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Formation of Alkyl Radicals by Photoionization of Alcohol Radicals Trapped in Glassy Matrices

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Experiments were carried out in order to elucidate the formation mechanism of $C_2H_5\cdot$ radicals formed by the UV irradiation ($250<\lambda<350$ nm) of $CH_3\dot{C}HOH$ radicals. The kinetics of the formation of the $C_2H_5\cdot$ radical was examined by means of ESR in neutral, acidic, and alkaline ethanol glasses at 77 K. The initial rate of the formation of $C_2H_5\cdot$ was nearly independent of the concentration of added acid (H_2SO_4), but it decreased sharply with that of added NaOH. Moreover, the limiting yield of $C_2H_5\cdot$ decreased with the concentrations of both the acid and the base. Our experimental results suggest that the $C_2H_5\cdot$ radicals are formed by this reaction:

$$C_2H_5OH_2^+ + e^- \longrightarrow C_2H_5\cdot + H_2O$$

The $C_2H_5OH_2^+$ ion and the electron result from the photoionization of $CH_3\dot{C}HOH$ radicals according to these reactions:

$$CH_3\dot{C}HOH \xrightarrow{h\nu} (CH_3CHOH)^+ + e^-$$
$$(CH_3CHOH)^+ + C_2H_5OH \longrightarrow CH_3CHO + C_2H_5OH_2^+$$

The free radicals produced by the abstraction of α hydrogen atoms from aliphatic alcohols have an absorption band between 200 and 350 nm.[1,2] Under irradiation in this wavelength range, $R\dot{C}HOH$ radicals are photolyzed, giving rise to $R\cdot$ and/or $RCH_2\cdot$ alkyl radicals.[3-6] The mechanism of the formation of $RCH_2\cdot$ radicals has not yet been definitely established, however.

By the photolysis of the $CH_3\dot{C}HOH$ radical (generated by the γ-irradiation of ethanol and trapped in the glassy state), which has been the most extensively studied,[3-6] both $\dot{C}H_3$ and $\dot{C}_2H_5$[3,5] are produced. The former disappears quickly upon hydrogen abstraction, whereas $C_2H_5\cdot$ reaches a stationary concentration. Moreover, it has been calculated[7] and confirmed experimentally[8] that $CH_3\dot{C}HOH$ trapped in polar solids may be photoionized in the near UV region, since its ionization potential is lowered from 7 eV in the gas phase to 2.5 eV in the solid state (2.5 eV corresponds to 495 nm).

The present work has been designed to show, using the example of $CH_3\dot{C}HOH$, that the photolytic formation of $RCH_2\cdot$ from $R\dot{C}HOH$ radicals trapped in glassy alcohols is a consequence of the photoionization rather than of the reaction of excited hydroxyalkyl radicals on the substrate, as has been suggested.[9]

Experimental

The ethanol was purified by fractional distillation. Neutral, acidic, and alkaline samples of ethanol containing 5% of water were degassed in "spectrosil" silica tubes and then γ-irradiated at 77 K in the glassy state, using a ^{60}Co source and a dose of 8×10^{19} eV ml^{-1}.

After irradiation, the samples were bleached by visible light to remove the trapped electrons. The ESR spectra were then recorded with a "STRAND Labs" 601 BX Spectrometer operating at 9.3 GHz. The concentration of radicals was determined by double integration and by comparison with a reference sample of pure glassy ethanol, taking $G(CH_3\dot{C}HOH)=8$[6] after bleaching. The UV irradiation was carried out by focusing the output of a 500 W mercury arc (Phillips SP. 500) onto the sample placed in a liquid-nitrogen Dewar vessel located in the cavity. Two intensities of illumination were used: 10^{17} quanta cm^{-3} s^{-1} and 2×10^{16} quanta cm^{-3} s^{-1} ($250\ nm<\lambda<400$ nm).

Results and Discussion

The rate of the formation and the limiting yield of $C_2H_5\cdot$ from UV-irradiated $CH_3\dot{C}HOH$ produced by γ irradiation have been studied in neutral ethanol, as well as in acidic and alkaline media, as a function of the concentrations of the added H_2SO_4 and NaOH.

