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Polarized Absorption Spectra of Aromatic Radicals in Stretched Polymer Film. V. The Benzophenone Radicals

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Benzophenone radical anions and ketyl radicals have been prepared in poly(vinyl alcohol) [PVA] films by means of γ-ray irradiation at 77 K. The polarized absorption spectra have been measured and used to determine the resolved spectra of these radicals. The spectrum of radical anions in the PVA film is very similar to that of ketyl radicals and can also be well explained by the calculated results for the hydrogen-bonding model of radical anions. The intense near-UV and visible absorption bands of radical anions in the PVA film are both correlated with those of ketyl radicals.

In previous papers we have reported the polarized absorption spectra of some aromatic radicals, determined by the stretched polymer film technique combined with γ-irradiation.[1–4] It was shown that the information on the direction of transition moments is useful for the assignment of the electronic transitions of these radicals.

A number of investigations have been reported on the preparation and the electronic structure of benzophenone radicals.[5–18] Porter and Wilkinson studied the visible absorption spectra of benzophenone ketyl radicals and radical anions prepared in an acidic or alkaline solution by means of flash photolysis.[5] They also studied the equilibrium between these radicals and determined the pK_a value of this equilibrium. The molar-extinction coefficients of these radicals in an acidic or alkaline solution have been determined by Hayon *et al.*, using the technique of pulse radiolysis-absorption spectroscopy.[11] McCelland investigated the electronic spectra of metal ion-paired ketyls by taking into account the effect of alkali metal ions as the perturbing electrostatic potential and semiquantitatively showed the spectroscopic blue shift of the visible absorption band.[7] Shida *et al.* measured the electronic absorption spectra of benzophenone radicals prepared by γ-irradiation in rigid glassy matrices and discussed the visible and near-UV bands in comparison with the results of MO calculations.[14] They suggested that the near-UV absorption bands of benzophenone radical anions and ketyl radicals have different polarization directions, though their spectra are quite similar in appearance. The polarization study of the electronic transition, however, has not been carried out for these radicals. It is desirable to determine experimentally the assignments of these absorption bands from the point of view of the direction of the transition moment.

In this study we investigate the polarized absorption spectra of benzophenone ketyl radicals and radical anions, prepared by the γ-irradiation of benzophenone in poly(vinyl alcohol) [PVA] films. The results are discussed in comparison with the results of MO calculations.

Experimental

Guaranteed reagent-grade benzophenone and methanol from Tokyo Kasei Co. Ltd., were used as received. PVA films were prepared by the method described previously.[2] Benzopheone was introduced into PVA films with the aid of methanol. The acidic sample film was prepared by immersing a PVA film into an acidic methanol solution of benzophenone containig 2 vol% of concd hydrochloric acid. The alkaline sample film was prepared by immersing a PVA film into an alkaline methanol solution of benzophenone containing 0.05 mol dm^{-3} of sodium hydroxide. These sample films were irradiated by ^{60}Co γ-ray for 2 h at a dose rate of 1.0×10^6 rad/h in liquid nitrogen. To control the concentrations of the ketyl radicals and radical anions of benzophenone, the irradiated films were taken out from liquid nitrogen and kept for tens of seconds. After this warming at room temperature, the films were again immersed in liquid nitrogen. The absorption spectrum of the radicals produced in the film was determined as the difference in the absorbances of the film before and after irradiation. In this experiment, the error introduced by the decrease of the parent molecule by the formation of radicals is less than 2% in absorbances below 360 nm because of the small molar-extinction coefficient ($\varepsilon \approx 300$)[19] of the parent molecule. The absorption spectra from 300 to 850 nm were measured with a spectrophotometer (JASCO SS-50) equipped with a Rochon polarizer. For the polarization measurements, the sample films were stretched about 4 times before irradiation.[2]

Roothaan's restricted Hartree-Fock open-shell calculations were carried out in the pi-electron approximation for benzophenone ketyl radicals and radical anions. The configuration interaction calculations were limited to all the singly excited and ground configurations. In order to take into account the effects of the hydrogen bond, the point charge, $Z_{\mathrm{eff}}\,e$, was located at the distance of 1.72 Å from the oxygen atom. The value of Z_{eff} was changed from 0 to 0.8. The valence-state ionization potentials (I_{p}), electron affinities (E_{a}), and resonance integrals (β) used were as follows; $I_{\mathrm{p}}(\mathrm{C})=11.22$, $E_{\mathrm{a}}(\mathrm{C})=0.62$, $I_{\mathrm{p}}(=\mathrm{O})=11.76$, $E_{\mathrm{a}}(=\mathrm{O})=3.87$, $I_{\mathrm{p}}(-\mathrm{OH})=33.00$, $E_{\mathrm{a}}(-\mathrm{OH})=11.47$, $\beta_{\mathrm{C-C}}=-2.318$, $\beta_{\mathrm{C=O}}=-2.70$, and $\beta_{\mathrm{C-OH}}=-2.30$ in eV.

