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Electron Spin Resonance Study of Short-Lived Free Radicals in Photoreduction of Benzophenone

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By observing electron spin resonance spectra during photolysis at room temperature, kinetic behaviors of short-lived free radicals are studied in photoreduction of benzophenone in alcohols, especially in ethanol, with and without sodium methoxide. In neutral solution, diphenylhydroxymethyl radicals and hydroxyethyl radicals are observed simultaneously. This is a firm evidence, obtained from ESR, of hydrogen abstraction of excited benzophenone from ethanol. Results indicate that (1) free radicals are the most efficiently generated by the light of ~350 nm, (2) hydroxyethyl radicals transform into diphenylhydroxymethyl radicals if the concentration of benzophenone is high, and (3) the latter radicals disappear following the second order reaction. In the presence of sodium methoxide, diphenylhydroxymethyl radicals transform into benzophenone ketyl anions.

Rate constants are determined, being 3×10^7 and $\sim10^4$ mole$^{-1}\cdot$l$\cdot$sec^{-1} for the combination reaction between diphenylhydroxymethyl radicals and the proton transfer reaction from diphenylhydroxymethyl radical to methoxide ion, respectively.

Photoreduction of benzophenone in alcohols is one of the most extensively studied subjects in photochemical reactions. Triplet excited benzophenone abstracts hydrogen from the solvent molecule to form diphenylhydroxymethyl radicals, which combines with each other to benzpinacol in neutral solutions.[1] Porter and Wilkinson proved directly by flash photolysis technique that the diphenylhydroxymethyl radicals were formed as intermediates in the photoreduction of benzophenone, and also that they converted to benzophenone ketyl anions in alkaline solutions.[2] Beckett and Porter determined the rate constant of reactions involving the diphenylhydroxymethyl radicals and ketyl anions.[3]

Since Livingston and Zeldes developed a technique of observing electron spin resonance (ESR) spectra of transient free radicals in liquids during photolysis,[4] the technique has been successfully employed to several photochemical reactions. Among them, Wilson studied free radicals photolytically generated from aromatic carbonyl compounds,[5-9] and found that diphenylhydroxymethyl radical was formed from benzophenone in alcohols, tetrahydrofuran,[6] and triethylamine.[9] From the observed hyperfine coupling constants, the structure of the free radical, especially the effect of hydrogen bond on the coupling constant of hydroxy proton, was studied in detail in referring to a molecular orbital calculation. The ESR observation gave an evidence that the photoreduction process involves the transient diphenylhydroxymethyl radical,

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[1] For example, (a) J. N. Pitts, Jr., B. L. Letsinger, R. T. Taylor, J. M. Patterson, G. Rectenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959); (b) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

[2] G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

[3] A. Beckett and G. Porter, *ibid.*, **59**, 2038 (1963).

[4] R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966)

[5] R. Wilson, *Can. J. Chem.*, **44**, 551 (1966).

[6] R. Wilson, *J. Chem. Soc. (B)*, **1968**, 84.

[7] R. Wilson, *ibid.*, **1968**, 1581.

[8] R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc. (C)*, **1969**, 2203.

[9] R. S. Davidson and R. Wilson, *J. Chem. Soc. (B)*, **1970**, 71.

though the counterpart radical formed from solvent was unable to be detected.

These investigations encouraged us to extend ESR study to kinetical behavior of transient free radicals during photolysis. In the present investigation, the ESR technique is employed to study the photoreduction of benzophenone in alcohols with the intention of elucidating the kinetical behavior of radicals, their formation and decay, in neutral and alkaline solutions.

Experimentals

Apparatus used was essentially the same as described by Livingston and Zeldes.[4] Illuminating light from a superhigh pressure mercury lamp (Philips, SP-500, 500 watts) passed throuth a quartz lens and a grid plate of a resonance cavity (Varian, Model E-4531), connected to a conventional ESR spectrometer (Varian, E-3), to a quartz flat cell. A glass cut-off filter or a mesh was inserted between the lens and the grid plate, if necessary, to regulate the illuminating light.

