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Spectroscopic Study of 10-Benzoyl-9-anthrol and Its Anion in Basic Media. An Estimation of Microscopic Polarity of PMMA

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The acid-base equilibrium of the title compound (BAOH) was studied in various media containing 4% triethylamine (TEA) by volume as a base. As the polarity of solvents increases, the equilibrium shifts toward the base form (BAO^-) and 100% yield of BAO^- is achieved in solvents with dielectric constant (ε) greater than 20. The equilibrium is also affected by temperature, favoring the base form at lower temperatures. The associated enthalpy change is estimated to be -14.6 kJ mol^{-1}. Of particular interest is the dominant existence of BAO^- in poly(methyl methacrylate) (PMMA), since the acid form (BAOH) dominates in a monomeric solvent (MMA). The microscopic effective dielectric constant of PMMA is estimated to correspond to that of a solvent with $\varepsilon=22$—30 by comparing spectral data in PMMA with those in various solvents. No base form is formed in polystyrene, indicating that not only rigidity but also polar groups in PMMA may be responsible for the anomalously large dielectric constant of PMMA.

In our study on photochemical reaction of nitroanthracenes (9-cyano- and 9-benzoyl-10-nitroanthracene) in various fluid solutions and poly (methyl methacrylate) (PMMA),[1)] we have found that the form of the final photoproducts (10-cyano-9-anthrol (CAOH) or its anion (CAO^-) and 10-benzoyl-9-anthrol (BAOH) or its anion (BAO^-)) is very dependent on the basicity, polarity, and rigidity of medium as well as temperature. Of particular interest is the formation of BAO^- in basic PMMA, since in a basic monomeric medium the main photoproduct is BAOH.

According to the results of Kosower,[2)] a solvent-environmental effect on a solute molecule is supported by a result of spectral shift which indicates that the molecular energy level is generally sensitive to the matrix. The primary polymer matrix effect is therefore manifested by changes in intermolecular interactions brought about by a decrease in the average separation between solute and solvent molecules and by an alteration of relative orientations of solvent molecules against solute molecule, all of which lead to a change in the coordination number of solvent shells. For this reason the effect of polymer matrix is frequently compared with solvent effects and discussed in the light of tsolven shift theories.[3—10)]

Thus, our observation of the medium effect on the form of the final photoproducts of nitroanthracenes leads us to an extensive spectroscopic study on the interchange between BAOH and BAO^- in a wide variety of media. Detailed information on this acid-base equilibrium is not only interesting in itself but also valuable in understanding photochemical processes of the nitroanthracenes.[1)]

We will also point out a possibility of utilizing the present acid-base pair of BAOH–BAO^- to estimate the microscopic polarity of polymers which is unaffected by the way of doping probe molecules.

Experimental

Chemicals. BAOH was synthesized from 9-benzoyl-10-nitroanthracene. The details of the methods of preparation of this material have been given in our previous paper.[1)] Uvasol diethyl ether was purchased from E. Merck A. G. and used without further purification. Methyl methacrylate monomer (MMA) was of guaranteed grade (Wako Pure Chemical Industries, Ltd.) and was distilled by the method of Collins *et al.*[11)] The purified monomer was stored in the dark in a refrigerator.

All the other chemicals used were of guaranteed grade (Wako Pure Chemical Industries, Ltd.) and were used without further purification, unless otherwise stated. In the following, "basic solvent" means a solvent which contains 4 vol% TEA.

To get a basic polymer sample, a solution of BAOH in 5 cm^3 of basic MMA and 0.5 mg of α,α'-azobisisobutyronitrile were poured into a 1 cm rectangular Pyrex cell, and degassed by seven freeze-pump-thaw cycles. After sealing the cell the sample solution was polymerized in bulk at 348 K for 24 h.

