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ESR Studies on the Reaction of an OH Radical in α,β-Unsaturated Aldehyde[*1]

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ESR studies on the UV irradiated α,β-unsaturated aldehyde - hydrogen peroxide mixtures have been done at low temperature in order to examine the reactions of an OH radical with aldehyde: formyl hydrogen-abstraction, methyl hydrogen-abstraction, and addition to an olefinic bond. It has been shown that abstraction of a methyl hydrogen by an OH radical occurs in crotonaldehyde, whereas β-addition of an OH radical to an olefinic bond takes place in methacrolein and acrolein. A formyl hydrogen is unreactive with an OH radical in any case. The distribution of unpaired electron in the radicals was also discussed.

Several ESR studies were carried out in this laboratory concerning the reaction of an OH radical at low temperature with an organic compound having hydroxyl groups.[1] It was found that the OH radical abstracts mainly an α-hydrogen. In some cases the possibility of hydrogen-abstraction from

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[1] K. Kuwata, T. Ichikawa and K. Hirota, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 652 (1962); K. Kuwata, K. Nishikida, H. Kawazura and K. Hirota, This Bulletin, **36**, 925 (1963); T. Ichikawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 736 (1964); T. Ichikawa and K. Kuwata, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1516 (1965); K. Nishikida and K. Kuwata, *J. Phys. Chem.*, in press.

a hydroxyl group was discussed. In derivatives of glycol, successive reactions, RCHOH–RCHOH $\xrightarrow{\dot{O}H}$ RCHOH–R$\dot{C}$OH $\xrightarrow{h\nu}$ R$\dot{C}$OH–RCO, were considered on the basis of ESR spectral changes and analysis of evolved gas. In connection with these results, it is interesting to examine the reaction of an OH radical in α,β-unsaturated aldehyde systems, because the aldehyde has a formyl hydrogen, methyl hydrogens, and an olefinic bond, which is expected to bring about a competition among formyl hydrogen-abstraction, methyl hydrogen-abstraction, and addition to an olefinic bond.

Experimental

Materials. Hydrogen peroxide (30 wt%) was concentrated under reduced pressure to 95 wt%, and the antioxidant was removed by distillation before use. Reagent-grade crotonaldehyde, methacrolein, and acrolein were purified by fractional distillation under reduced pressure.

Procedure. The aldehyde containing 10 mol% hydrogen peroxide was introduced into a quartz sample tube and deaerated by freezing and thawing under vacuum. The sample in a clear glassy state was illuminated in a quartz Dewar vessel at 77°K with the light from a low pressure mercury lamp. After illumination for 3hr the sample was transferred quickly into a cavity which was immersed in liquid nitrogen. Warming of the sample was carried out inside the cavity in the range 77—300°K. Details of the cavity have already been shown.[2] Measurements were done at X-band with a homemade spectrometer using 450kc/sec field modulation.

Results and Discussion

Crotonaldehyde. Figure 1a shows the ESR spectrum of an illuminated glass of a crotonaldehyde-hydrogen peroxide mixture at 80°K. On warming the sample to 160°K the spectrum changed as shown in Fig. 1b. The intensity of the signal was not reduced lower than 50% of the initial state. The spectrum consists of equally spaced four lines with the separation of 12.9 G, the intensity ratios of the lines being 1.2 : 2.8 : 2.8 : 1.0. Since the ratios are closer to 1 : 3 : 3 : 1, the radical should have equally interacting three protons.

The four line spectrum can be interpreted by the radical formed by abstraction of a methyl hydrogen; $\dot{C}H_2$-CH=CH-CHO↔CH_2=CH-$\dot{C}$H-CHO↔CH_2=CH-CH=CH-$\dot{O}$. The identification is based upon the following arguments. The molecular orbital calculation of pi-electron spin densities using McLachlan procedure[3] gave the values as follows;

	C_1	C_2	C_3	C_4	O_5
$\rho=$	0.6456	−0.1704	0.5051	−0.0324	0.0521
a(G)=	14.6	3.9	11.4	0.7	

