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Transfer-free Energy Aspect on the Keto-enol Tautomerization Rate of Benzoylacetone in Water-Dimethyl Sulfoxide Mixtures

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Synopsis. The transfer-free energies of the keto form, the enol form, and the transition state of benzoylacetone from water to water–dimethyl sulfoxide (DMSO) mixtures have been evaluated on the basis of kinetic and partition experiments at 25 °C. The results were compared with those of acetylacetone, and the substituent effects of methyl and phenyl groups on the transfer-free energies have been discussed in terms of the group transfer-free energy.

The study of solvent effect on the kinetic behavior of β-diketone is necessary in order to elucidate the formation reaction of metal chelates with β-diketone and the solvent extraction mechanisms of these compounds. In the course of our study of the solvent effect on the keto-enol tautomerization rate of acetylacetone, we pointed out the usefulness of the partition coefficient in interpreting the kinetic solvent effect.[1] When the extent of solvent effect on a reactant is measured as a function of the change in the partition coefficient, the solvent effect on a transition state can be conveniently evaluated by simultaneous knowledge of the rate constant and the partition coefficient of the reactant. In this study, the solvent effect on the keto-enol tautomerization rate of benzoylacetone (BA) in a water–DMSO mixture will be described in terms of the transfer-free energy and the estimated free energies will be compared with those of acetylacetone (AA) in order to examine the substituent effects of methyl and phenyl groups.

Experimental

Chemicals. Benzoylacetone (Wako Junyaku Co., G. R.) was purified by recrystallization from diethyl ether. Heptane and DMSO were purified by a method described previously.[1] All the mixed solvents were prepared from the purified DMSO and the doubly distilled water by weight.

Kinetic Measurements. The tautomerization reaction was initiated by injecting a minute amount of a dioxane solution of BA into the mixed solvent in an optical cell thermostated at 25±0.1 °C. Since BA exists solely as the enol form in dioxane, the decreasing absorbance of the enol form is observed at 310 nm immediately after the injection. From the decrease in the absorbance recorded on a spectrophotometer, a first-order rate constant (k_{obsd}) was obtained. The concentration of BA was below 10^{-4} M in all measurements.

Equilibrium Measurements. The enol fractions (f) of BA in the mixed solvents were estimated from the apparent molar absorptivity at 310 nm. The molar absorptivity of the enol form of BA in water has been determined to be 1.62×10^4 at 310 nm by means of a stopped-flow technique.[2] The apparent partition coefficients (P_{obsd}) of BA between heptane and the mixed solvents were determined photometrically at 25±0.05 °C by the same method as was used for AA.[1] All the photometric measurements were carried out by means of a Hitachi 356 spectrophotometer.

Results and Discussion

The kinetic and equilibrium results are shown in Fig. 1. Both k_{obsd} and P_{obsd} decrease rapidly with an increase in the DMSO, while the enol fraction f increases moderately.

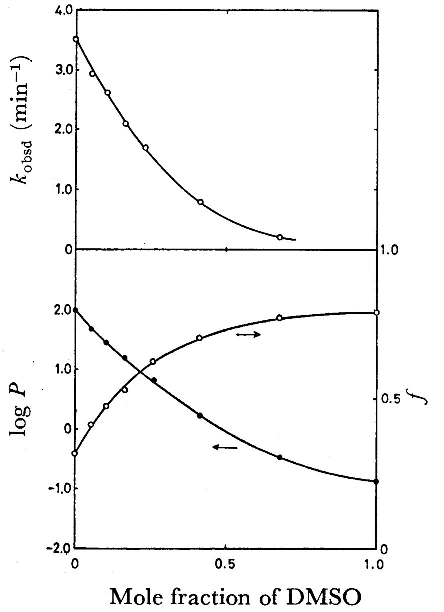

Fig. 1. Observed rate constant (k_{obsd}), enol fraction (f) and partition coefficient (P) of BA as a function of the mole fraction of DMSO.