Measurements of Absorption Spectra and Z-Values. Using a Hitachi 200-20 spectrophotometer, absorption spectra were taken at room temperature and at low temperatures down to 143 K. To get a given low temperature a cold nitrogen gas, generated by heating liquid nitrogen in a metal Dewar vessel, was introduced into a quartz Dewar vessel in which a 1 cm rectangular sample cell made of Suprasil was mounted. The temperature was measured with a copper-constantan thermocouple which was inserted into a sample cell.

For the estimation of medium polarity, Z-values were determined with 1-methyl-4-(methoxycarbonyl)pyridinium iodide, which was recrystallized twice from methanol, yielding the melting point of 175—176 °C. The charge-transfer band of this salt was measured in a 1 cm rectangular quartz cell. (For a polymeric sample, 5 cm^3 of sample solution in MMA was polymerized by the same method as described before.)

Results and Discussion

Acid-base Equilibrium between BAOH and BAO^-. The pK_a value of BAOH has been determined to be 8.8 in water–ethanol mixed solvent by the ordinary spectroscopic method.[12)] From this value it is expected that BAOH easily dissociates to BAO^- in slightly basic organic media.

In Fig. 1, we show the absorption spectral change of BAOH in ethanol caused by addition of triethylamine (TEA), which indicates that there exists an acid-base equilibrium between BAOH and BAO^-. The absorption

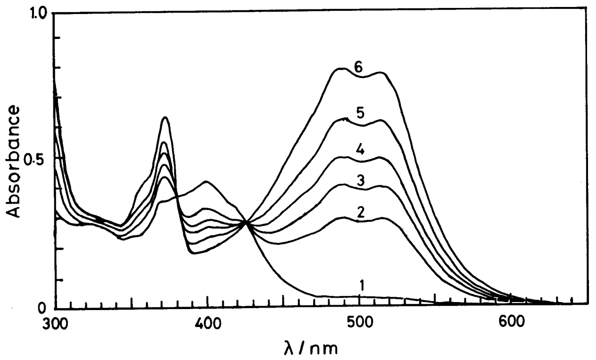

Fig. 1. Absorption spectral change of BAOH in ethanol (initial concentration 1.5×10^{-4} mol dm^{-3}) by the addition of different amount of TEA.
TEA volume ratio: 1; 0%, 2; 0.05%, 3; 0.1%, 4; 0.2%, 5; 0.5%, 6; 4%.

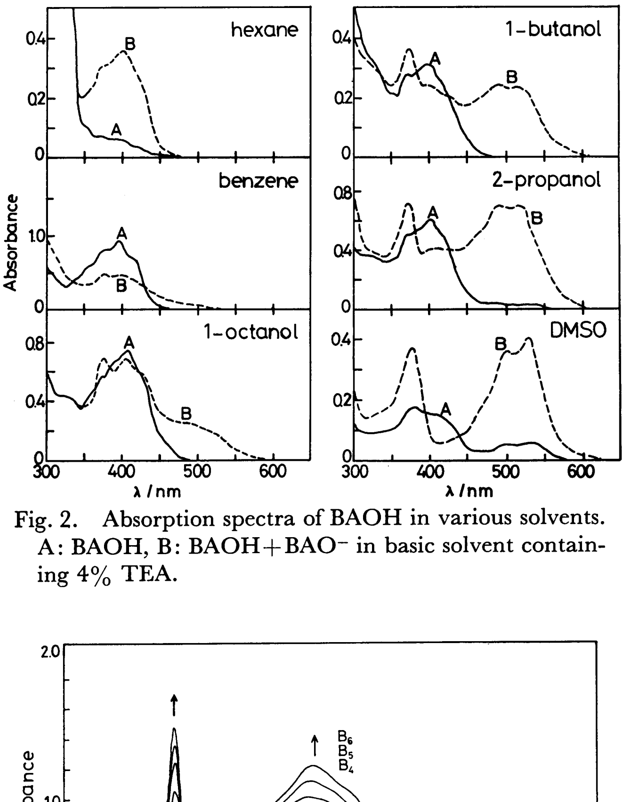

Fig. 2. Absorption spectra of BAOH in various solvents.
A: BAOH, B: BAOH+BAO$^-$ in basic solvent containing 4% TEA.