During photolysis the overall concentration of radicals ($CH_3\dot{C}HOH$ and $C_2H_5\cdot$) was determined by integration, as has been indicated previously.

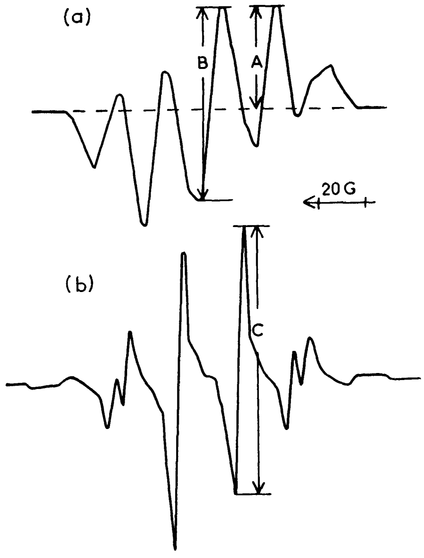

Fig. 1. a) ESR spectrum of $CH_3\dot{C}HOH$ radical observed at 77 K after γ irradiation of pure C_2H_5OH and subsequent bleaching to trapped electrones.
b) Spectrum of $C_2H_5\cdot$ observed at 77 K after UV photolysis of $CH_3\dot{C}HOH$.

The relative concentration of radicals was determined by measureing the amplitude of Bands A and B for $CH_3\dot{C}HOH$ (Fig. 1a) and of Band C for $C_2H_5\cdot$ (Fig. 1b). These amplitudes were correlated with the true concentration of radicals by calibration with the spectra of both radicals obtained separately, and then integrated.

The variations in the concentrations of the $CH_3\dot{C}HOH$ and $C_2H_5\cdot$ radicals with the time of UV irradiation are represented in Figs. 2 and 3.

In the case of neutral ethanol, the signal amplitude of $CH_3\dot{C}HOH$ falls to an undetectable level after 5 to 15 min of illumination, the rate of decrease depending on the UV-light intensity, while the concentration of $C_2H_5\cdot$ passes through a maximum and decays slowly by recombination after the complete consumption of $CH_3\dot{C}HOH$. The logarithmic plot of $CH_3\dot{C}HOH$ against the time of illumination is linear the slope being proportional to the intensity of UV irradiation, indicating a first-order decay of this radical (Fig. 4). This means that the optical density of the $CH_3\dot{C}HOH$ radical may be very small. Under the same conditions, the rate of the formation of $C_2H_5\cdot$ and its limiting yield are drastically reduced as the concentration of NaOH is increased (Fig. 2). On the other hand, the initial rate of the formation of $C_2H_5\cdot$ is about the same in acidic and neutral media, while its limiting yield is lowered by the presence of H_2SO_4.

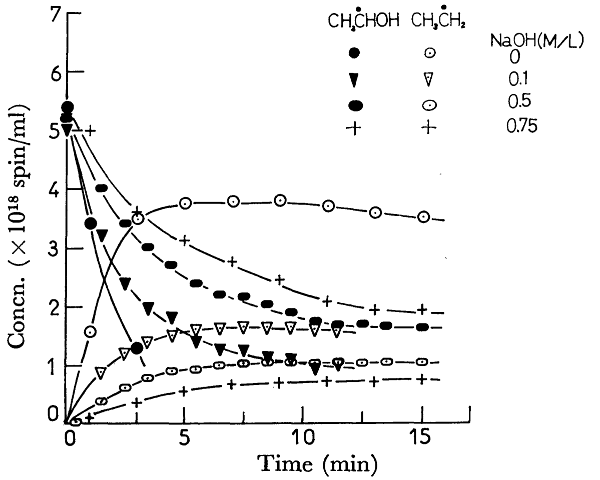

Fig. 2. Variation of the concentration of $CH_3\dot{C}HOH$ and $C_2H_5\cdot$ radicals in the course of UV photolysis ($I=2\times10^{16}$ quanta $cm^{-3}s^{-1}$): neutral and alkaline matrices.

