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SPECTROPHOTOMETRIC INVESTIGATIONS OF THE TAUTOMERIC REACTION BETWEEN ANTHRONE AND ANTHRANOL—I

THE KETO-ENOL EQUILIBRIUM

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Abstract—The equilibrium of the tautomeric reaction between anthrone and anthranol has been investigated in isooctane and benzene by means of absorption and fluorescence spectrophotometry, on the basis of the finding that the keto-enol reaction is catalysed by basic substances, e.g. triethylamine. For the enolization reaction the equilibrium constant at 20° and the enthalpy change are, respectively, 0·0021 and 3·3 kcal/mol in isooctane and 0·0025 and 2·6 kcal/mol in benzene, indicating that the keto form is more stable in inert solvents. Addition of increasing amount of triethylamine leads to a gradual shift of the equilibrium toward the enol form, which fact is quantitatively interpreted in terms of the formation of a hydrogen-bond between anthranol and the amine.

INTRODUCTION

ALTHOUGH the interconversion between anthrone and anthranol is typical of the keto-enol tautomerism, comparatively few quantitative studies have been made of the rate and equilibrium of this tautomeric reaction. Bansho and Nukada[1,2] studied the kinetics of the isomerization of anthranol to anthrone in various solvents by dielectrical and analytical techniques, and Löber[3] investigated the keto-enol equilibrium by means of fluorescence spectrometry. The results of these studies indicate that the reaction is of the first order and both its rate and equilibrium are strongly dependent upon the solvent employed.

From the viewpoint of the quantum-mechanical resonance, considerable attention has been paid to the relative stability of anthrone and anthranol.[4,5] In connection with this problem, it should be desirable to determine experimentally the energy difference between the two forms in inert solvents like hydrocarbons. Unfortunately, in hydrocarbon solvents the tautomeric reaction is very slow and the equilibrium is on the side of the keto form. These facts make it practically impossible to measure the equilibrium constant and determine the energy difference in such solvents.

As reported in a preliminary communication, the authors[6] observed spectroscopically that the reaction is catalysed by basic substances, e.g. triethylamine. By developing this observation the anthrone-anthranol equilibrium has been studied in detail and quantitatively in hydrocarbon solvents, the resulting data being given in this paper. In the presence of a relatively large amount of the basic substance, the enol form was found to increase appreciably; and this phenomenon is interpreted in terms of hydrogen-bonding between anthranol and the base. The following paper of this series will deal with the base-catalysed reaction itself.

RESULTS AND DISCUSSION

The intrinsic keto–enol equilibrium. The near UV absorption spectra of anthrone in isooctane and benzene are shown in Fig. 1. Of the two electronic absorption bands, the weaker one located at the longer wavelengths has been assigned to an $n \rightarrow \pi^*$ transition, and the other stronger band to a $\pi \rightarrow \pi^*$.[7] In conformity with this assignment, the weaker band is displaced to the blue and the stronger to the red on changing the solvent from isooctane to benzene, that is, on increasing the solvent refractive index.[8]

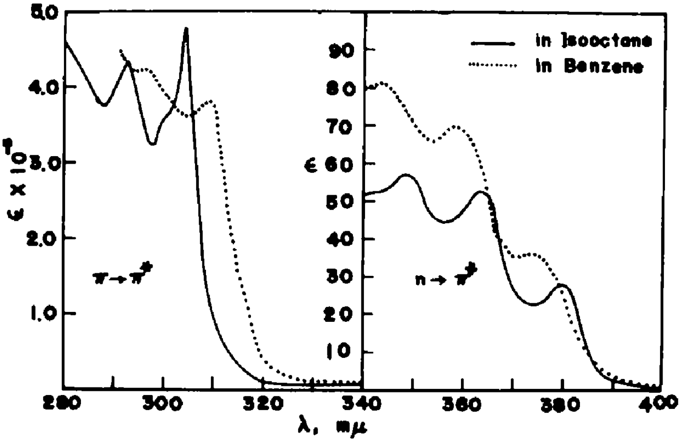


FIG. 1 The near UV absorption spectra of anthrone in isooctane and benzene.