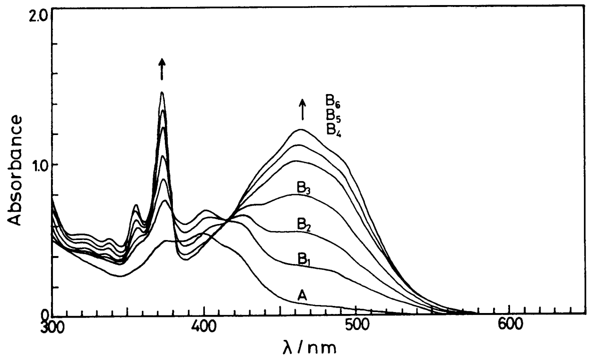

Fig. 3. Absorption spectral change of BAOH in basic EPA at low temperature.
A: At room temperature, B_1: 253 K, B_2: 233 K, B_3: 213 K, B_4: 193 K, B_5: 173 K, B_6: 143 K.

spectrum due to BAO$^-$ lies on the longer wavelength side and has two band maxima around 370 and 500 nm. Although the addition of 4% TEA to the ethanol solution is enough to dissociate BAOH into BAO$^-$ almost completely, which form of BAOH and BAO$^-$ dominates in other solvents depends on the nature of solvents even in the presence of TEA, as shown in Fig. 2. Since the standard free energy change associated with the equilibrium is a function of dielectric constant, it is fully expected that the acid-base equilibrium is affected by the polarity of solvents. However, instead of trying to formulate the general equation to give the standard free energy change, which would be extremely difficult, we measured absorption spectra of the acid-base pair in more than thirty organic solvents, whose dielectric constants range from 1.84 to 46.7, in order to find the threshold of dielectric constant above which BAO$^-$ dominates.

The obtained results indicate that the equilibrium between BAOH and BAO$^-$ is strongly dependent on the dielectric constant ε of solvents, that is, the amount of BAO$^-$ increases as the polarity of solvent increases and nearly 100% yield of BAO$^-$ is obtained in such basic solvents as acetone, ethanol, benzonitrile, methanol, *N*,*N*-dimethylformamide, acetonitrile, and dimethyl sulfoxide, all of which have dielectric constants greater than 20. No pure BAO$^-$ exists in neat TEA or in pure polar solvents even when their dielectric constants exceed 20.

The stability of BAO$^-$ is found to depend not only on the polarity and basicity of solvents but also on the temperature. A typical example is illustrated in Fig. 3. The spectra were taken for BAOH in basic EPA (ether : isopentane : ethanol=5 : 5 : 2 in volume ratio). At room temperature, one can see that the spectrum is mainly due to BAOH, being slightly superposed by that of BAO$^-$. This is because the polarity of EPA is much less than 20. As the temperature decreases, the absorbance of a new spectrum with a band maximum at 466 nm (Spectra B_1—B_6) increases, accompanied by two isosbestic points at 380 and 420 nm. The isosbestic point at 420 nm is not so clear. Spectra B_1—B_6 are similar to that of BAO$^-$ observed in basic ethanol at room temperature, but the former are appreciably blue-shifted compared with the latter. By changing the volume ratio of ethanol in basic EPA, the spectral shift of BAO$^-$ was examined at 196 K. The result shows that the absorption band maximum of BAO$^-$ which lies around 500 nm in basic ethanol shifts to the blue with decrease in the content of ethanol and gradually arrives at Spectrum B_4 in Fig. 3 as the ratio of ethanol approaches to that in EPA, *i.e.*, 5 : 5 : 2. Thus, it is concluded that Spectra B_1—B_6 are not due to new species but to BAO$^-$ (though blue-shifted because of the lower polarity of EPA), and that the spectral change of B_1 to B_6 with lowering temperature is due to a shift in equilibrium between BAOH and BAO$^-$.

