Pulse Radiolysis and E.S.R. Evidence for the Formation of an Alkene Radical Cation in Aqueous Solution

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Direct pulse radiolysis evidence, complemented by e.s.r. experiments, establishes that the radical cation $Me_2\overset{+}{C}-\dot{C}Me_2$ ($\lambda_{max.}$ *ca.* 290 nm) is formed by acid-catalysed elimination of OH^- from $\cdot CMe_2CMe_2OH$; the radical cation deprotonates to give $\cdot CH_2CMe{=}CMe_2$ with *k* 3.9×10^5 s^{-1}.

E.s.r. results have established[1] that isomerism of β-hydroxyalkyl radicals (*e.g.* the conversion of $\cdot CH_2CMe_2OH$ into $\cdot CMe_2CH_2OH$) can be brought about in acid solution. Although it has been suggested that the reaction proceeds *via* a short-lived radical cation, only circumstantial evidence could be obtained. We now present direct evidence that radical cations are indeed involved. Our approach has been to study the oxidation of 2,3-dimethylbutane-2-ol (**1**) using time-resolved pulse radiolysis and to complement this by steady-state e.s.r. measurements to identify the radicals involved.

Reaction of (**1**) with ·OH (from Ti^{III}–H_2O_2) in the e.s.r. cavity at pH >3 gave signals from the radicals (**2**) [*a*(2H) 2.18, *a*(H) 2.58 mT; *g* 2.0027] and (**3**) [*a*(2H) 2.28 mT; *g* 2.0027], together with (**4**) [*a*(6H) 2.30, *a*(6H) 0.05 mT; *g* 2.0027], which comprises *ca.* 25% of the mixture . As the pH was lowered to *ca.* 1, the spectrum of (**4**) was replaced by a new signal which characterizes the allyl radical (**5**) [*a*(3H) 1.575, 1.245, 0.30, *a*(1H) 1.31, 1.28 mT; *g* 2.0026]; no corresponding changes occurred in the concentrations of (**2**) and (**3**). Radicals (**4**) and (**5**) were also obtained by reaction of tetramethylethylene (**6**) with ·OH at pH > 3, with (**5**) dominant; at pH < 2, (**4**) again disappeared and the concentration of (**5**) increased slightly. The implication is that acid-catalysed loss of hydroxide has occurred, leading eventually to the formation of the allyl radical (**5**) by deprotonation of an intermediate radical cation (see Scheme 1).

Reaction of both (**1**) and (**6**) with ·OH was then carried out by pulse radiolysis of aqueous solutions at pH values in the range 5 to < 0; spectra were recorded in the range 240—600 nm (see *e.g.* ref. 2), but significant absorption was detected only in the range 240—340 nm.§ Under the conditions employed, reaction of ·OH and ·H with the substrate is essentially complete within the pulse. With substrate (**1**), two strong absorptions, with $\lambda_{max.}$ 250 and 290 nm respectively, were detected. The former of these was observed only at pH <2; as the pH was lowered below this value (to <0) both its yield and rate of formation increased [as shown by comparison of Figures 1(a) and 1(b)]. Its decay was observed to be bimolecular. The latter absorption was short-lived and observed only at very low pH (<0.3), where its first-order decay corresponded to the formation of the absorption at 250 nm [see *e.g.* Figure 1(c) and Figure 2].

The absorption at 250 nm was also detected following pulse radiolysis of solutions of (**6**) both at low pH and at pH >3; under these conditions, the e.s.r. results indicate that the allyl radical (**5**) is the major product, and we assign the absorption accordingly. It follows that the absorption at 290 nm arises from an intermediate in an acid-catalysed reaction which, as indicated by the e.s.r. results, involves the conversion of (**4**) into (**5**). We believe that this intermediate is the radical cation