From the equilibrium data, the transfer-free energies of the keto form ($\delta\Delta G_{\mathrm{s,K}}$) and the enol form ($\delta\Delta G_{\mathrm{s,E}}$) from water to the mixed solvents can be evaluated by means of Eqs. 1 and 2 respectively:

$$\delta\Delta G_{\mathrm{s,K}} = RT\ln\frac{(1-f^\circ)}{(1-f)}\cdot\frac{P}{P^\circ} \tag{1}$$

$$\delta\Delta G_{\mathrm{s,E}} = RT\ln\frac{f^\circ}{f}\cdot\frac{P}{P^\circ} \tag{2}$$

where the superscript ° denotes the values in water, chosen as the reference solvent. Moreover, the transfer-free energies of the transition state can be estimated by means of the following equation:

$$\delta\Delta G^{\mathrm{t}} = RT\ln\left(\frac{P}{P^\circ}\cdot\frac{1-f^\circ}{1-f}\cdot\frac{f^\circ}{f}\cdot\frac{k^\circ_{\mathrm{obsd}}}{k_{\mathrm{obsd}}}\right) \tag{3}$$

By using the partition coefficient on the mole fraction scale which is calculated from P_{obsd} and the density data of the mixed solvent in the literature,[3] we can obtain the transfer-free energies, $\delta\Delta G_{\mathrm{s,K}}$, $\delta\Delta G_{\mathrm{s,E}}$, and

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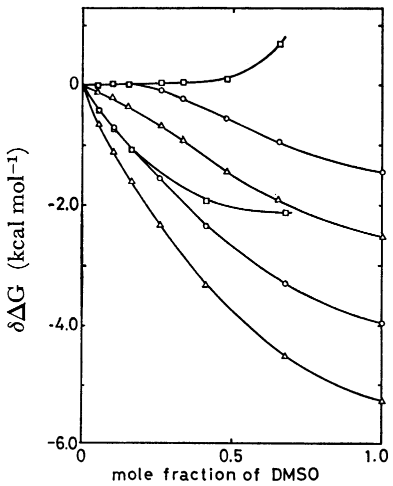

Fig. 2. Estimated transfer-free energies of AA (the upper three plots) and BA (the lower three plots) as a function of the mole fraction of DMSO. □: $\delta\Delta G^t$, ○: $\delta\Delta G_{s,K}$, △: $\delta\Delta G_{s,E}$.

$\delta\Delta G^t$, expressed as on the mole fraction scale. The estimated values, together with those for AA, are shown in Fig. 2 as a function of the DMSO mole fraction.

Figure 2 points to the following: (i) all the transfer-energy values of BA are smaller than those of AA; (ii) the $\delta\Delta G_{s,K}$ of AA is nearly zero in the composition region of $X_S < 0.2$, whereas that of BA decreases with the increase in DMSO in the same region; (iii) the $\delta\Delta G^t$ of AA is zero or a positive value, whereas that of BA is negative. These differences are considered to be mainly due to the destabilization of BA in water, which is caused by the substitution of the phenyl group for one methyl group of AA.

The substituent effect on the transfer-free energy should be discussed in terms of the group transfer-free energy. The $\delta\Delta G_{s,K}$ values, for example, of AA and BA may be divided into the corresponding free energies of the groups as follows:

$$\delta\Delta G^{A}_{s,K} = \delta\Delta G^{A}_{s}(\text{-COCH}_2\text{CO-}) + 2\delta\Delta G^{A}_{s}(\text{CH}_3\text{-}) \tag{4}$$

$$\delta\Delta G^{B}_{s,K} = \delta\Delta G^{B}_{s}(\text{-COCH}_2\text{CO-}) + \delta\Delta G^{B}_{s}(\text{CH}_3\text{-}) + \delta\Delta G^{B}_{s}(\text{C}_6\text{H}_5\text{-}) \tag{5}$$