In isooctane or benzene as solvent, especially when it is deaerated, the highly purified anthrone is stable so that almost no change is produced in its spectrum in a day or two, indicating that the enolization reaction is extremely slow. However, the reaction is accelerated by addition of a small amount of a basic compound. Thus, in the presence of triethylamine the concentration of which is as low as 10^{-4} mol/l., the keto–enol equilibrium is reached in hydrocarbons within several hours, starting from anthrone. It should be noted that triethylamine of such a low concentration has virtually no effect on the keto–enol equilibrium itself, as will be shown later.

In Fig. 2 is shown the absorption spectrum of the equilibrium mixture of anthrone and anthranol in benzene, which was attained in the above-mentioned manner, together with the spectrum of anthrone alone. It is seen that the transformation of the keto form to the enol causes an increase of absorption in the $n \rightarrow \pi^*$ region of the ketone; specifically a distinct peak is seen to appear at 405 mμ which does not exist in the spectrum of the ketone itself.

The absorption difference as obtained by subtracting the absorption of the ketone from that of the equilibrium mixture is represented in Fig. 2 by spectrum 3, and the absorption of anthranol in toluene by spectrum 4. The scale of the ordinate for spectrum 4 is so chosen that its maximum at 386 mμ may coincide with the corresponding maximum of spectrum 3. Taking into account the difference between the

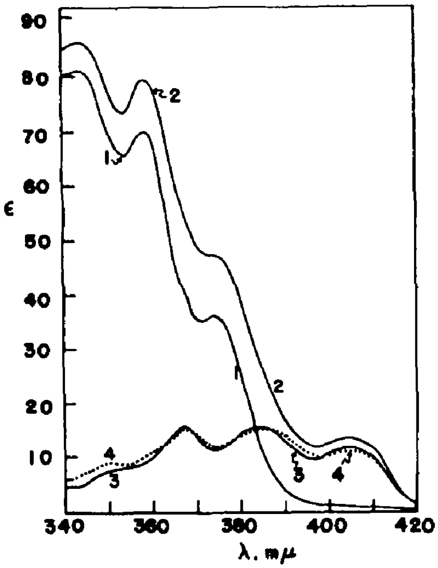


FIG. 2 The absorption spectra of anthrone, anthranol and their equilibrium mixture: 1, anthrone in benzene; 2, the equilibrium mixture of anthrone and anthranol in benzene; 3, difference of spectra 2 and 1; 4, anthranol in toluene.

solvents employed, one may says that spectrum 3 agrees well with spectrum 4; namely, spectrum 3 represents the enol form.

In contrast to anthrone in benzene, which gives no fluorescence, the equilibrium mixture corresponding to spectrum 2 of Fig. 2 does exhibit fluorescence. Figure 3 shows the fluorescence spectrum along with the excitation spectrum associated with the fluorescence. It is reasonable to consider that the fluorescence originates from

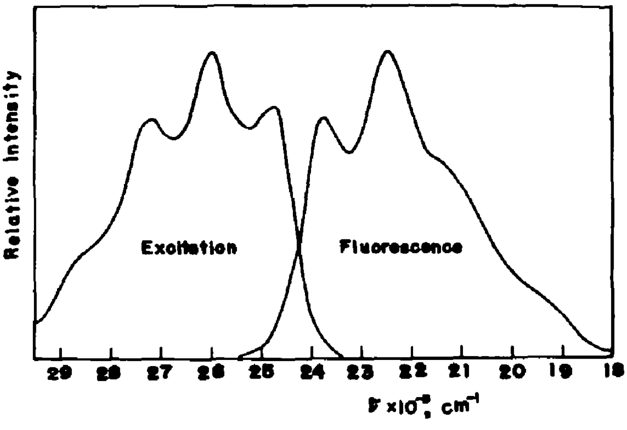


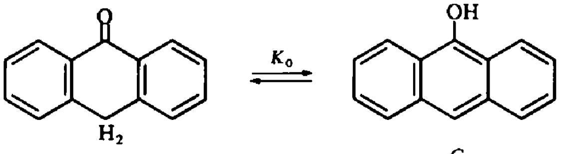
FIG. 3 Fluorescence and excitation spectra of the equilibrium mixture of anthrone and anthranol in benzene.

the enol form. In fact, the excitation spectrum agrees with the absorption spectrum of anthranol (cf. spectra 3 and 4 of Fig. 2), and besides there is a mirror-image relationship between excitation and fluorescence spectra.

It may be noted that results essentially similar to those shown in Figs 2 and 3 have been obtained with solutions of anthrone in isooctane.

