these plots for the build-up of the absorption from the appropriate carbonyl-conjugated radicals derived from all 1,2-dihydroxyalkyl radicals studied except those from glucose and ribose. The overall rate constants for dehydration k_d (*i.e.* k_1/K) have been calculated on the assumption that the establishment of the equilibrium is rapid compared with dehydration. The k_d values are very similar to those obtained from the initial slopes of the plots of k_{obs} *versus* $[H^+]$. For those species (*e.g.* propane-1,2-diol) where isomeric radicals are formed, the reaction of the different radicals could not be distinguished (unlike the steady-state e.s.r. experiments, see above), except for myoinositol where the kinetic distinction between the two isomeric radicals is facilitated by the significant difference in their reactivity.

In the case of ethane-1,2-diol both the build-up of Y· and the decay of the primary radical (at 260 nm) were observable and analysable. The results of the kinetic analysis of the build-up of $\cdot CH_2CHO$ are presented in Table 1. Though the value of k_1 obtained (7.5×10^5 s^{-1}) is similar to that previously reported[6] (8.6×10^5 s^{-1}), the appropriate values of K differ appreciably (4.6×10^{-2} dm^3 mol^{-1} as compared with[5] 1.8×10^{-1} dm^3 mol^{-1}): this difference may reflect the lower radical concentrations (by a factor of *ca.* 3) in the present study, which makes a distortion of the equilibrium due to radical-radical reactions less likely.

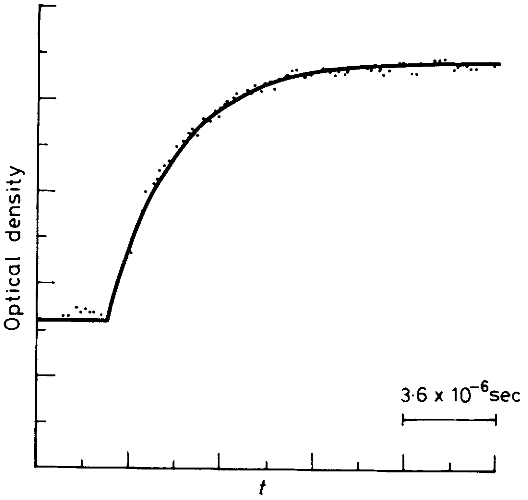


Figure 2. Build-up of the optical density (arbitrary units) at 240 nm (for the absorption assigned to the radical $\cdot CMe_2CHO$) in experiments with 2-methylpropane-1,2-diol at pH 3.25

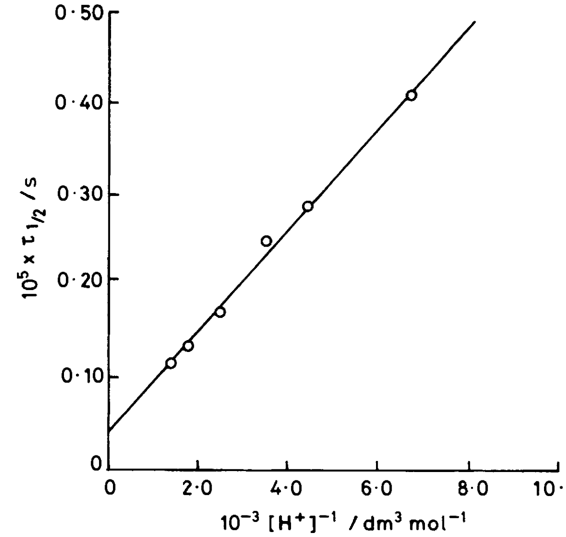


Figure 3. Dependence on $1/[H^+]$ of $\tau_{1/2}$ for the build-up of the dehydrated radical from cyclohexane-1,2-diol

We also studied the acid-catalysed loss of an alkoxy group[11] from α-hydroxy-β-alkoxy-substituted radicals, a process previously demonstrated *via* e.s.r. experiments.[16] With both $MeOCH_2CH_2OH$ and tetrahydrofurfuryl alcohol the acid-catalysed rearrangement of the initial radical into the appropriate secondary radical could only be monitored kinetically by the decay of the initial radical; the values of k_1 and K for the loss of the alkoxyl group from these two substrates are also given in Table 1.