Results and Discussion

Curve a in Fig. 1 shows the absorption spectrum of the benzophenone radicals at 77 K produced by the γ-irradiation of the sample PVA films. By making reference to the spectra of benzophenone radical anions [BP$^{-\cdot}$] and ketyl radicals [BPH$^{\cdot}$] reported by Porter and

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Wilkinson,5) this is ascribed to the mixture of $BP^{-\cdot}$ and $BPH^{\cdot}$. The absorption maxima appearing at about 18×10^3 cm^{-1} and 16×10^3 cm^{-1} are assigned to $BPH^{\cdot}$ and $BP^{-\cdot}$ respectively. Assuming the values of the molar-extinction coefficients reported by Hayon *et al.* for these peaks,11) the concentrations of $BP^{-\cdot}$ and $BPH^{\cdot}$ are estimated to be $(2.8\pm0.2)\times10^{-3}$ mol dm^{-3} and 1.1 ± 0.1 mol dm^{-3} respectively. Curve a′ in Fig. 1 is the spectrum measured at 77 K after a slight warming. The concentrations of $BP^{-\cdot}$ and $BPH^{\cdot}$ are estimated to be $(1.3\pm0.1)\times10^{-3}$ mol dm^{-3} and $(1.9\pm0.2)\times10^{-3}$ mol dm^{-3} respectively. It should be noted here that $BP^{-\cdot}$ was converted to $BPH^{\cdot}$ by warming, though some of the radicals disappeared. This change has been attributed to the acid-base equilibrium between benzophenone radicals.5)

Curve b in Fig. 1 shows the spectrum of the γ-irradiated benzophenone in the PVA film containing methanol and hydrochloric acid. It is similar to curve a′ in appearance. The concentrations of $BP^{-\cdot}$ and $BPH^{\cdot}$ are estimated to be $(3.0\pm0.3)\times10^{-3}$ mol dm^{-3} and $(2.8\pm0.3)\times10^{-3}$ mol dm^{-3} respectively. After a slight warming, the spectrum of curve b′ was also observed. This is similar to that of $BPH^{\cdot}$ in an ethanol glass reported by Shida *et al.*14) The peak of $BP^{-\cdot}$ disappeared. The concentration of $BPH^{\cdot}$ is $(6.0\pm0.5)\times10^{-3}$ mol dm^{-3}. Curve c in Fig. 1 shows the spectrum of the γ-irradiated benzophenone in the PVA film containing methanol and sodium hydroxide. After a slight warming, the spectrum of curve c′ was observed. Though there remains a shoulder at about 18×10^3 cm^{-1} which is assigned to $BPH^{\cdot}$, $BP^{-\cdot}$ is predominant after this warming. The concentrations of $BP^{-\cdot}$ and $BPH^{\cdot}$ are estimated to be $(2.2\pm0.2)\times10^{-3}$ mol dm^{-3} and $(0.2\pm0.1)\times10^{-3}$ mol dm^{-3} respectively. It should be noted that only 5% of the absorbance of the intense near-UV band at 29.5×10^3 cm^{-1} (curve c′) is due to $BPH^{\cdot}$.

Thus, under acidic or alkaline conditions benzophenone ketyl radicals or radical anions are predominantly prepared in the PVA films. The sample films for the polarization measurements of $BPH^{\cdot}$ and $BP^{-\cdot}$ were prepared in the same manner as those of b′ and c′ in Fig. 1.