Analytical grade chemicals were used without further purification. Air dissolved in solutions was removed by bubling helium gas for at least half an hour before photolysis.

Flow rate of solutions was 4.3 m*l* per min. As the effective volume of the cell was 0.052 m*l*, the resident time of the solution in the cell was estimated to be 0.7 sec, during which free radicals were generated by light, and their ESR spectra were detected. Flowing through the cell, the solutions were heated by the light to about 5° higher than the room temperature (20°±2°C).

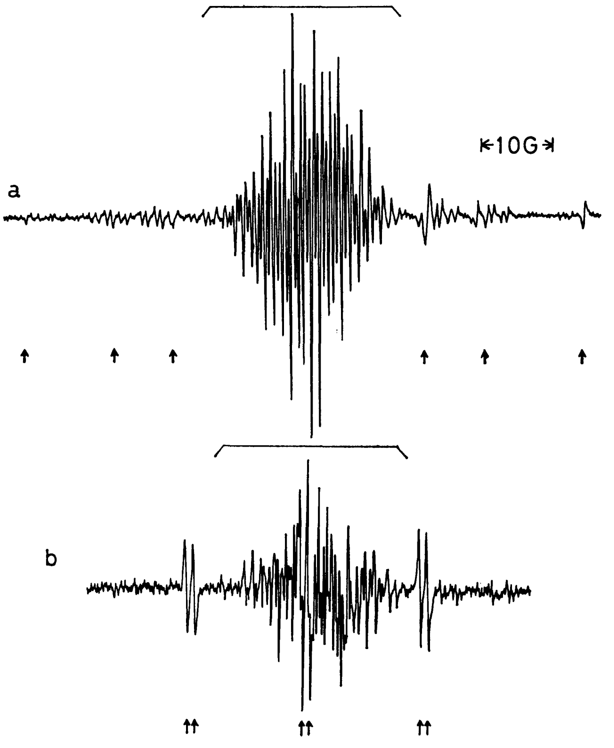

Fig. 1. Electron spin resonance spectra observed during the photolysis of benzophenone (0.44 mol·l^{-1}) in (a) ethanol and (b) methanol at room temperature. Brackets and arrows indicate the spectra of free radicals formed from benzophenone and those formed from alcohols, respectively. Amplitude of magnetic field modulation: 0.5G.

Results

Figure 1 shows the ESR spectra observed from solutions of benzophenone in ethanol and methanol. They are composed of three components: the spectra indicated with arrows due to free radicals, $CH_3\dot{C}HOH$ and $\dot{C}H_2OH$, formed by hydrogen abstraction from ethanol and methanol, respectively, central complex spectra indicated with blackets due to free radicals formed from benzophenone, and other spectra which are rather weak and are not identified. The free radicals fromed from solvent molecules are identical with those reported by Livingston and Zeldes.[4]

The yield of free radicals was larger in ethanol than in methanol. Therefore, ethanol is used as solvent in all experiments described below.