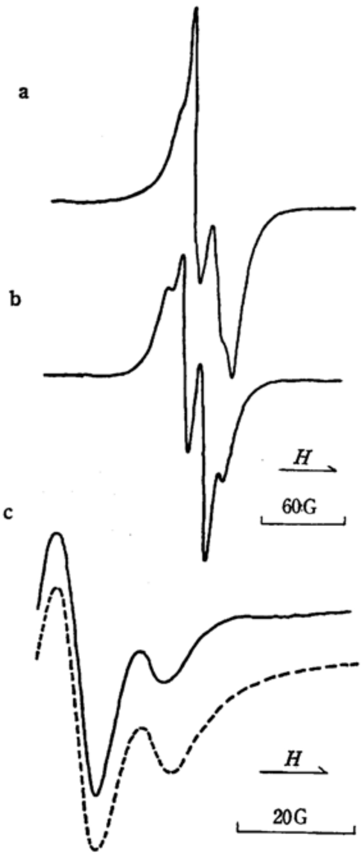

Fig. 1. ESR spectra of an illuminated glass of crotonaldehyde containing 10 mol% hydrogen peroxide.
a) Spectrum measured at 80°K
b) Spectrum measured at 160°K
c) Computed curve (dotted lines)

Hfs constants were estimated by taking into account McConnell's relation[4]

$$a = Q\cdot\rho \qquad (1)$$

where Q is a constant (23 G) and ρ is the spin density on the carbon. The results indicate that the C_2 and C_4 protons do not contribute strongly to the hfs and the difference between C_1 and C_3 proton hfs constants is not larger than the observed line width (5 G). Thus it seems probable that the postulated radical gives the four line spectrum due to the predominant interaction with two C_1

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[2] K. Kuwata and K. Hirota, This Bulletin, **34**, 458 (1961).

[3] A. D. McLachlan, *Mol. phys.*, **3**, 233 (1960). The parameter λ in the procedure was given $\lambda=1.2\beta$. The coulomb integrals and the resonance integrals were assumed to be $\alpha_O=\alpha_C+1.5\beta$, $\alpha_C=\alpha_{C'}-0.15\beta$, $\beta_{CO}=1.6\beta$, and $\beta_{CC'}=\beta$, which were used in the calculation on the anion radicals of aromatic carbonyl compounds (P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962)).

[4] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

and one C_3 protons. The computed curve with Lorentzian line shapes in consideration of these results is shown in Fig. 1c.

It is apparent that another possible radical such as CH_3–CH=CH–$\dot{C}$=O (hydrogen-abstraction from a formyl group) and CH_3–CHOH–$\dot{C}$H–CHO (OH-addition to an olefinic bond) can not give the four line spectrum. The reason for this is that the former is a sigma radical in which an unpaired electron is localized on a sigma orbital of a carbon atom⁵⁾ and has only one interacting proton, and the latter has unequally interacting three protons, *i. e.*, α-, β-, and formyl protons.

Although the spectrum before warming of the sample exhibits asymmetric line shapes, it apparently already contains the characteristic features of the four lines in the spectrum, which suggests that the initial spectrum consists of the four lines and some additional lines. The spectral change, therefore, is likely due to the disappearance of more unstable radicals.

An ESR spectrum of illuminated crotonaldehyde without hydrogen peroxide was also examined, the results showing a relatively small radical yield, *i. e.*, one twentieth in the case containing hydrogen peroxide.

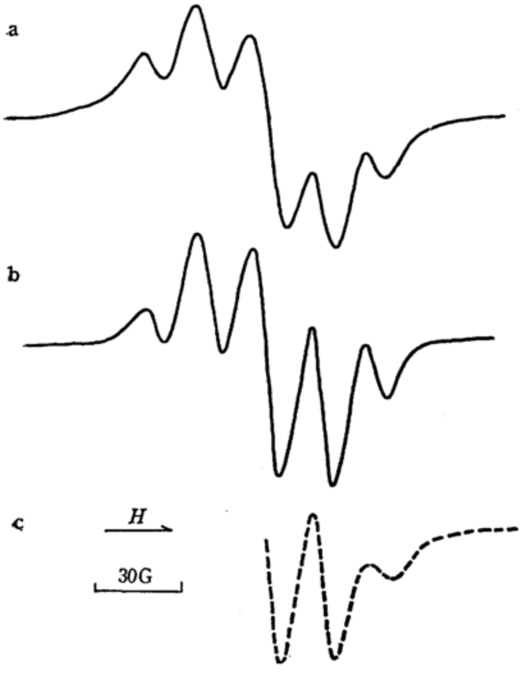

Fig. 2. ESR spectra of an illuminated glass of methacrolein containing 10 mol% hydrogen peroxide.
a) Spectrum measured at 80°K
b) Spectrum measured at 180°K
c) Computed curve