Figure 2 shows the polarized absorption spectra of $BPH^{\cdot}$ (a) and $BP^{-\cdot}$ (b) in the stretched PVA films. The sample films (a) and (b) contain hydrochloric acid and sodium hydroxide respectively, as in curves 1b and 1c. In Fig. 2b there remains the absorption due to $BPH^{\cdot}$ and the molar ratio of $BPH^{\cdot}$ to $BP^{-\cdot}$ is about 0.13. The behavior of the dichroic ratio ($R_d=A_{/\!/}/A_{\perp}$) of these spectra is similar; the R_d values in the regions of the intense near-UV and visible bands are large. It is usually admitted that the molecular long axis is preferentially inclined to the stretching direction of the film. This has been confirmed by the analysis of the polarized absorption spectra for the radicals produced in the PVA films by γ-irradiation and for the parent molecule, benzophenone.1-4,19) This means that the transition moments of these bands are polarized parallel to the molecular long axis. In order to show this situation more clearly, the resolved spectra were determined by making use of the polarized absorption spectra, according to a method described in a previous paper.4) Figure 3 shows the resolved spectra of $BPH^{\cdot}$ (a) and $BP^{-\cdot}$ (b). The extreme values used to determine the resolved spectra were as follows; $R_d^1=1.86$ and

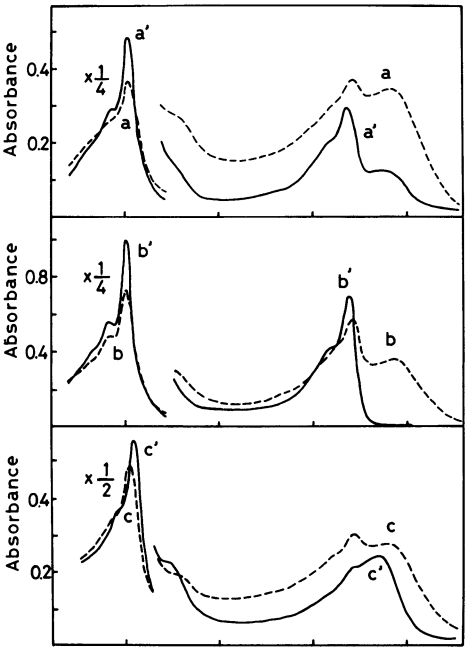

Fig. 1. Absorption spectra of the γ-irradiated benzophenone in the neutral (curve a), acidic (b) and alkaline (c) PVA films. Curves a′, b′, and c′ are the spectra observed after slight warming at room temperature.

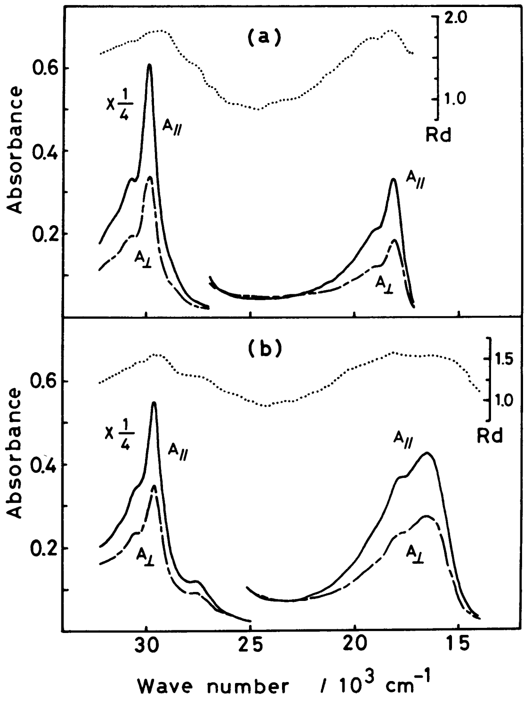

Fig. 2. Polarized absorption spectra of benzophenone ketyl radicals (a) and radical anions (b) in the stretched PVA films.