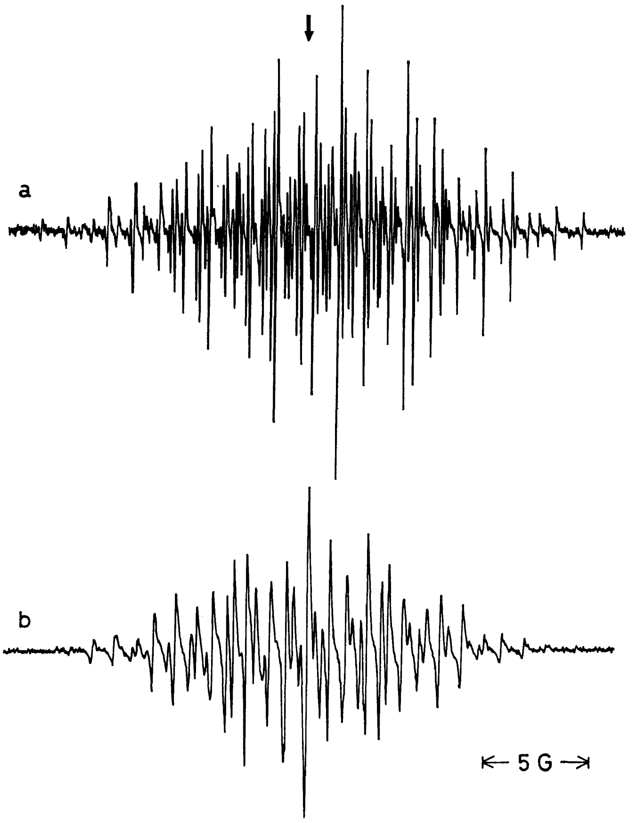

Fig. 2. Electron spin resonance spectra observed during the photolysis of benzophenone (0.44 mol·l^{-1}) in ethanol at room temperature. Amplitude of magnetic field modulation: 50 mG. (a) Diphenylhydroxymethyl radical formed in neutral solution and (b) benzophenone ketyl anion formed in the presence of sodium methoxide. Arrow indicates the center of spectra.

When the central spectrum is recorded with a small amplitude of magnetic field modulation, well resolved hyperfine structure is observed as shown in Fig. 2, *a*. The structure is described by equivalent four protons at the ortho-positions of the rings with hyperfine coupling constant of 3.1G, four protons at meta-positions with the coupling constant of 1.2G, two protons at the para-positions of the rings with the constant of 3.6G, and a proton in hydroxy group with the constant of 2.9G, and it is reasonably attributed to diphenyl-

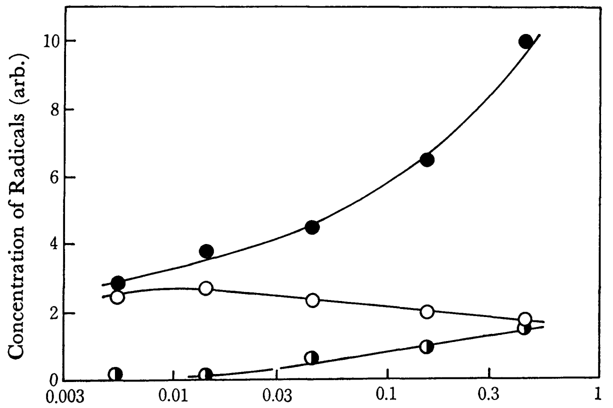

Fig. 3. Dependence of observed concentration of free radicals formed during the photolysis of benzophenone in ethanol on the concentration of benzophenone. ●; Diphenylhydroxymetyl radical, ○; hydroxyethyl radical, ◑; unidentified radical.

hydroxymethyl radical. The observed hyperfine coupling constants are compared with those reported, 3.23, 1.23, 3.64, and 2.91G, respectively.[6] The spectrum of $CH_3\dot{C}HOH$ vanishes if recorded with the small amplitude of field modulation, because of its larger width of hyperfine lines.

Observed intensity of the three spectra are plotted as a function of the concentration of benzophenone in solution, as shown in Fig. 3. At the lowest concentration examined, the observed yield of diphenylhydroxymethyl radical is about the same as that of $CH_3\dot{C}HOH$. With the increasing concentration of benzophenone, the yield of diphenylhydroxymethyl radical increases remarkably, while that of hydroxyethyl radical reaches the maximum and then gradually falls down.

The unidentified spectrum also increases in its intensity with the increasing concentration of benzopheneone. It is probably due to free radicals formed by the reaction between the primarily formed radicals and benzophenone.

The intensity of observed spectra was calibrated with reference to that of diphenylpicrylhydrazyl solution in ethanol. The concentration of diphenylhydroxymethyl radical was estimated to be 4.5×10^{-7} mol·l^{-1} for the highest concentration of benzophenone examined (0.44 mol·l^{-1}), though the value includes the uncertainty factor of 2.

The yield of diphenylhydroxymethyl radical was studied as a function of light intensity, at the benzophenone concentration of 0.14 mol·l^{-1}. It was found to be proportional to the 0.37th power of the light intensity. The radicals disappear probably in combining with each other following the second order kinetics rather than the first order one. The deviation of exponent from 0.5 may have been caused by the fact that the resident time of solution in the resonance cavity is so short that the steady state concentration of the radicals is not completely attained.