Although the proton transfer in *p*-nitrophenol–TEA system has been studied quantitatively by Baba *et al.*,[13] we have roughly estimated the enthalpy change of BAOH into BAO$^-$ from the temperature dependence of the absorbance at 466 nm, by assuming that the absorbance at 143 K is due to BAO$^-$ alone. The estimated value is -14.6 kJ mol^{-1}. Since in basic EPA there is no spectral change in either BAOH or BAO$^-$ at various temperatures and since no change in Kosower's *Z*-value is observed for basic EPA, one can

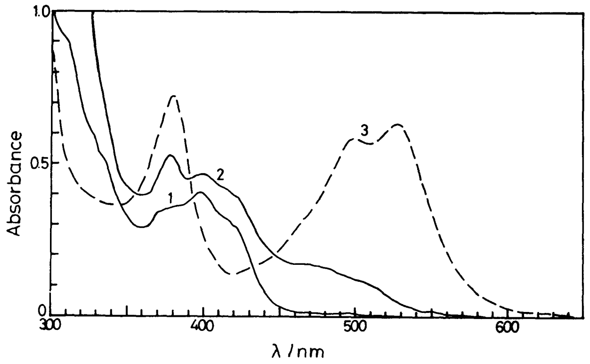

Fig. 4. Absorption spectral change of BAOH.
1: BAOH in MMA, 2: BAOH+BAO$^-$ in basic MMA, 3: BAO$^-$ in basic PMMA.

say that the polarity of EPA is not affected by lowering temperature. Consequently, it can be said that in basic EPA, the observed temperature effect on the equilibrium emerges purely through an enthalpy change ΔH of constant negative value, but not through a change in the dielectric constant of EPA with temperature.

Spectral Shift in PMMA. In our study on the photochemistry of 9-cyano- or 9-benzoyl-10-nitroanthracene in basic PMMA, it was found that absorption spectra of photoproducts (CAO$^-$ and BAO$^-$) in polymeric media are more red-shifted and become more structured than those in the monomer solution (MMA).[1]

Figure 4 shows the absorption spectral change of BAOH when the properties of medium (MMA) are modified. Only BAOH exists in MMA and it dissociates only slightly to BAO$^-$ by the addition of TEA. After the polymerization of this basic sample solution at 348 K for 24 h, BAO$^-$ is obtained in 100% yield. Of particular interest is the appearance of absorption spectra of BAO$^-$ in a basic polymeric medium, since in a basic monomeric medium the observed absorption spectrum is dominated by BAOH, being superposed only slightly by that due to BAO$^-$. Moreover, the absorption band of BAO$^-$ obtained in basic PMMA is red-shifted compared with that in a basic monomeric medium and the spectral shape of the Franck-Condon envelope is rather similar to those in pyridine, 2-propanol, *N,N*-dimethylformamide, and dimethyl sulfoxide, each containing TEA.

In relation to this anomalous medium effect of PMMA, it is interesting to know the effect of the rigidity of basic PMMA on the dominant existence of BAO$^-$. Upon polymerizing a basic MMA solution of BAOH gradually, a growth of the absorption of BAO$^-$ was observed. Initially the almost colorless solutions became red as the medium became viscous and its color deepened upon further polymerization untill such a spectrum as given in Fig. 4 was obtained. This could be interpreted as follows: PMMA may not necessarily be extremely hard to favor the presence of BAO$^-$ and even a soft rubber-like PMMA may exhibit a dielectric constant high enough for BAO$^-$ to dominate it.

As described above, the equilibrium between BAOH and BAO$^-$ is strongly dependent on the dielectric constant of solvents, giving 100% yield of BAO$^-$ in basic solvents which have ε greater than 20. The dominant existence of BAO$^-$ in basic PMMA can not be interpreted in terms of the formation of small cavities (filled with TEA) created in the polymeric medium in which most of the solute molecules might be located, because BAOH is the main form in both neat TEA and basic MMA.