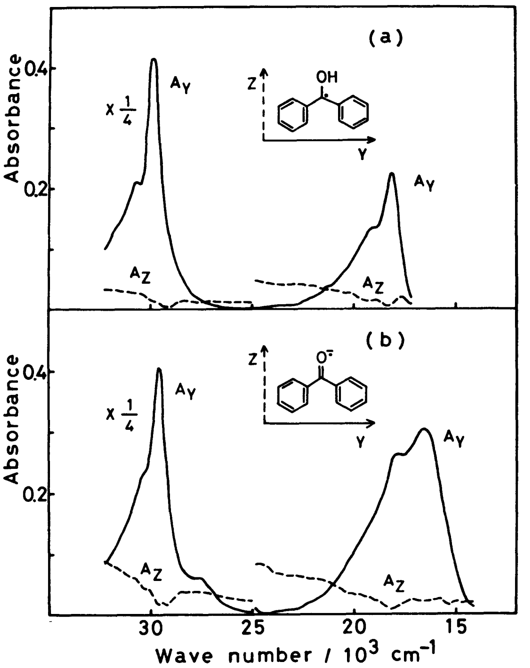

Fig. 3. Resolved spectra of benzophenone ketyl radicals (a) and radical anions (b). A_Y and A_Z curves are the molecular long- and short-axis polarized components, respectively.

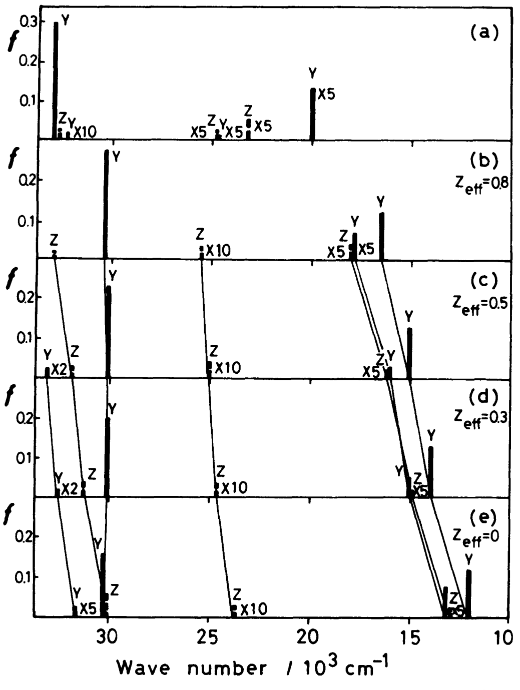

Fig. 4. Calculated results for benzophenone ketyl radicals (a) and radical anions (b)—(e). A point charge, Z_{eff} e, was set at the distance of 1.72 Å from the oxygen atom in order to take into accounts the effects of hydrogen bond.

$R_d{}^s=0.87$ for BPH$^{\cdot}$, and $R_d{}^1=1.60$ and $R_d{}^s=0.94$ for BP$^{-\cdot}$. As may be seen in Fig. 3, the main parts of the intense UV and visible bands of both radicals are long-axis (Y-) polarized components. No intense peak is found for the short-axis (Z-) polarized component.

The calculated results for BPH$^{\cdot}$ are shown in Fig. 4a. The results are similar to those obtained by the Longuet-Higgins and Pople type MO calculation.[10,14)] By comparison of Figs. 3a with 4a, it may be seen that the calculated transition energies are greater than the experimental values by (2—3)×10³ cm⁻¹, but the correspondence of the intense bands is fairly good. The Y-polarized bands at 18×10³ cm⁻¹ and 30×10³ cm⁻¹ are assigned to the first and seventh transitions respectively. The upper-state wave functions of these electronic transitions are represented by the following two main configurations; $\Psi_{\mathrm{I}}=0.638\,\Phi_{8\to9}-0.383\,\Phi_{6\to8}+\cdots$ and $\Psi_{\mathrm{VII}}=0.504\,\Phi_{8\to9}+0.424\,\Phi_{6\to8}+\cdots$, where the subscripts 6, 7, and 8 refer to the number of MO's and where MO ϕ_8 is the singly occupied orbital. Thus, these transitions originate mainly from two configurations, $\Phi_{8\to9}$ and $\Phi_{6\to8}$, and are similar to each other in characteristics. This assignment agrees well with those of other authors.[10,14)]

The calculated results for BP$^{-\cdot}$ are shown in Fig. 4e. As BP$^{-\cdot}$ is considered to form a hydrogen bond in the PVA film, model calculations were carried out by locating a point charge, Z_{eff} e, at a distance of 1.72 Å from the oxygen atom of radical anions. These results are shown in Fig. 4b—d ($Z_{\mathrm{eff}}=0.8$ to 0.3). On going from $Z_{\mathrm{eff}}=0$ (Fig. 4e) to $Z_{\mathrm{eff}}=0.8$, the first four transitions shift to blue, whereas the intense UV transition does not. The results for $Z_{\mathrm{eff}}=0.8$ explain well the resolved spectra of Fig. 3b. The intense Y-polarized visible and near-UV bands at about 16.5×10³ cm⁻¹ and 29.5×10³ cm⁻¹ are, respectively, assigned to the first and the fifth transitons, the excited states of which are represented by the following two charge-resonance configurations; $\Psi_{\mathrm{I}}=0.837\,\Phi_{8\to9}-0.278\,\Phi_{7\to8}+\cdots$ and $\Psi_{\mathrm{V}}=0.402\,\Phi_{8\to9}+0.637\,\Phi_{7\to8}+\cdots$, where MO ϕ_8 is the singly occupied orbital.