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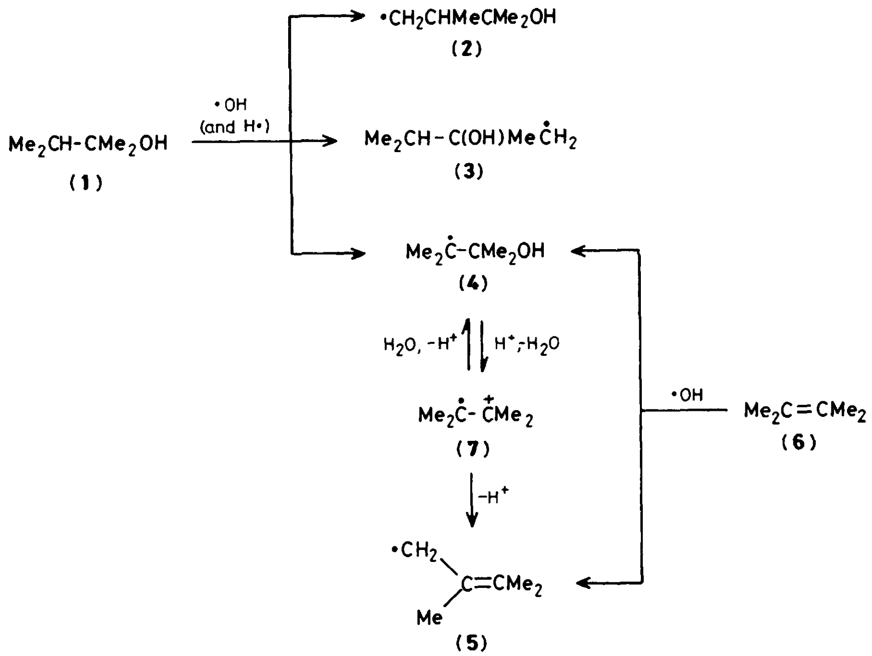
§ It should be noted that under these conditions formation of H· accompanies that of ·OH below pH *ca.* 2.5 (see *e.g.* ref. 3); the nature of the radicals formed from (**1**) should be unaffected.



Scheme 1

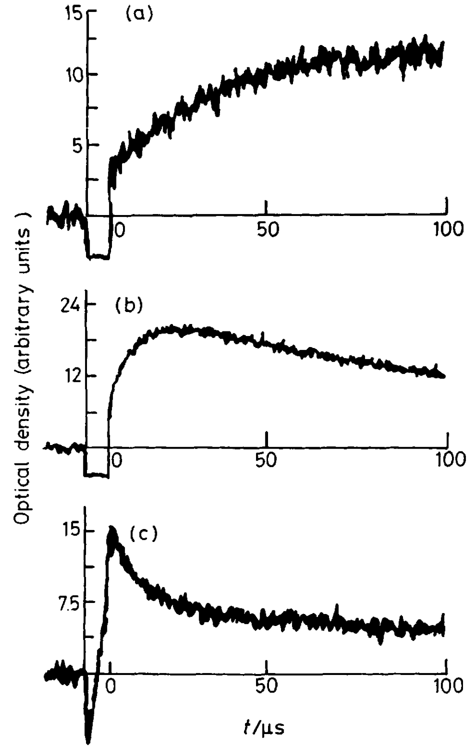


Figure 1. The variation of optical density with time following pulse irradiation of an aqueous solution (N_2O-saturated) of 2,3-dimethylbutane-2-ol (**1**) (0.01 mol dm^{-3}). (a) λ 250 nm, pH 1.1; (b) λ 250 nm, pH 0.1; (c) λ 295 nm, pH −0.1.