The keto–enol equilibrium with which we are concerned here is free from the influence of the base added as a catalysing agent, so that it is to be called the intrinsic equilibrium.

Now, let us consider the equilibrium



C_k C_e (1)

where K_0 is the equilibrium constant, with the subscript zero referring to the intrinsic equilibrium. C_k and C_e are the equilibrium concentrations of anthrone and anthranol, respectively. Assuming that their respective initial concentrations are C_k^0 and zero, one obtains

$$C_k + C_e = C_k^0 \tag{2}$$

$$K_0 = \frac{C_e}{C_k} \tag{3}$$

The absorbance A of the equilibrium mixture is given by

$$A = (\epsilon_k C_k + \epsilon_e C_e) d \tag{4}$$

where ϵ_k and ϵ_e are the molar extinction coefficients of the keto and enol forms, respectively, and d is the cell length. It follows from Eqs (2), (3) and (4) that

$$\epsilon_0 \equiv \frac{A}{C_k^0 d} = \frac{\epsilon_k + K_0 \epsilon_e}{1 + K_0} \tag{5}$$

ϵ_0 is the apparent molar extinction coeficient of the equilibrium mixture; it corresponds to spectrum 2 of Fig. 2. The difference $\epsilon_0 - \epsilon_k$ which corresponds to spectrum 3 of the same figure is expressed as

$$\epsilon_0 - \epsilon_k = \frac{K_0}{1 + K_0}(\epsilon_e - \epsilon_k) \tag{6}$$

As has already been stated, anthrone shows only a weak $n \rightarrow \pi^*$ transition in the region from 340 to 420 mμ, whereas anthranol has a relatively strong $\pi \rightarrow \pi^*$ transition in the same spectral region. Thus, in this region, ϵ_k is less than one hundred, but ϵ_e amounts to several thousand; that is, $\epsilon_e \gg \epsilon_k$. Equation (6) can then be written as

$$\epsilon_0 - \epsilon_k \simeq \frac{K_0}{1 + K_0}\epsilon_e \tag{7}$$

which means that the difference $\epsilon_0 - \epsilon_k$ is approximately proportional to ϵ_e.

TABLE 1. THERMODYNAMIC QUANTITIES FOR THE ISOMERIZATION OF ANTHRONE TO ANTHRANOL IN HYDROCARBON SOLVENTS

Solvent	K_0				ΔH_0 (kcal/mol)	ΔS_0 (cal/deg. mol)	ΔF_0 (kcal/mol)
Isooctane	$1{\cdot}70 \times 10^{-3}$ (285°K)	$2{\cdot}07 \times 10^{-3}$ (293°K)	$2{\cdot}47 \times 10^{-3}$ (303°K)		3·3	−1·0	3·6 (300°K)
Benzene	$1{\cdot}98 \times 10^{-3}$ (278°K)	$2{\cdot}30 \times 10^{-3}$ (289°K)	$2{\cdot}77 \times 10^{-3}$ (299°K)	$3{\cdot}07 \times 10^{-3}$ (308°K)	2·6	−3·0	3·5 (300°K)

Further, it follows from Eq. (7) that $K_0 \ll 1$, since $\epsilon_e \gg \epsilon_0 - \epsilon_k$ (cf. Fig. 2). Therefore Eq. (7) becomes

$$K_0 \simeq \frac{\epsilon_0 - \epsilon_k}{\epsilon_e} \tag{8}$$

The value of ϵ_e can be determined in the manner described later, so that the equilibrium constant K_0 is easily obtained from Eq. (8).

The K_0 values thus determined with isooctane and benzene as solvents at various temperatures are given in Table 1. Plots of log K_0 against $1/T$ show a good linear relationship (Fig. 4). From these data the changes of the enthalpy, entropy and free energy (ΔH_0, ΔS_0 and ΔF_0) for the isomerization of anthrone to anthranol were obtained in the ordinary way, the results being listed in Table 1.