The lifetime of diphenylhydroxymethyl radical was determined, for the benzophenone concentration of 0.44 mol·l^{-1} by recording the transient change of the intensity of its spectrum, when the illuminating light was rapidly shut off and lit on repeatedly. Representative results are shown in Fig. 4, *a*. The most probable curve of transient change is obtained as Fig. 4, *b*, which gives the rise and decay times of 0.8 and 0.2 sec, respectively. Difference between the rise time and the decay time is resulted from an effective lifetime due to the flowing of radicals out of the cell, t_f. They are approximated by the following relations:

$$1/t_d = 1/\tau + 1/t_f \qquad (1)$$

$$1/t_r = 1/\tau - 1/t_f, \qquad (1')$$

where t_d and t_r stand for the decay and rise time, and τ is true half life of the radical.[10] The half life is determined from Fig. 4, *b*, being 0.3 sec. The calculated t_f is 0.5 sec, which is in agreement with the resident time of solution in the cell (a half of the resident time, 0.7/2=0.35 sec, is the expected value for t_f).

To determine the wavelength of light effective to

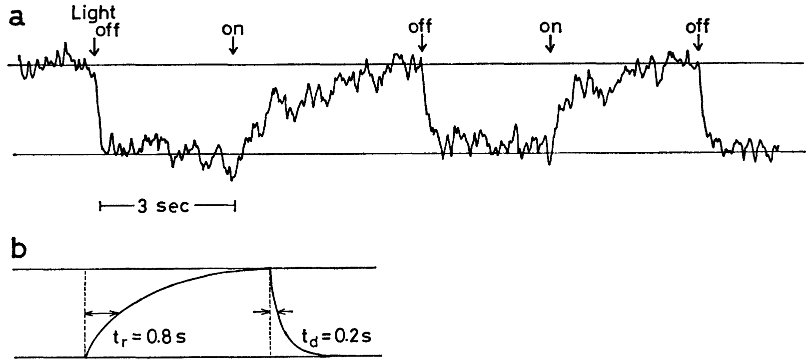

Fig. 4. Transient change in the intensity of electron spin resonance specta due to short-lived free radicals during the photolysis of benzophenone (0.14 mol·l^{-1}) in ethanol, when the light is shut off and lit on rapidly, recorded with response time of 0.1 sec. (a) An example of recorded curves, (b) the most probable curve estimated from several observations.

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[10] When the plateau of curves in Fig. 4 indicates the steady state concentration under the photo-illumination, the relations (I) and (I′) enable us to estimate the value of $\tau(\approx 1/\sqrt{k_3R}$, R is the rate of radical formation and k_5 is the rate constant of bimolecular decay of free radicals, as seen in eq. (7)) and t_f. If the plateu value is much less than the steady state concentration, the relations should be replaced by $1/t_d > 1/\tau + 1/t_f$ and $1/t_r < 1/\tau - 1/t_f$. However, in this experiment, the calculated t_f of 0.5 sec is rather close to the expected value of 0.35 sec. Therefore, the relations are thought to be valid for rough estimation of τ.

generate free radicals, the intensity of ESR spectra was examined by inserting a cut-off filter to the light path. The relative values of intensity were 100, 92, 83, 60, and 14 for $\lambda > 250$ (without filter), >270, >310, >350, and >390 nm, respectively. Referring a factory-provided datum of the lamp, relative quantum efficiencies are estimated, being 0.3, 1.0, and 1.0 for the wavelength region of 270~310, 310~350, and 350~390 nm. The light of wavelength around 350 nm is the most effective.