The coefficients of the atomic orbitals of MO's, ϕ_6, ϕ_8, and ϕ_9 of BPH$^{\cdot}$, and ϕ_7, ϕ_8, and ϕ_9 of BP$^{-\cdot}$, are shown schematically in Fig. 5. As can be seen in Fig. 5, the

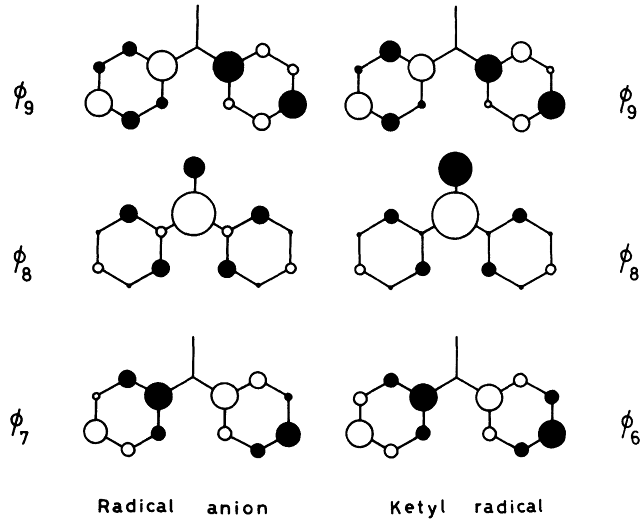

Fig. 5. Correlations of MO's ϕ_6, ϕ_8, and ϕ_9 of benzophenone ketyl radicals with the corresponding ones of radical anions ($Z_{\mathrm{eff}}=0.8$). MO ϕ_8 is the singly occupied orbital. The size of the circle represents the relative value of the coefficient of the atomic orbitals. Open circles indicate positive sign and full circles negative sign.

MO's ϕ_6, ϕ_8, and ϕ_9, of BPH$^{\cdot}$ are similar to the ϕ_7, ϕ_8, and ϕ_9 of BP$^{-\cdot}$ respectively. Therefore, the $\Phi_{8\to9}$ and $\Phi_{7\to8}$ configurations of BP$^{-\cdot}$ are correlated with the $\Phi_{8\to9}$ and $\Phi_{6\to8}$ of BPH$^{\cdot}$ respectively. As a result,the Ψ_{I} and Ψ_{V} of BPH$^{\cdot}$ are correlated with the Ψ_{I} and Ψ_{VII} of BPH$^{\cdot}$. According to the results of the polarization measurement and the above discussion, the near-UV and visible bands of BPH$^{\cdot}$ in the PVA films can be said to be similar to those of BP$^{-\cdot}$ not only in spectral appearance, but also in the direction of the transition moments.

According to the Longuet-Higgins and Pople type MO calculation on BP$^{-\cdot}$, two transitions with large oscillator strengths are calculated to be located in the near-UV region.[14,20] The intense near-UV band observed in an MTHF glass was assigned to the Z-polarized transition by Shida *et al.*[14] However, in our caluclation (Fig. 4e, $Z_{\mathrm{eff}}=0$) the Y-polarized transition is calculated to appear in this region with an oscillator strength larger than that of the Z-polarized one by a factor of 3. On going from $Z_{\mathrm{eff}}=0$ to 0.8, this Z-polarized transition shifts to blue, while the Y-polarized one remains. Furthermore, the direction of the transition moment of the near-UV band of BP$^{-\cdot}$ in the PVA film is parallel to the molecular long axis (Y). Therefore, the main part of the intense near-UV band in an MTHF glass may be assigned to the Y-polarized transition.

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20) The MO diagram of ϕ_9 in Fig. 7 in Ref. 14 is erroneous (private communication).