where the superscripts A and B denote AA and BA respectively. If the next assumption is valid:

$$\begin{aligned} \delta\Delta G^{A}_{s}(\text{-COCH}_2\text{CO-}) &= \delta\Delta G^{B}_{s}(\text{-COCH}_2\text{CO-}) \\ \delta\Delta G^{A}_{s}(\text{CH}_3\text{-}) &= \delta\Delta G^{B}_{s}(\text{CH}_3\text{-}) \end{aligned} \tag{6}$$

the difference between Eqs. 4 and 5 becomes:

$$\delta\Delta G^{A}_{s,K} - \delta\Delta G^{B}_{s,K} = \delta\Delta G^{B}_{s}(\text{CH}_3\text{-}) - \delta\Delta G^{B}_{s}(\text{C}_6\text{H}_5\text{-}) \tag{7}$$

Similar treatments of $\delta\Delta G_{s,E}$ and $\delta\Delta G^t$ lead to Eq. 8:

$$\begin{aligned} \delta\Delta G^{A}_{s,K} - \delta\Delta G^{B}_{s,K} &= \delta\Delta G^{tA} - \delta\Delta G^{tB} \\ &= \delta\Delta G^{A}_{s,E} - \delta\Delta G^{B}_{s,E}\ . \end{aligned} \tag{8}$$

This equation shows that the transfer-free energy differences between the corresponding states of the two diketones are independent of the solvent composition and equal each other. However, the experimentally estimated values of the differences do not show an equality as in Eq. 8. The estimated values are as follows:

$$\begin{aligned} &\delta\Delta G^{A}_{s,K} - \delta\Delta G^{B}_{s,K} : \delta\Delta G^{tA} - \delta\Delta G^{tB} : \delta\Delta G^{A}_{s,E} - \delta\Delta G^{B}_{s,E} \\ &= 1 : 1.6 : 1.7 \end{aligned} \tag{9}$$

The discrepancy between these data and the prediction in Eq. 8 may be due to a difference in the charge delocalization of the keto forms, the enol forms, and the transition states of the two diketones, which is caused by substituting the phenyl group for one methyl group of AA. The result of Eq. 9 suggest that the charge distribution in the transition state is closer to that for the enol form than to that for the keto form.

The reaction indices for the enolization and the ketonization, α_e and α_k,[1] which are defined as:

$$\alpha_e = \frac{\delta\Delta G^t}{\delta\Delta G_{s,K}}, \quad \alpha_k = \frac{\delta\Delta G^t}{\delta\Delta G_{s,E}} \tag{10}$$

respectively, were estimated in the low-mole-fraction region of DMSO as follows: $\alpha_e = -0.17$ and $\alpha_k = -0.05$ in AA and $\alpha_e = 1.07$ and $\alpha_k = 0.69$ in BA. The signs of α in the two diketones are opposite, according to the sign of $\delta\Delta G^t$.

From the above results, it seems that the effect of the mixed solvent on the transfer-free energies is more striking in AA than in BA. Recently, Symons[4] has investigated the hydrogen-gas solubility in the water–DMSO mixed solvent at 25 °C and has observed a distinct minimum of the solubility expressed on the molar scale in the region of 25—35 mol % DMSO. In a previous study of the liquid-liquid partition of AA between heptane and the mixed solvent, a distinct maximum in the partition coefficient of the keto form has been observed at $X_S = 0.2$.[1] However in the case of BA no such phenomenon is observed at all. Although the hydrogen-gas solubility has been interpreted in terms of a changing entropy and energy of "hole" formation in the solvent with the composition,[4] the transfer-free energy of β-diketone is not likely to be solely interpreted by this factor. In the case of β-diketone, a solute-solvent interaction energy including a size contribution of solute and solvent[5] seems to be a possible factor governing the transfer-free energy, in addition to the "hole" formation energy which may be related to such a property as an internal pressure of the solvent.[6,7]

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