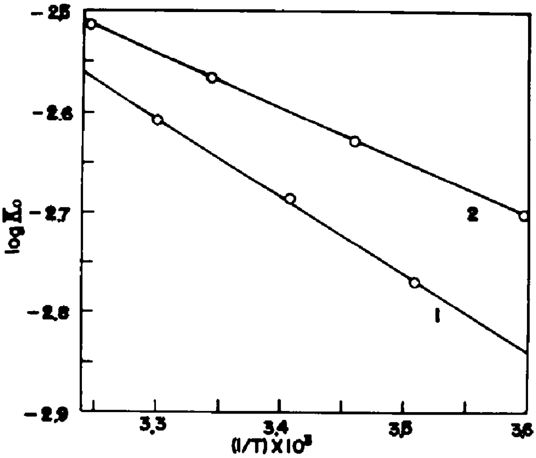


FIG. 4 Plots of log K_0 vs. $1/T$: 1, in isooctane; 2, in benzene.

As to the relative stability of anthrone and anthranol, it has been supposed that the two tautomeric forms have approximately the same energy.[5] Table 1 shows that the keto form is more stable by 3·3 kcal/mol in isooctane and by 2·6 kcal/mol in benzene. The energy difference is thus small in ether case, but it is sufficient to locate the equilibrium definitely on the side of the keto form.

Effects of basic substances on the keto–enol equilibrium. As may be seen in Fig. 5, in hydrocarbons as solvents, the increase of the concentration of triethylamine was found to lead not only to an increase of the rate of the conversion but also to an intensification of the absorption in the long wavelength region (>340 mμ). Figure 6 shows plots of absorbance values at 367 mμ and 385 mμ against the initial concentration, C_B^0, of the catalysing base, triethylamine. (We are here concerned with relatively low values of C_B^0.)

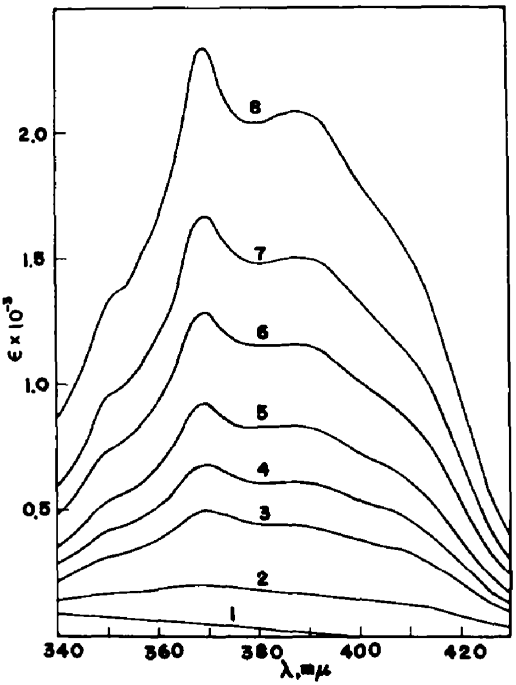


Fig. 5 Changes in the absorption spectrum of anthrone in benzene at 20° caused by addition of triethylamine. The concentrations of triethylamine (C_B^0): 1, 10^{-4}; 2, 0·21; 3, 0·63; 4, 0·94; 5, 1·41; 6, 2·12; 7, 3·17; 8, 4·76 mol/l.

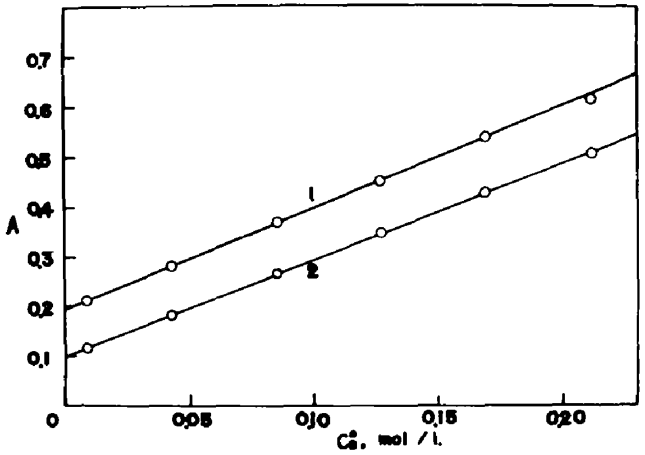
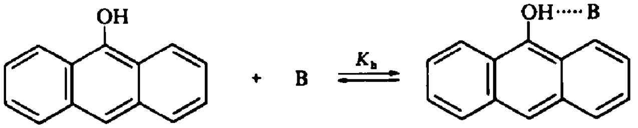


Fig. 6 Plots of A vs. C_B^0: 1, at 367 mμ; 2, at 385 mμ. In benzene at 20° with triethylamine as the base. C_K^0, 3·32 × 10^{-3} mol/l.; cell length, 10 mm.