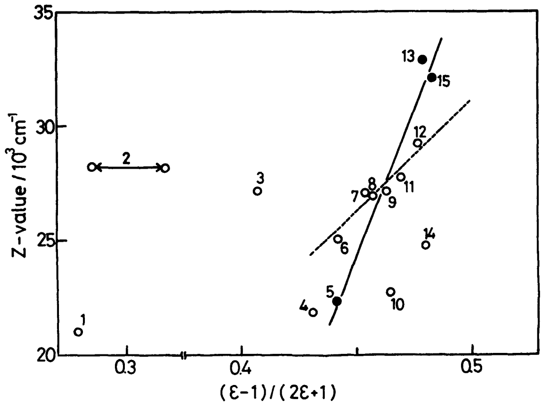

Fig. 5. Plot of Z-value against $(\varepsilon-1)/(2\varepsilon+1)$ for various solvents.
1: MMA, 2: PMMA, 3: tetrahydrofuran, 4: 1,2-dichloroethane, 5: pyridine, 6: 2-methyl-2-propanol, 7: 2-butanol, 8: 1-butanol, 9: 2-propanol, 10: acetone, 11: ethanol, 12: methanol, 13: *N,N*-dimethylformamide, 14: acetonitrile, 15: dimethyl sulfoxide.

It is obvious that the solvent molecules immediately around a solute molecule can no longer be described by the same parameters as those used for the bulk solvent. The more polar the solute, the greater would be the divergence between the properties of the solvent molecules near the solute and those of the bulk solvent. Since dielectric constants obtained by the usual macroscopic measurement reflect an average of solvent arrangements over macroscopic distances, they are inappropriate at the microscopic level to represent the solvent properties particularly when highly polar solute molecules are involved. Considering that the values of macroscopic dielectric constants are 2.9 for MMA[14] and 3.0—3.6 for PMMA,[15] one may envisage that the microscopic medium polarity in basic PMMA is much greater than that in basic MMA solution.

In order to scale the polarity of PMMA with another solvent-polarity parameter, we have measured the wave number of the longest wavelength charge-transfer absorption band of 1-methyl-4-(methoxycarbonyl)pyridinium iodide in various solvents. It is obvious that the obtained values, when expressed in energy, should correspond to Kosower's Z-values. Thus we call them simply Z-values for convenience. The obtained Z-values are plotted in Fig. 5 against $(\varepsilon-1)/(2\varepsilon+1)$ for various solvents to see the correlation between Z-value and ε. (For PMMA, ε is the macroscopic dielectric constant, *i.e.*, 3.0—3.6.) As is well known, the points are scattered too much to draw a single correlation line, but two lines can be drawn if the data are restricted to those in akin solvents. The dotted line shows a correlation in basic alcohols and the solid line is drawn for the data in basic pyridine, *N,N*-dimethylformamide, and dimethyl sulfoxide. From these different lines, however, one can estimate similar effective dielectric constants 25.4

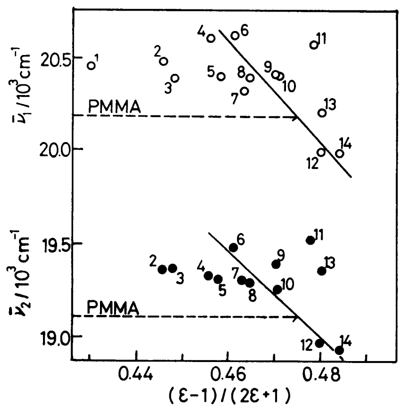

Fig. 6. Plot of two absorption peaks of BAO⁻ ($\tilde{\nu}_1$, $\tilde{\nu}_2$) against $(\varepsilon-1)/(2\varepsilon+1)$ for various solvents.
1: 1-Octanol, 2: 1-hexanol, 3: 1-pentanol, 4: 2-butanol, 5: 1-butanol, 6: 2-butanone, 7: 2-propanol, 8: acetone, 9: ethanol, 10: benzonitrile, 11: methanol, 12: *N,N*-dimethylformamide, 13: acetonitrile, 14: dimethyl sulfoxide.