Methacrolein. An illuminated glass of methacrolein-hydrogen peroxide mixture gave the spectrum as shown in Fig. 2a. On warming the sample to 180°K, the spectrum became well resolved five lines with separations of 19.5 G whose intensity ratios were 1.1 : 3.7 : 5.5 : 3.4 : 1.0. The radical should have equally interacting four protons because the theoretical intensity ratios are 1 : 4 : 6 : 4 : 1.

If a methyl hydrogen is abstracted by an OH radical, the radical CH_2=C(CHO)–$\dot{C}H_2$↔$\dot{C}H_2$–C(CHO)=CH_2 would be formed. This radical would be essentially the allyl type with equally interacting four protons. The hfs constants of 19.5 G, however, are considerably larger than the expected value, *i. e.*, 14.4 G observed in the allyl radical.⁶⁾ It seems difficult to attribute the five line spectrum to the supposed radical.

In β-addition to an olefinic bond, the radical CH_2OH–$\dot{C}$(CH_3)–CHO↔CH_2OH–C(CH_3)=CH–$\dot{O}$ is formed. The five line spectrum may be accounted for by this radical on the assumption of a conformation as follows: 1) The methyl group rotates so rapidly that as all the hfs constants of the methyl protons are substantially equivalent. 2) The methylene group is fixed on such positions that one of the methylene protons has a hfs constant around 19.5 G, while the other less than the observed line width (8 G). According to Heller and McConnell,⁷⁾ the hfs constant of each β-proton is given by

$$a_{\beta_i} = 2Q_\beta \cdot \rho_\alpha \cdot \cos^2\theta_i \qquad (2)$$

where Q_β is a constant, ρ_α a spin density on an α-carbon, and θ_i an angle between a H_i–C_β–C_α plane and an axis of a p_z orbital occupied by an unpaired electron. For a rapidly rotating methyl proton, a value of $\cos^2\theta_{av}$ is equal to 1/2. Hence the hfs constants of the methyl protons are given by $a_\beta(CH_3) = Q_\beta \cdot \rho_\alpha = 19.5$ G. Substitution of the values given above for a_{β_1} and $Q_\beta \cdot \rho_\alpha$ into Eq. (2) leads to a value of 45° for θ_1. Provided that the difference between θ_1 and θ_2 is 120°, θ_2 is either 75° or 15°. Taking the former, we found a value $a_{\beta_2} = 2.6$ G from Eq. (2).

It is added here that as the π-electronic system of this radical resembles that of the allyl radical,⁶⁾ the spin density on the formyl carbon is expected to be small and also the hfs constant of a hydrogen attached to the formyl carbon is expected to be less than the observed line width. The computed curve is also shown in Fig. 2c for comparison with the observed spectrum.

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5) F. J. Adrian, E. L. Cochran and V. A. Bowers, *ibid.*, **36**, 1661 (1962); *ibid.*, **43**, 462 (1965).

6) J. E. Bennett and A. Thomas, *Proc. Roy. Soc.*, **208A**, 123 (1964).

7) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

Fessenden and Schuler⁸⁾ evaluate a value $Q_\beta = 29.3$ G from their results of a number of aliphatic hydrocarbon radicals. Using the value, we found 0.667 for ρ_α. Fischer⁹⁾ showed experimentally that ρ_α in a substituted alkyl radical $X_1-\underset{\substack{|\\ X_2}}{\dot{C}}-X_3$ can be calculated by use of a product rule

$$\rho_\alpha = \prod_{i=1}^{3} (1 - \Delta(X_i)), \tag{3}$$

where $\Delta(X_i)$ is a fraction which expresses the spin-density withdrawing-power of an X_i group. Substituting the values given by Fischer⁹⁾ ($\Delta(CH_3) = 0.081$ and $\Delta(CH_2OH) = 0.079$) and authors¹⁰⁾ ($\Delta(CHO) = 0.198$) into Eq. (3), we obtain a value $\rho_\alpha = 0.678$, which is very close to the experimentally derived value.