The experimental results shown in Figs 5 and 6 can be best understood by considering the following hydrogen-bonding equilibrium:

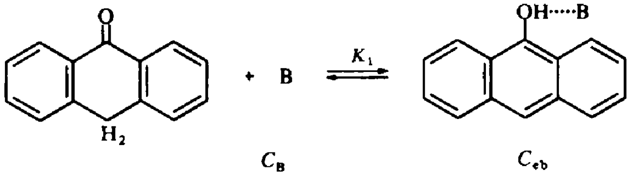


(9)

in which B stands for the base. The formation of the hydrogen bond between anthranol and the base must result in a stabilization of the enol form. The keto–enol equilibrium will then be displaced to the side of the enol form.

The spectra in Fig. 5 for the higher concentrations of triethylamine differ appreciably from the spectrum of the free anthranol (cf. Fig. 2). This can be explained by attributing the former spectra to the hydrogen-bonded complex.[9] It may be noted that the absorbance values obtained by extrapolating the lines of Fig. 6 to $C_B^0 = 0$ are practically equal to those observed with $C_B^0 = 10^{-4}$ mol/l. (cf. Fig. 2), but are different from the corresponding absorbance values observed for anthrone in the pure hydrocarbon solvents, i.e. with $C_B^0 = 0$.

In order to quantitatively treat the keto–enol equilibrium in the presence of the base, let us assume the following equilibrium in addition to (1):



(10)

in which K_1 is the equilibrium constant, and C_B and C_{eb} are, respectively, the concentrations at equilibrium of the base and the hydrogen-bonded complex of anthranol with the base. One will then have

$$C_k + C_e + C_{eb} = C_k^0 \tag{11}$$

$$K_1 = \frac{C_{eb}}{C_k C_B} \tag{12}$$

The absorbance value at equilibrium is given by

$$A = (\epsilon_k C_k + \epsilon_e C_e + \epsilon_{eb} C_{eb})\, d \tag{13}$$

where ϵ_{eb} is the molar extinction coefficient of the complex. It follows from Eqs (3) and (11)–(13) that

$$\epsilon = \frac{A}{C_k^0 d} = \frac{\epsilon_k + K_0 \epsilon_e + K_1 C_B \epsilon_{eb}}{1 + K_0 + K_1 C_B} \tag{14}$$

The ratio $(C_e + C_{eb})/C_k$ represents the apparent equilibrium constant, K_{app}, for the keto–enol reaction in the presence of the base. From Eqs (3) and (12)

$$K_{\mathrm{app}} = \frac{C_e + C_{eb}}{C_k} = K_0 + K_1 C_B \tag{15}$$

It is to be noted that, if $C_B^0 \rightarrow 0$, then $C_B \rightarrow 0$; so that $K_{\mathrm{app}} \rightarrow K_0$ and $\epsilon \rightarrow \epsilon_0$ (cf. Eq. (5)).

The equilibrium constant K_h for the hydrogen-bond between the enol and the base is given by

$$K_h = \frac{C_{eb}}{C_e C_B} \tag{16}$$

Combination of Eqs (3) and (16) leads to

$$K_1 = K_0 K_h \tag{17}$$

Now, with the use of the extinction coefficient ϵ_0 defined by Eq. (5), Eq. (14) can be rewritten as

$$\epsilon = \epsilon_0 + \frac{K_1 C_B}{1 + K_0 + K_1 C_B}(\epsilon_{eb} - \epsilon_0) \tag{18}$$

Since K_0 is known to be far smaller than unity (Table 1), Eq. (18) becomes

$$\epsilon \simeq \epsilon_0 + \frac{K_1 C_B}{1 + K_1 C_B}(\epsilon_{eb} - \epsilon_0) \tag{19}$$