(dotted line) and 21.6 (solid line) for that of PMMA and they are close to that which was estimated before, by comparing the spectral data of the acid-base pair of BAOH–BAO⁻ in PMMA with those in various solvents.

BAO⁻ provides a possibility of estimating the polarity of PMMA, since the solvent effect on the spectral shift of BAO⁻ is significant. Although solvent effects on absorption spectra have been studied for more than a century, it is difficult to understand these effects in terms of only one macroscopic physical solvent parameter. In general, most of the empirical solvent scales constitute a more comprehensive measure of solvent polarity than dielectric constant, and it can be said that only a multiparameter approach which includes terms corresponding to all possible solute-solvent interaction mechanisms is sufficient for the development of a quantitative model for medium effects of all kinds of solvents.[16] Since a large *Z*-value is obtained in PMMA, *i.e.*, $28.2\times10^3\,cm^{-1}$ in PMMA and $21.1\times10^3\,cm^{-1}$ in MMA, and since BAO⁻ is dominated in basic PMMA, it is evident that the microscopic medium polarity in PMMA is actually greater than that in MMA. Therefore, we have made a tentative plot of the wave number of two absorption peaks of BAO⁻ around 500 nm ($\tilde{\nu}_1$,$\tilde{\nu}_2$) against $(\varepsilon-1)/(2\varepsilon+1)$ for various solvents, and a good correlation is found for aprotic solvents as shown in Fig. 6. From this, one can estimate the effective dielectric constant of the basic PMMA to be 28.9—29.5.

All the values estimated so far for the effective dielectric constant of PMMA are much larger than the macroscopic dielectric constant of PMMA (ε=3.0—3.6) or MMA (ε=2.9), indicating the existence of a very polar microscopic region in PMMA. Thus there will be no doubt that the microscopic effective medium polarity of MMA will increase upon polymerization, resulting in the dominant existence of BAOH in basic MMA but of BAO⁻ in basic PMMA. Although the reason for this is not clear,[17] it may very well be related not only to the rigidity but also to the methoxycarbonyl group of PMMA, since it was confirmed that BAO⁻ could not exist in a basic polystyrene medium which was prepared similarly to PMMA. Further study on this problem is now in progress.

Finally, it would be worth mentioning that the present acid-base pair has an advantage as a probe to examine the microscopic dielectric constant of polymeric medium in the sense that it can be photochemically produced without modifying the microscopic environment. When a polar molecule is doped in a medium to probe its microscopic property, it is very likely that the molecules around the probe reorient to minimize the potential energy. This would make it impossible to know the "true face" of the polymer environment. Our "pre-probe" molecule, 9-benzoyl-10-nitroanthracene is, however, expected to behave as an inert molecule when doped in basic PMMA and upon irradiation it would generate BAO⁻ without modifying the environment; there will be an environment which is different from the polymer environment of BAO⁻ produced chemically from BAOH. Taking it into account that the two different ways of producing BAO⁻ yielded the same result, the anomalously high value of ε obtained for PMMA appears to reflect the true microscopic dielectric constant. Consequently, "photochemically producible probes" as described here will open a more reliable way for probing microscopic properties of polymeric media.

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17) One possibility might be the existence of a small amount of water in PMMA, which come together around a solute molecule as the polymerization proceeds. We have prepared a sample in a vacuum system, and MMA was dried using molecular sieves 3A (Wako Pure Chemical Industries, Ltd.) which was baked out at *ca.* 7×10^{-3} Pa and 500 °C for 20 h. However, we have obtained the same result.