(**7**), which is formed by acid-catalysed elimination of OH^- from (**4**) and which is ultimately deprotonated, presumably by reaction with water. (We also assume that hydration can occur: *cf.* ref. 1.) In support of this assignment we note that the absorption maximum is close to that (λ 280 nm) reported for the cyclohexene radical cation (in n-heptane solution)[4] and is in agreement with that predicted on the basis of photoelectron spectroscopic studies of (**6**) itself.[5]

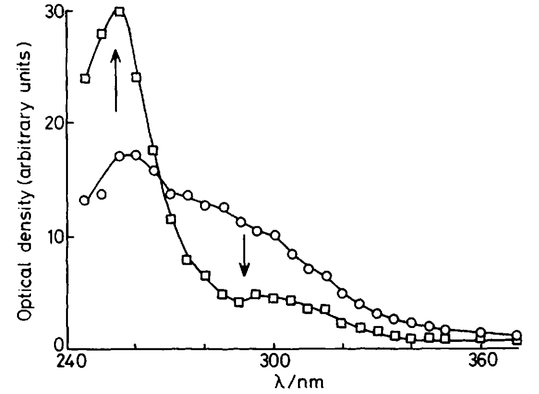


Figure 2. Absorption spectra recorded 0.5 μs (○) and 10 μs (□) after pulse irradiation of an aqueous solution (N_2O-saturated) of (**1**) (0.01 mol dm^{-3}) at pH *ca.* 0 ($HClO_4$, 1 mol dm^{-3}).

The pulse radiolysis results can be used to estimate both the rate constant for deprotonation of the radical cation (**7**) and the overall equilibrium constant for its formation from (**4**); on a micro-second time-scale the important reactions are (1) and (2). Assuming that equilibrium (1) is established before deprotonation takes place, equation (3) is then derived for the formation of (**5**).

$$(\mathbf{4}) + H^+ \xrightleftharpoons{K} (\mathbf{7}) + H_2O \qquad (1)$$

$$(\mathbf{7}) \xrightarrow{k} (\mathbf{5}) + H^+ \qquad (2)$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} + \frac{\ln 2}{kK[H^+]} \qquad (3)$$

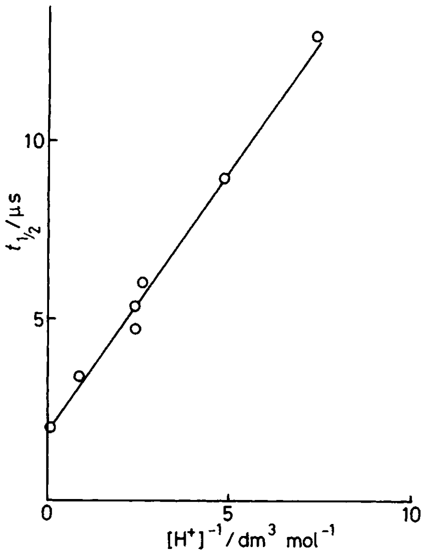


Figure 3. Variation with $[H^+]^{-1}$ of $t_{\frac{1}{2}}$ for the build-up of the absorption at 250 nm, in pulse radiolysis of solutions of (**1**) (0.01 mol dm^{-3}).

From the variation of $t_{\frac{1}{2}}$ [for the formation of (**5**)] with $[H^+]^{-1}$ at ambient temperature (see Figure 3) we calculate values of k and K as 3.9×10^5 s^{-1} and 1.2 respectively. These values also allow calculation of the pH required for 50% depletion of (**4**) [and conversion into (**5**)] in steady-state e.s.r. experiments (under which conditions it can be shown[1] that $[H^+]kK = k_t[R\cdot]_{tot}$, where k_t is the radical termination rate constant); estimating $[R\cdot]_{tot}$ as 3×10^{-6} mol dm^{-3} and assuming k_t as 10^9 mol^{-1} s^{-1} the predicted value is 2.2, in good agreement with that observed.

In corresponding pulse radiolysis experiments with Et_3COH there is a similar build-up of an absorption at 250 nm (but only at significantly lower pH). This evidently corresponds to the formation of the allyl radical $\dot{C}$HMe–C(Et)=CHMe (formed from the precursors $\cdot$CHMeCEt$_2$OH and Me$\dot{C}$H–$\overset{+}{C}$Et$_2$, see ref. 1). Kinetic analysis gives values for k' and K' of 2.5×10^5 s^{-1} and 0.1 respectively. The lower value for the equilibrium constant is presumably a consequence of the reduced stability, compared with (**7**), of the trialkyl-substituted radical cation.

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