For two substrates, namely 2-methylpropane-1,2-diol and 2-methylbutane-2,3-diol, it was found that, even at pH 6.5, the optical absorptions assigned to the 1,2-dihydroxyalkyl radicals were rapidly replaced (within the first 50 μs after the pulse) by those assigned to carbonyl-conjugated radicals characterized by maxima in the range 220—235 nm (see *e.g.* Figure 1). In each case the build-up of this secondary radical was monitored at

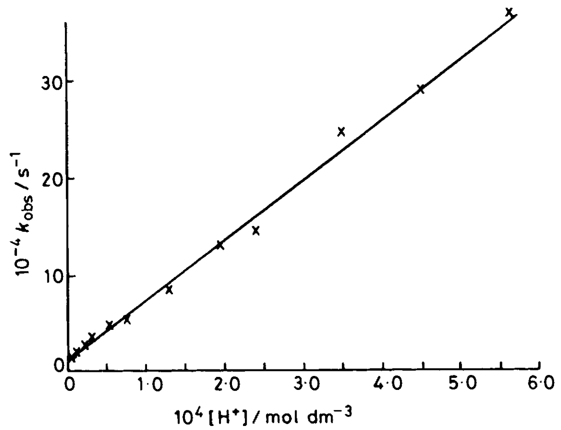


Figure 4. Variation of the pseudo-first-order rate constant (k_{obs}) for build-up of the absorption assigned to the dehydrated radical $^{\bullet}CMe_2CHO$ (obtained from 2-methylpropane-1,2-diol) with $[H^+]$

both 240 and 290 nm and kinetic analysis was possible after signal averaging. A plot of the experimentally determined rate constants (k_{obs}) for the former substrate *versus* $[H^+]$ is shown in Figure 4. A straight line through the origin would be expected if the only process occurring is an acid-catalysed dehydration, but this is clearly not so: even at $[H^+] \simeq 0$ the observed rate constant is *ca.* 1×10^4 s^{-1}, so that some other process which is independent of $[H^+]$ is occurring. For the radical from 2-methylbutane-2,3-diol the appropriate rate constant is 2×10^4 s^{-1}.

It is known that base-catalysed dehydration of 1,2-dihydroxyalkyl radicals can occur,[5-7] the initial step being ionization of the α-hydroxy group [equation (1)]. However, at pH 6.5 the concentration of OH^- is $< 10^{-7}$ mol dm^{-3}, which gives a maximum possible rate constant of *ca.* 10^3 s^{-1} for the OH^--induced dehydration [*i.e.* 10^7 (mol dm^{-3}) × *ca.* 10^{10} (dm^3 mol^{-1} s^{-1})]. Since this is an order of magnitude less than k_{obs} it is concluded that the process giving rise to the dehydrated radical is *spontaneous* elimination of water from the initial 1,2-dihydroxyalkyl radical. No similar reaction was seen with the other dimethyl-substituted radical studied (from butane-2,3-diol), suggesting that any spontaneous elimination from the latter must be appreciably slower than with 2-methylpropane-1,2-diol and 2-methylbutane-2,3-diol.

Confirmation of the rapid spontaneous dehydration of $^{\bullet}CH(OH)CMe_2OH$ and $^{\bullet}CMe(OH)CMe_2OH$ was obtained *via* photolysis experiments (*cf.* ref. 20) in which aqueous solutions of the parent diols (0.5% v/v) containing 2% propanone at pH 6 (and 3—5 °C) were irradiated in the cavity of an e.s.r. spectrometer. In each case signals were detected only from the radicals formed by *rearrangement* of first-formed α,β-dihydroxyalkyl radicals, namely $\bullet CMe_2CHO$ [*a* (3 H) 1.780, *a* (3 H) 2.073, and *a* (1 H) 0.280 mT, *g* 2.004 18, *cf.* ref. 21] and $\bullet CMe_2C(O)Me$ [*a* (3 H) 1.895, *a* (3 H) 2.045, and *a* (3 H) 0.203 mT, *g* 2.003 82, *cf.* ref. 22], rather than their precursors;* somewhat more intense (though otherwise identical) spectra were obtained in the presence of potassium peroxydisulphate (6 mmol dm^{-3}) (see *e.g.* Figure 5*a*). In contrast, when the photolysis was carried out for solution of the diols (0.5%) in propanone containing 1% di-t-butyl peroxide, only the parent radicals $\bullet CH(OH)CMe_2OH$ [*a* (1 H) 1.525 and *a* (6 H) 0.073 mT, *g* 2.002 97] and $\bullet CMe(OH)CMe_2OH$ [*a* (3 H) 1.935, *a* (OH) 0.010, and *a* (6 H) 0.035, *g* 2.002 93] were detected (see Figure 5*b*). These results clearly establish that the uncatalysed dehydration reaction occurs much more rapidly in the highly polar environment provided by the aqueous solution; since only the rearranged (and not the precursor) radicals are then detected we can place a lower limit on the rate of fragmentation as *ca.* 10^3 s^{-1}, which is consistent with the pulse-radiolysis results.