When the solution was made alkaline by adding sodium methoxide, the spectrum of diphenylhydroxymethyl radical was replaced by the spectrum shown in Fig. 2, *b*. The latter has the hyperfine structure due to four equivalent protons with the coupling constant of 2.8G, four protons with 1.0G and two protons with 3.5G, and is identical with that of benzophenone ketyl anion reported previously.[11] The *g*-factor of ketyl anion is found to be larger than that of diphenylhydroxymethyl radical by 0.0003. Therefore, $g=2.0033$ for the ketyl anion, because $g=2.0030$ for the latter radical.[6]

At small concentration of sodium methoxide added, ESR spectra show the coexistence of both diphenylhydroxymethyl radical and bonzophenone ketyl anion. With the increasing concentration of sodium methoxide, the former decreases and the latter increases in their concentration. Concurrently, the sum of them increases from 4.5×10^{-7} mol·l^{-1} to a plateau value of 4×10^{-6} mol·l^{-1}, for 0.44 mol·l^{-1} of benzophenone, as shown in Fig. 5.

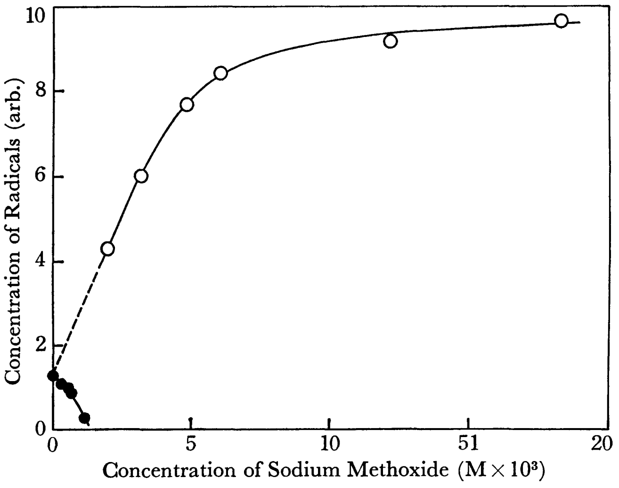

Fig. 5. Observed concentration of diphenylhydroxymethyl radical (●) and benzophenone ketyl anion (○) formed during the photolysis of benzophenone (0.44 mol·l^{-1}) in ethanol as a function of sodium methoxide added to the solution.

Discussion

Photoreduction of benzophenone in alcohols has been studied by means of conventional photochemical analysis method and, later on, by flash photolysis technique. Generally accepted mechanism, for ethanol as solvent, is as follows:[1,3]

$$(C_6H_5)_2C{=}O \xrightarrow{h\nu} (C_6H_5)_2{=}O^* \tag{2}$$

$$(C_6H_5)_2C{=}O^* + CH_3CH_2OH \longrightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}HOH \tag{3}$$

$$CH_3\dot{C}HOH + (C_6H_5)_2C{=}O \longrightarrow CH_3CH{=}O + (C_6H_5)_2\dot{C}OH \tag{4}$$

$$2(C_6H_5)_2\dot{C}OH \xrightarrow{k_5} (C_6H_5)_2COHCOH(C_6H_5)_2 \tag{5}$$

Very primary process is the excitation of benzophenone. Radicals are generated the most efficiently by the light of wavelength around 350 nm, which indicates that $n\rightarrow\pi$ transition of benzophenone is responsible for the hydrogen abstraction reaction (3), as the transition has the band maximum at about 340 nm in alcoholic solutions. The reaction (3) is directly evidenced by observing simultaneously the ESR spectra of both diphenylhydroxymethyl radical from benzophenone and hydroxyethyl radical from ethanol.

Results shown in Fig. 3 strongly suggest the conversion of hydroxyethyl raidcal to diphenylhydroxymethyl radical, by the reaction (4). If the concentration of benzophenone, and therefore that of diphenylhydroxymethyl radical, is enough high, the radical disappear following the second order reaction, as expected from the reaction (5). In the presence of sodium methoxide, the reaction competes with its conversion to benzophenone ketyl anion,

$$(C_6H_5)_2\dot{C}OH + CH_3O^- \xrightarrow{k_6} (C_6H_5)_2CO^- + CHO_3H. \tag{6}$$

As the ketyl anion is much more stable than diphenylhydroxymethyl radical,[3,5] the sum of both the anion and the radical increases in their yield with the increasing concentration of added sodium methoxide. The plateau of curve in Fig. 5 is thought to be attained by the complete conversion to the ketyl anion without loss of diphenylhydroxymethyl radical; $k_5[(C_6H_5)_2\dot{C}OH] \ll k_6[CH_3O^-]$.