If the base is triethylamine, K_h is considered to be of the order of 10^2 l./mol,[10] so that K_1 should be less than 1 l./mol; moreoever C_k^0 is of the order of 10^{-3} mol/l. under the present experimental conditions. Therefore it follows that

$$\frac{C_{eb}}{C_B^0} < \frac{C_{eb}}{C_B} = K_1 C_k < K_1 C_k^0 \ll 1$$

since $C_B^0 > C_B$ and $C_k^0 > C_k$; in other words $C_{eb} \ll C_B^0$. Combination of this relation with $C_B = C_B^0 - C_{eb}$ results in an approximate equation $C_B \simeq C_B^0$. It may be noted that this approximate equation holds regardless of the magnitude of C_B^0. If it is assumed that C_B^0 is so small that $K_1 C_B^0 \ll 1$, Eq. (19) is reduced to

$$\epsilon \simeq \epsilon_0 + K_1(\epsilon_{eb} - \epsilon_0) C_B^0 \tag{20}$$

It is to be expected from Eq. (20) that a plot of ϵ versus C_B^0 should lead to a straight line, with the intercept equal to ϵ_0. The results shown in Fig. 6 are in agreement with this expectation. Also, the slope of the line should give $K_1(\epsilon_{eb} - \epsilon_0)$, from which K_1 can be determined, since the ϵ_{eb} value is known as will be described later. The constants K_1 thus obtained are listed in Table 2, together with the values of ΔH_1, ΔS_1 and ΔF_1 for the reaction in Eq. (10). The linearity of the plots of log K_1 versus $1/T$ is good, as is seen in Fig. 7.

Inspection of the values of K_0 and K_1 in Tables 1 and 2 will reveal that $K_0 \gg K_1 C_B$ if C_B^0 is of the order of 10^{-4} mol/l. It can then be concluded from Eq. (15) that the

TABLE 2. THERMODYNAMIC QUANTITIES FOR THE FORMATION OF THE ANTHRANOL–TRIETHYLAMINE HYDROGEN-BONDED COMPLEX FROM ANTHRONE AND TRIETHYLAMINE IN HYDROCARBON SOLVENTS

Solvent		K_1 (l./mol)		ΔH_1 (kcal/mol)	ΔS_1 (cal/deg. mol)	ΔF_1 (kcal/mol)
Isooctane	0·182 (285°K)	0·149 (293°K)	0·109 (303°K)	−5·2	−21·4	1·3 (300°K)
Benzene	0·117 (286·5°K)	0·095 (293°K)	0·073 (303°K)	−5·2	−22·4	1·5 (300°K)

keto–enol equilibrium undergoes hardly any change by the existence of triethylamine of such a low concentration.

Quantities for the hydrogen-bond. The equilibrium constant K_h and the enthalpy change ΔH_h for the formation of the hydrogen-bond between anthranol and triethylamine (Eq. (9)) can be derived from the corresponding quantities for the reactions represented by Eqs (1) and (10). Thus, from the relation $K_h = K_1/K_0$, the values of K_h at 25° were determined to be 57 and 31 l./mol, respectively, in isooctane and benzene. These are somewhat smaller than the equilibrium constants for the hydrogen-bonds in which naphthols or phenol are used in place of anthranol;[11] this is probably due to the steric hindrance which is considered to exist at the 9-position of anthracene. Reasonable values of ΔH_h were obtained by combining the data given in Tables 1 and 2. The results are as follows: −8·5 and −7·8 kcal/mol in isooctane and benzene, respectively.

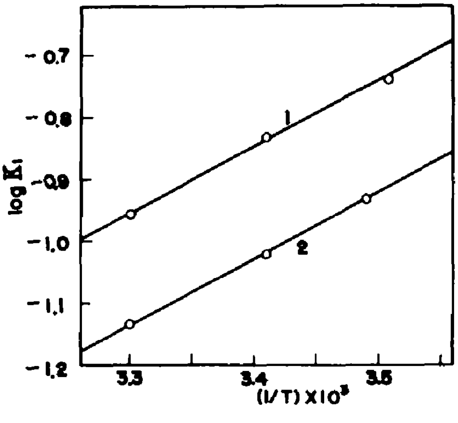


FIG. 7 Plots of log K_1 vs. $1/T$: 1, in isooctane; 2, in benzene.

Conversely, these observations indicate that the hydrogen-bond is responsible for the displacement of the equilibrium toward the enol form in the presence of triethylamine. It is to be noted that the absolute value of the entropy change ΔS_1 is markedly large as compared with that of ΔS_0. This is quite reasonable since the former corresponds to a bimolecular association.

It would be of interest to point out here that the amount of the enol form is greater in polar solvents than in hydrocarbons.[2] It can now be suggested that in the former solvents the formation of a hydrogen-bond between anthranol and the solvent molecule should lead to a shift of the equilibrium in favor of the enol form.