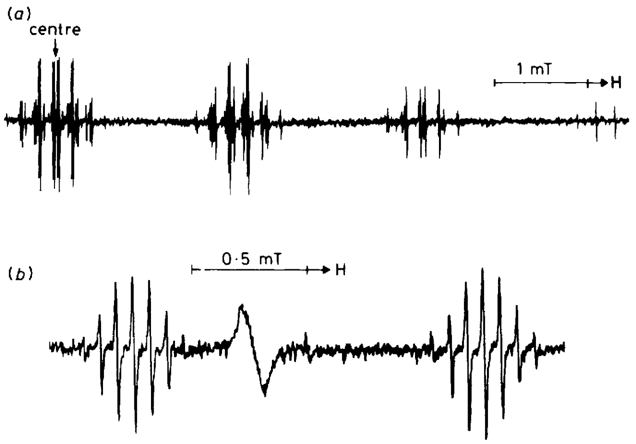


Figure 5(*a*). E.s.r. spectrum of $^{\bullet}CMe_2C(O)Me$ obtained by photolysis of an aqueous solution containing propanone (2% v/v), 2-methylbutane-2,3-diol (0.5%), and potassium peroxydisulphate (6 mmol dm^{-3}) at pH 3.2 and 3—5 °C; the same (but weaker) spectrum was obtained without the peroxydisulphate at pH 6; (*b*) E.s.r. spectrum of $^{\bullet}CH(OH)CMe_2OH$ obtained by photolysis at 3—5 °C of a solution of 2-methylpropane-1,2-diol (0.5% v/v) in propanone containing di-t-butyl peroxide (1%); the broad peak is the central line from $^{\bullet}CH_2COMe$, produced by hydrogen-abstraction from the solvent

For the radical from 2-methylbutane-2,3-diol, the activation parameters for the spontaneous dehydration were determined by employing pulse radiolysis (as above) to measure the rate constants at pH 6.5 as a function of temperature in the range −3—40 °C. The Arrhenius activation energy E_A was found to be 19 kJ mol^{-1} and $\Delta S^{\ddagger} = -93$ J mol^{-1} K^{-1}.

(ii) *Scavenger experiments.* To test the results and conclusions described in the previous sections, competition experiments were carried out using 1,1-dimethyl-4,4′-bipyridinium dichloride (methyl viologen, MV^{2+}) to scavenge the initial 1,2-dihydroxyalkyl radicals. We established that 1,2-dihydroxyalkyl radicals are readily oxidized by this substrate (which is converted into the long-lived radical-cation $MV^{+\bullet}$) while the carbonyl-conjugated radicals which result from acid-catalysed dehydration are unreactive [these radicals are weak oxidants (see *e.g.* ref. 7), in contrast to the reducing nature of 1,2-dihydroxyalkyl radicals].

A competition scheme was arranged in which oxidation of the initial radicals competes with acid-catalysed loss of water. Kinetic analysis of equations (13) and (14) leads to equation (15), where $[MV^+]_0$ and $[MV^+]$ are the concentrations (which are directly proportional to the observed optical densities) of the methyl viologen radical-cation at pH values where there is no competition and significant competition, respectively. Values of k_{14}, the rate constant for the production of $MV^{+\bullet}$ in the absence of competition, were obtained from kinetic analysis of the build-up of its absorption at 600 nm in experiments at pH 6 (see Table 3).

$$S^{1\bullet} + H^+ \longrightarrow Y^\bullet \qquad (13)$$

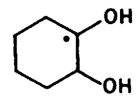
$$S^{1\bullet} + MV^{2+} \longrightarrow MV^{+\bullet} + S^{1+} \qquad (14)$$

$$\frac{[MV^+]_0}{[MV^+]} - 1 = \frac{k_d[H^+]}{k_{14}[MV^{2+}]} \qquad (15)$$

---

* Diols lacking the (β) dimethyl substituent give spectra from first-formed radicals under these conditions.