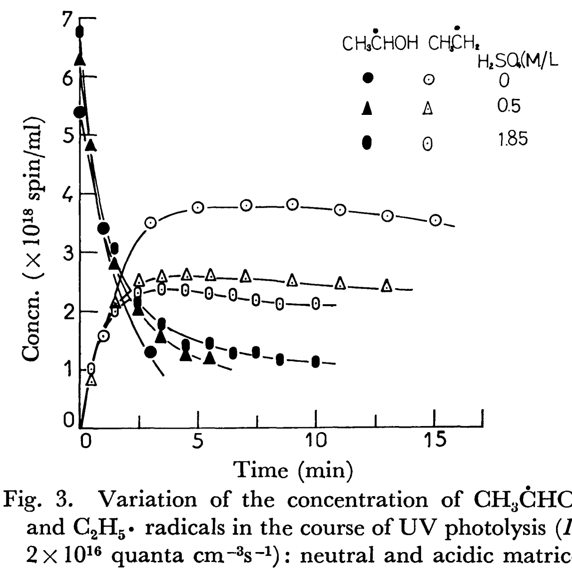

Fig. 3. Variation of the concentration of $CH_3\dot{C}HOH$ and $C_2H_5\cdot$ radicals in the course of UV photolysis ($I=2\times10^{16}$ quanta $cm^{-3}s^{-1}$): neutral and acidic matrices.

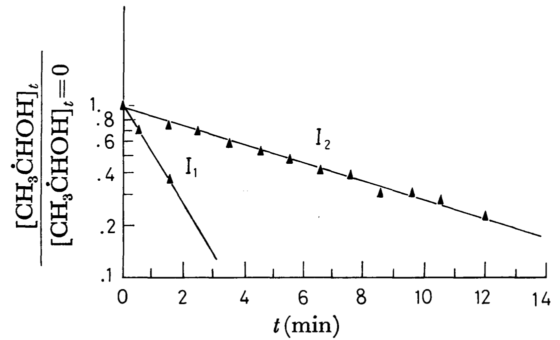

Fig. 4. Logarithmic plot of $[CH_3\dot{C}HOH]_t$ *versus* UV irradiation time, $[CH_3\dot{C}HOH]_{t=0}$ being the initial concentration. $I=10^{17}$ quanta cm^{-3} s^{-1}, $I_2=2\times10^{16}$ quanta cm^{-3} s^{-1}.

In order to interpret these results, which are summarized in Figs. 5 and 6, the reaction scheme proposed in a previous paper[8] by one of the present authors has been somewhat modified as follows.

The photoionization of $CH_3\dot{C}HOH$ and the consecutive ion-molecule reactions are:

$$CH_3\dot{C}HOH \xrightarrow{h\nu} (CH_3CHOH)^+ + e^- \tag{1}$$

$$(CH_3CHOH)^+ + C_2H_5OH \longrightarrow C_2H_5OH_2{}^+ + CH_3CHO \tag{2}$$

An increase in the concentration of $CH_3\dot{C}HO$ has actually been observed in the course of the photolysis of $CH_3\dot{C}HOH$.[9]

The released electron can participate in the competitive reactions:

$$e^- + 2C_2H_5OH \longrightarrow CH_3\dot{C}HOH + C_2H_5O^- + H_2$$

and/or

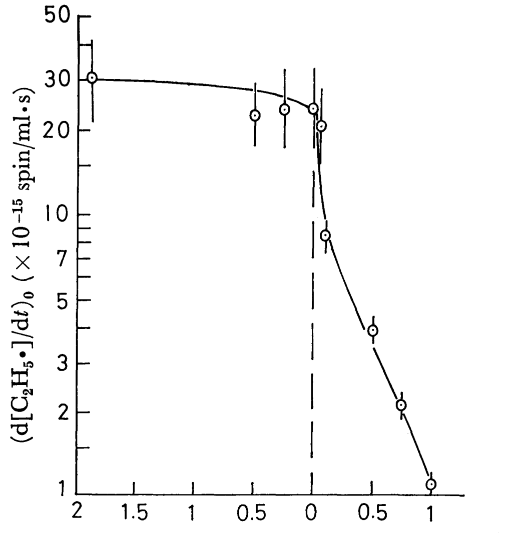

Fig. 5. Initial rate of formation of $C_2H_5\cdot$ as a function of H_2SO_4 and NaOH concentrations.