The competing reactions are described by the following kinetical relations:

$$\frac{d[(C_6H_5)_2\dot{C}OH]}{dt} = R - k_5[(C_6H_5)_2\dot{C}OH]^2 - k_6[(C_6H_5)_2\dot{C}OH][CH_3O^-] \tag{7}$$

$$\frac{d[(C_6H_5)_2CO^-]}{dt} = k_6[(C_6H_5)_2COH][CH_3O^-], \tag{8}$$

where R stands for the rate of formation of diphenylhydroxymethyl radical. In the absence of sodium methoxide, the concentration of diphenylhydroxymethyl radical follows eq. (9) obtained by integrating eq. (7) with the initial condition of null concentration for $t=0$,

$$[(C_6H_5)_2\dot{C}OH] = \sqrt{\frac{R}{k_5}}\cdot\frac{\exp(2\sqrt{k_5R\cdot t})-1}{\exp(2\sqrt{k_5R\cdot t})+1}, \tag{9}$$

For the concentration of sodium methoxide enough high, the loss of free radical may be ignored, and

$$[(C_6H_5)_2CO^-] = R\cdot t. \tag{10}$$

Flowing solutions are photolyzed for their resident time in the cell, t_0. Therefore, the observed intensity of spectra is proportional to

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[11] P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, **1963**, 5412.

$$\int_0^{t_0}[(C_6H_5)_2\dot{C}OH]dt = \frac{1}{k_5}\cdot\ln\{\exp(2\sqrt{k_5R}\cdot t_0)+1\} - \sqrt{\frac{R}{k_5}}\cdot t_0 \tag{11}$$

and

$$\int_0^{t_0}[(C_6H_5)_2CO^-]dt = \frac{R}{2}\cdot t_0^2. \tag{12}$$

The observed concentration without sodium methoxide (the left hand side of eq. (11), 4.5×10^{-7}) and that at the plateau of curve (the left hand side of (12), 4×10^{-6}) both indicated in Fig. 5 and $t_0=0.7$ sec lead to $k_5=3\times10^7$ mol$^{-1}\cdot l\cdot$sec^{-1}. Thus obtained k_5 is compared with the value derived from flash photolysis study, 5.9×10^7 mol$^{-1}\cdot l\cdot$sec^{-1}, in 50 vol% isopropanol-water mixture.[3]

On the other hand, the value of k_5 can be roughly estimated from the true half life of diphenylhydroxymethyl radical in the absence of sodium methoxide (see Fig. 4). From the relation,

$$k_5 = 1/[(C_6H_5)_2\dot{C}OH]_0\cdot\tau, \tag{13}$$

$[(C_6H_5)_2\dot{C}OH]_0\approx4.5\times10^{-7}$ mol$\cdot l^{-1}$ and $\tau\approx0.3$ sec, k_5 is calculated to be 0.7×10^7 mol$^{-1}\cdot l\cdot$sec^{-1}. If one consider local sensitivity of ESR depending on the sinusoidal distribution of microwave magnetic field, H_1, along the flow of solution, which is ignored in the above treatments, and the uncertainty involved in eqs. (1) and (1′), this value of k_5 is thought to agree rather well with the value of 3×10^7 mol$^{-1}\cdot l\cdot$sec^{-1}.

The yield of benzophenone ketyl anion reaches to 50% of its plateau value at 2.5×10^{-3} mol$\cdot l^{-1}$ of sodium methoxide. At this concentration, the following realtion can be used to evaluate the rate constant, k_6;

$$k_5[(C_6H_5)_2COH] = k_6[\dot{C}H_3O^-], \tag{14}$$

Assuming that sodium methoxide dissociates completely in ethanol at this low concentration, estimation of the order of magnitude gives 10^4 mol$^{-1}\cdot l\cdot$sec^{-1} for the rate constant of proton transfer from diphenylhydroxymethyl radical to methoxide ion, reaction (6).

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