Table 3. Rate constants (k_{14})[a] for the reduction of methyl viologen (MV^{2+}) by α,β-dihydroxyalkyl and related radicals

Reducing radicals	$[R^{1\bullet}]/[R^{2\bullet}]$	k_{14}/dm^3 mol^{-1}s^{-1}	k_d/k_{14}
		1.3×10^9	1.0
$\cdot CMe(OH)CHMe(OH)$		1.1×10^9	0.9
$^{\bullet}CH(OH)CHMe(OH)$ ($R^{1\bullet}$)	0.35	*ca.* 1×10^8	1.8[b]
$HOCH_2\dot{C}Me(OH)$ ($R^{2\bullet}$)		*ca.* 5×10^8	0.9[b]
$^{\bullet}CH_2OH$		3×10^8[c]	
$^{\bullet}CH(OH)CH_2OH$		1.8×10^8	0.06
$^{\bullet}CH(OH)CH(OH)CH_2OH$		1.2×10^8	0.08[b]
$HOCH_2\dot{C}(OH)CH_2OH$			0.04[b]
$^{\bullet}CH(OH)CH(OH)CH(OH)CH_2OH$/ $HOCH_2\dot{C}(OH)CH(OH)CH_2OH$		7.2×10^7	0.04
Myoinositol ($R^{1\bullet}$)[d]	0.45	1×10^8	0.007
Myoinositol ($R^{2\bullet}$)[e]		2×10^7	0.007

[a] The errors in the rate constants are estimated to be ±10%. [b] k_d taken from e.s.r. experiments (Table 1). [c] *cf.* L. K. Patterson, R. D. Small, and J. C. Scaiano, *Radiat. Res.*, 1977, **72**, 218. [d] Isomer with axial β-OH. [e] Isomer with only equatorial β-OH.

Plotting ($[MV^+]_0/[MV^+]$) − 1 *versus* $[H^+]/[MV^{2+}]$ for some representative diols gave straight lines provided low values of $[H^+]$ were used, allowing k_d, the overall rate constants for dehydration, to be determined. The values obtained for the substrates studied by this method are shown in Table 1. At higher $[H^+]$ there were significant deviations from a straight line in the competition plots. This is interpreted in terms of the reversibility of the protonation of $S^{1\bullet}$ [equation (13)] (see Scheme 1).

We also note at this stage that the rate constants k_{14} decrease on replacing alkyl by hydroxyalkyl substituents in the glycol moiety. Further, for certain unsymmetric diols such as propane-1,2-diol and myoinositol, two independent exponential components were observed in the build-up of the absorption from $MV^{+\bullet}$. In these cases the kinetics of the build-up of $MV^{+\bullet}$ were analysed using a computer program that simultaneously analyses for the rate constants and the ratios of the two components (see Table 3).[23] The two components are attributed to reaction of isomeric 1,2-dihydroxyalkyl radicals formed by attack of HO· (showing that the structure of the radical has a marked effect on its ease of one-electron oxidation).

Discussion

The overall rates of acid-catalysed dehydration obtained by the three methods employed are in reasonable agreement (see Table 1), suggesting that the procedures used in obtaining these values are justified. We believe that the absolute magnitudes of the values obtained by the *direct* pulse-radiolysis methods are the most reliable, but note that this approach does not normally allow the distinction to be made between slightly different values for mixtures of isomeric radicals. However, this can be accomplished using e.s.r. (*e.g.* the evidence[12] that it is the radical from myoinositol with an axial β-OH that reacts by dehydration faster than the isomers with only equatorial β-OH groups).