Acrolein. An illuminated glass of an acrolein-hydrogen peroxide mixture gave the spectrum as shown in Fig. 3a together with the spectrum observed after warming of the sample to 160°K (Fig. 3b). The spectrum at 160°K consists of unequally spaced four lines with the separations of 17.0, 13.0, and 17.0 G in turns and the intensity ratios of 1.0 : 1.4 : 1.5 : 1.2. The results suggest that the radical formed has two unequally interacting protons with the hfs constants of 17.0 and 30.0 G, respectively.

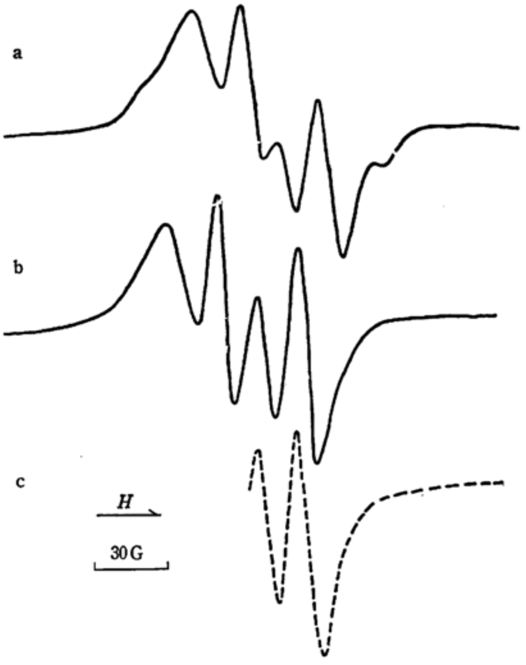

Fig. 3. ESR spectra of an illuminated glass of acrolein containing 10 mol% hydrogen peroxide.
a) Spectrum measured at 80°K
b) Spectrum measured at 160°K
c) Computed curve

The spectrum can be attributed to the radical produced by β-addition to an olefinic bond; $CH_2OH\text{-}\dot{C}H\text{-}CHO \leftrightarrow CH_2OH\text{-}CH{=}CH\text{-}\dot{O}$. The molecular orbital calculation³⁾ leads to predicted values for pi-electron spin densities on the radical as follows:

	C_1 —	C_2 —	O_3
$\rho =$	0.758	0.048	0.194
a(G) $=$	17.4	1.1	

On substituting a value $a_1 = 17.0$ G into Eq. (1), the spin density on C_1 is found to be 0.739, which shows good accordance with the calculated value.

The angle, θ_1 and θ_2 for the methylene proton can be calculated from Eq. (2) by using the values $a_{\beta_1} = 30.0$ G, $Q_\beta = 29.3$ G, and $\rho_\alpha = 0.739$, which gives the values 34° and 86°, respectively. As a result, the angle $\theta_2 = 86°$ leads to a value $a_{\beta_2} = 0.22$ G. The computed curve is shown in Fig. 3c.

Application of the values $\rho_\alpha = 0.739$ and $\Delta(CH_2OH) = 0.079$ to the Eq. (3) leads to a value $\Delta(CHO) = 0.198$, which may be compared with the value $\Delta(CRO) = 0.162$ given by Fischer.⁸⁾

Summary and Conclusion

We have attempted to study by the ESR method the reaction of an OH radical in α,β-unsaturated aldehyde at low temperature. It has been found that abstraction of a methyl hydrogen by an OH radical occurs in crotonaldehyde, whereas β-addition of an OH radical to an olefinic bond takes place in methacrolein and acrolein. A formyl hydrogen seems to be unreactive with an OH radical in any case. Further work will be necessary to determine what factors are in favor of abstraction or addition especially in crotonaldehyde and methacrolein.

The values of pi-electron spin-densities obtained by the molecular orbital calculation using McLachlan procedure have shown good accordance with those estimated from experimental data on the radicals in crotonaldehyde and acrolein. Application of Fischer's treatment has been helpful for discussions on spin densities and hfs constants.

The authors wish to express their thanks to Professor Kozo Hirota for his encouragement throughout this study.

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8) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2141 (1963).

9) H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964); *ibid.*, **20a**, 428 (1965).

10) See the next section of the text.