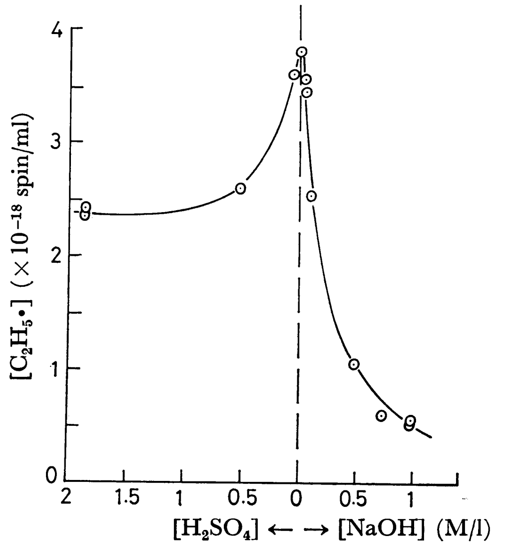

Fig. 6. Maximum yield of $C_2H_5\cdot$ as a function of H_2SO_4 and NaOH concentrations.

$$\left\{\begin{array}{l} e^- + C_2H_5OH \longrightarrow C_2H_5O^- + H\cdot \\ H\cdot + C_2H_5OH \longrightarrow CH_3\dot{C}HOH + H_2 \end{array}\right. \qquad (3)$$

$$e^- + C_2H_5OH_2{}^+ \longrightarrow H_2O + C_2H_5\cdot \qquad (4)$$

Reaction (3) is supported by the experimental finding that the $CH_3\dot{C}HOH$ radicals are formed by the decay of electrons formed when alkali metals are added to C_2H_5OH glass at 77 K,[10] while Reaction (4) has been suggested by Yoshida *et al.*[11] However, in the present case, the rate of Reaction (4) is most likely larger than that of Reaction (3).

A reaction similar to (4) has been proposed by Symons *et al.*[12] to account for the formation of methyl and isopropyl radicals in γ-irradiated solutions of methanol and isopropanol in glassy acidic ice. It may be pointed out that Reaction (4) is energetically favourable, the electron affinity of H_2O^+ being markedly larger than the C–O bond energy (12.6 eV against 4 eV[13]).

In the alkaline matrix, the $C_2H_5OH_2{}^+$ ions, precursors of $C_2H_5\cdot$, are scavenged by an excess of $C_2H_5O^-$ and/or OH^- ions:

$$\begin{array}{l} C_2H_5O^- + C_2H_5OH_2{}^+ \longrightarrow 2C_2H_5OH \\ \text{and/or} \\ OH^- + C_2H_5OH_2{}^+ \longrightarrow C_2H_5OH + H_2O \end{array} \qquad (5)$$

$CH_3\dot{C}HOH$ being regenerated by Reaction (3). The failure to observe the ESR spectrum of the solvated electron, even in the alkaline medium may be attributed to its high quantum yield of untrapping by UV light.[2]

It could be expected that, in the acidic matrix, the contribution of Reaction (4) would be enhanced by the increase in the concentration of $C_2H_5OH_2{}^+$. The decay in the yield of $C_2H_5\cdot$ as the concentration of H_2SO_4 is increased suggests that the electrons released by Reaction (1) are partially scavenged by $HSO_4{}^-$, producing $CH_3\dot{C}HOH$ radicals according to these reactions:

$$e^- + HSO_4{}^- \longrightarrow SO_4{}^{2-} + H\cdot \qquad (6)$$

$$H\cdot + C_2H_5OH \longrightarrow CH_3\dot{C}HOH + H_2 \qquad (7)$$

The hypothesis of an ionic contribution to the near-UV photolysis of hydroxyalkyl radials, trapped in glassy alcohols, seems, therefore, supported by the effect of added acids and bases presented here.

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