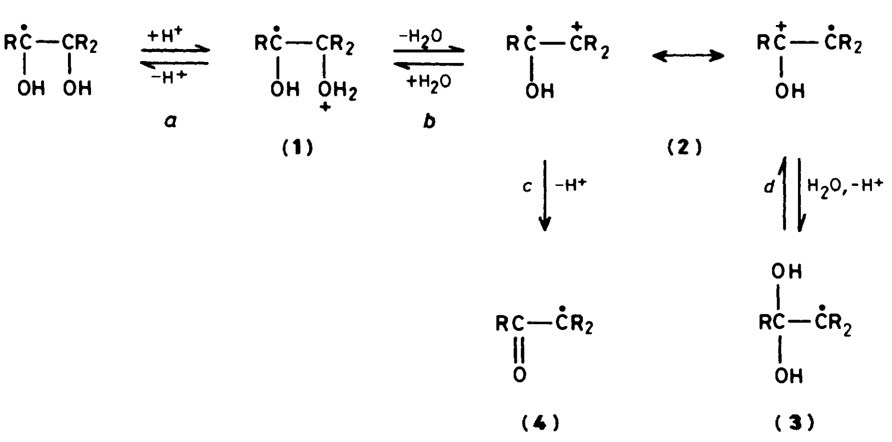
The results establish that the reaction is much faster for, *e.g.*, cyclohexane-1,2-diol (for which the value obtained from the direct pulse-radiolysis study is 1.2×10^9 dm^3 mol^{-1} s^{-1}) and butane-2,3-diol (9.8×10^8 dm^3 mol^{-1} s^{-1}) than for the radicals from polyhydric compounds (*e.g.* erythritol, 4.2×10^6 dm^3 mol^{-1} s^{-1}) and alkoxyalcohols (*e.g.* 2-methoxyethanol, 2.2×10^6 dm^3 mol^{-1} s^{-1}). These results are consistent with a reaction in which a radical-cation is formed (Scheme 1), since its formation would be expected to be assisted by the incorporation into the radical of $+I$ groups (Me), and retarded by the presence of further ($-I$) hydroxymethyl substituents. It also appears that alkoxy groups are less effective as leaving groups than hydroxy groups.

The separate values of K and k_1 as obtained from the treatment[5] of the kinetic data from the pulse-radiolysis experiments (Table1) can, in principle, provide greater insight into the role of substituents. For example, the values of k_1, the rate constant for loss of water from the protonated radical, show a variation in the direction anticipated if stabilization of the incipient radical-cation is important (*cf.* ref. 24). The decrease in k_1 observed on substituting a methyl group by a hydroxymethyl group, *e.g.* in going from propane-1,2-diol to glycerol, or from butane-2,3-diol to erythritol, suggests that the variation in k_1 is predominantly due to electronic factors (since the radicals from these compounds should have similar geometries, with the β-hydroxy group eclipsing the singly occupied orbital[8]).

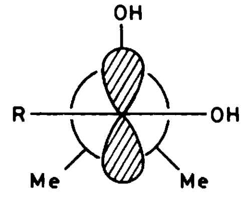
Parallel but more dramatic changes are found in the magnitude of K; however, whilst the structural dependence of the values of the pK_a's for the protonated radicals is in the direction which would have been predicted (*i.e.* $+I$ substituents decrease the acid strength and $-I$ substituents cause a significant increase), the absolute magnitudes (up to 3.1) are generally much larger than would be expected by comparison with the parent compounds[25] ($\leqslant 0.34$). Two factors might be expected to increase the base strength of the radicals in comparison with the parent molecules. The first is the electron-releasing $+M$ effect of the α-conjugated oxygen atom in the radicals (which should make it easier for these species to accept a positive charge). The second is the anticipated favourable interaction between the unpaired electron and the σ-bond of the β-OH_2^+ group; it is known[8] that an eclipsed geometry is favoured by α,β-dihydroxyalkyl radicals, as a result of the combination of $+M(\alpha)$ and $-I(\beta)$ effects, an interaction which should be enhanced by protonation. In support of the latter interpretation is the high value of K (2.35) – and hence the lowest basicity – for that isomer from myoinositol with only β-equatorial groups; the low rate of loss of β-OH in this species may well then reflect its comparative resistance to protonation.

It is also possible that the mechanism outlined in Scheme 1 (and used to derive the kinetic expression employed for analysis) is an oversimplification of a more complex overall scheme, so that the experimentally derived values of K and k_1 do not necessarily correspond to the acid strength of the appropriate protonated radical or its rate of dehydration, respectively. For example, Scheme 1 leads to the prediction that at very high acidity the rate of production of the carbonyl-conjugated radical should become independent of $[H^+]$: for glycerol and erythritol, for example, the limiting rate should be 6.5×10^5 and 3.5×10^5 s^{-1}, respectively (see Table 1). For these two compounds (chosen so as to keep the rates of dehydration within measurable range) the rates of formation of the dehydrated radicals were found to increase linearly from *ca.* 1.2×10^6 to *ca.* 4×10^6 s^{-1} in the range 0.5—2 mol dm^{-3} $HClO_4$. Though these rates are clearly above those calculated on the basis of Scheme 1 from data obtained at pH $\geqslant$ 1 (suggesting that Scheme 1 may be an oversimplification) it is also possible that the changes reflect protonation of γ-hydroxy groups in these radicals.

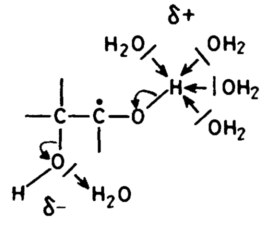
A more detailed overall mechanism (Scheme 2) should perhaps include firstly the possibility that the cation-radical (**2**),



Scheme 2.



(5)



Scheme 3.

produced from the protonated radical (1), may undergo rapid hydration in competition with proton loss from C_α-OH. It is also possible that reactions *b* and *d* are reversible and not unreasonable to assume that the rate of hydration of the carbocation-like intermediate (2) (*via* reverse reaction *b* and reaction *d* is comparable or greater than that for its deprotonation (*via c*). While further speculation is at this stage perhaps unjustified we nevertheless note that the good agreement between the values for k_d determined by the three different methods suggests that the values are significant, and that they describe the relative propensities of the series of diol radicals to be protonated and subsequently to undergo acid-catalysed dehydration.

From a comparison of the values of k_d (Table 1) and k_{14}, the rate constants for reduction of methyl viologen by the diol radicals (Table 3), it can be seen that both decrease as the substituents become more electron-withdrawing. This is as anticipated since with both reactions the positive charge developed in the transition state has to be accommodated within the framework of the diol. The ratio k_d/k_{14} (Table 3) decreases from *ca.* 1 for the radicals from cyclohexane-1,2-diol and butane-2,3-diol to a value of *ca.* 7×10^{-2} for the radicals from myoinositol, showing that the dehydration reaction is much more sensitive to substituent effects than the redox reaction with methyl viologen (*cf.* dehydration and oxidation reactions of hydroxycyclohexadienyl radicals[23-26]).

The rapid *uncatalysed* dehydration of the radicals from 2-methylpropane-1,2-diol [$\cdot$CH(OH)CMe$_2$OH] and 2-methylbutane-2,3-diol is of special note. It has been previously shown that in α,β-dioxygen-substituted radicals of this type the β-hydroxy group prefers to lie in the same plane as the orbital containing the unpaired electron,[8] a conformation (5) that will offer the smallest energy barrier to the formation of the radical-cation. We believe that the presence of the two β-methyl substituents will effectively lock the radical in this conformation (*cf.* the *gem*-dimethyl effect) and increase the overlap between the β-hydroxy group and the singly occupied orbital, thus lowering the energy barrier to loss of this group (the conformational effect of the methyl groups thus operates in the same direction as the electronic effect). A similar effect has been noted for loss of $HO_2\cdot$ from radicals of the type $R^1R^2C(OH)OO\cdot$ (where changing R^1 and R^2 from hydrogen to methyl leads to a 60-fold increase in rate[27]) as well as for base-catalysed dehydrations[7] [*cf.* equations (1) and (2)].

The low E_A-value for the spontaneous dehydration of (5; R = Me) (19 kJ mol^{-1}) is close to the energy of the hydrogen bond. The strongly negative $\Delta S^\ddagger$ value (-93 J mol^{-1} K^{-1}) is typical for reactions in which neutral molecules yield ions,[28,29] and in this case the magnitude suggests that the observed loss of entropy is largely attributed to the hydration entropy of the proton (-105 J mol^{-1} K^{-1}).[28,30] This leads to the suggestion that the dehydration proceeds by deprotonation of C_α-OH to give an ionized radical which undergoes a very rapid elimination[7] of OH^- from C_β (*i.e.* it is a base-catalysed reaction in which water is the base). On the other hand, if deprotonation of C_α-OH was the only rate-determining factor, the rate constant for the spontaneous dehydration should *decrease* on going from 2-methylpropane-1,2-diol to 2-methylbutane-2,3-diol, since the additional methyl group at C_α should decrease the acidity of C_α-OH. Since the opposite effect is observed (the rate constant for the radical from the latter is twice that from the former) we suggest that deprotonation of C_α-OH may be concerted with elimination of OH^- from C_β, a reaction which would be enhanced by the electronic and steric effects of the methyl group at C_α (Scheme 3).

Whether acid-catalysed processes similar to those described in the preceding section are of any significance in the radiation chemistry of DNA is dependent on the local hydrogen-ion concentration around the DNA helix. It is interesting to note that a recent report[31] suggests that in aqueous solution at an overall pH of 6—7 polyuridylic acid has a proton density, in the immediate vicinity of the strand, that corresponds to a concentration of 0.17 mol dm^{-1}, a concentration high enough to make these dehydration reactions rapid. However, we note that even if [H$^+$] is only *ca.* 10^{-7} mol dm^{-3} the dehydration reaction will still be fast (*ca.* 10^3 s^{-1}),[5,7] due to its efficient base catalysis.

Experimental

(*a*) *E.s.r. Experiments*.—Most of the e.s.r. experiments were carried out in York on a Varian E-104 spectrophotometer equipped with an X-band klystron and 100 KHz modulation. A mixing chamber was employed which allowed simultaneous mixing of three reagent streams, *ca.* 50 ms before passage through the cavity of the spectrometer. The flow was maintained with a Watson-Marlow 502S flow-inducer positioned on the inlet tubing, and pH measurements were made using a Pye-Unicam PW 9410 pH meter (with the electrode inserted into the effluent stream of the flow system). All solutions were extensively deoxygenated by the passage of oxygen-free nitrogen both prior to and during use. The first solution contained titanium(III) chloride (0.008 mol dm^{-3}), ethylenediaminetetra-acetic acid (3 g dm^{-3}), and either concentrated sulphuric acid or potasssium carbonate to give the desired pH, and the second contained hydrogen peroxide (0.033 mol dm^{-3}); the substrate was included in the third stream with a concentration typically in the range 0.01—0.1 mol dm^{-3}. Absolute radical concentrations were obtained by comparison of doubly integrated signals (using a Datalab DL 4000 microcomputer) with that from vanadyl sulphate (10^{-3} mol dm^{-3} $VOSO_4 \cdot H_2O$) obtained under identical spectrometer settings.

The photolytic e.s.r. experiments were carried out in Mülheim as previously described;[20] measurement of hyperfine splittings (to ± 7 μT) and *g*-values (to $\pm 2 \times 10^{-5}$) were obtained with an n.m.r. side-band technique, and second-order corrections have been made.

(*b*) *Pulse-radiolysis Experiments*.—The solutions typically contained 0.01—0.1 mol dm^{-3} substrate in triply distilled water, and they were saturated with N_2O in order to convert e_{aq}^- into HO•. The pH of the solution was adjusted with NaOH or $HClO_4$. The 3-MeV van de Graaff accelerator, and the optical detection and data collection systems have been previously described.[29,33] The solutions were irradiated at room temperature (20 ± 2 °C) with electron pulses of 0.1—0.4 μs duration that delivered doses corresponding to *ca.* 4 μmol dm^{-3} radicals. Dosimetry was performed with N_2O-saturated 10 mmol dm^{-3} KCNS solutions taking $\varepsilon[(SCN)_2^-]_{480\ nm}$ 760 m^2 mol^{-1} and *G*(OH) 6.0 molecules/100 eV (0.62 μmol J^{-1}).

The substrates were obtained from Aldrich, Fluka, and Merck and used as received except for 2-methylpropane-1,2-diol[34] and 2-methylbutane-2,3-diol which were synthesized as described previously.[35]

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