Evaluation of ϵ_e *and* ϵ_{eb}. According to Eq. (7) ϵ_e is proportional to $\epsilon_0 - \epsilon_k$ in the wavelength region longer than 340 mμ. Similarly, in the same region, it follows from Eq. (18) that ϵ_{eb} is proportional to $\epsilon - \epsilon_0$ for a given value of C_B (or C_B^0), under the reasonable assumption that $\epsilon_{eb} \gg \epsilon_0$. The relative values of ϵ_e and ϵ_{eb} are thus obtained as a function of the wavelength, since the values of $\epsilon_0 - \epsilon_k$ and $\epsilon - \epsilon_0$ are known from the experiment. The above procedure enables one to determine only the spectral forms or the relative spectra for the free and hydrogen-bonded anthranol. As regards the solution of anthranol in toluene, the absorption spectrum was directly observed for a wider wavelength region, but still the absolute intensity (i.e. ϵ_e itself) could not be determined because of the instability of anthranol. Therefore, in the present study ϵ_e and ϵ_{eb} were evaluated in an indirect way as follows.

It can be shown from Eq. (18) that the following equation holds for two given wavelengths λ_1 and λ_2, irrespective of the value of C_B^0:

$$\frac{\epsilon(\lambda_1) - \epsilon_0(\lambda_1)}{\epsilon(\lambda_2) - \epsilon_0(\lambda_2)} = \frac{\epsilon_{eb}(\lambda_1) - \epsilon_0(\lambda_1)}{\epsilon_{eb}(\lambda_2) - \epsilon_0(\lambda_2)} \tag{21}$$

where $\epsilon(\lambda_1)$, for instance, is the value of ϵ at λ_1. A plot of $\epsilon(\lambda_1)$ versus $\epsilon(\lambda_2)$ was found to give a straight line, in conformity with what Eq. (21) means. Consider a second straight line represented by

$$\frac{\epsilon(\lambda_1)}{\epsilon(\lambda_2)} = \frac{\epsilon_{eb}(\lambda_1)}{\epsilon_{eb}(\lambda_2)} \tag{22}$$

Then it is to be expected that

$$\epsilon(\lambda_1) = \epsilon_{eb}(\lambda_1) \quad \text{and} \quad \epsilon(\lambda_2) = \epsilon_{eb}(\lambda_2)$$

at the intersecting point of these two lines.

Now, the following assumptions are seen to be reasonable by reference to the results of studies on electronic spectra of some anthracene derivatives.[12] (1) The

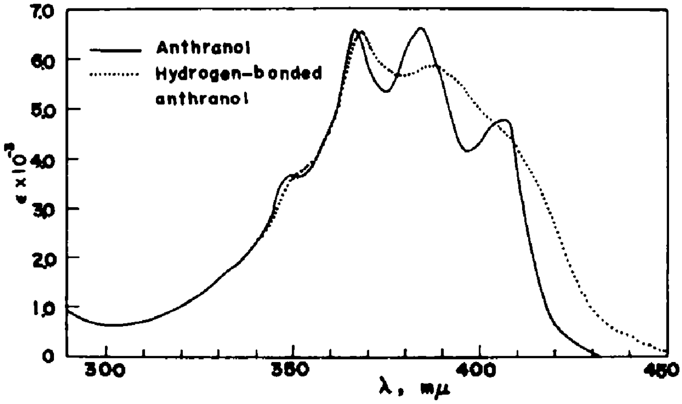


FIG. 8 The absorption spectra of anthranol in toluene (solid curve) and the hydrogen-bonded complex of anthranol with triethylamine in benzene (dotted curve).

absorption spectrum of anthranol in the region of 300 to 430 mμ consists of two different electronic bands. The one at the shorter wavelengths is due to the ^1L_b transition, which includes the vibrational peak at about 370 mμ, and the other is due to the ^1L_a transition. (2) The ^1L_b transition is insensitive to the environmental condition, so that no appreciable change is produced in both its location and intensity by changing the solvent. On the basis of these assumptions, $\epsilon_{eb}(\lambda_1)/\epsilon_{eb}(\lambda_2)$ for the hydrogen-bonded complex in benzene was evaluated to be 1/10 with $\lambda_1 = 309$ mμ and $\lambda_2 = 369$ mμ, from the spectral data on the free anthranol in toluene. The absolute value for ϵ_{eb} (369 mμ) was then determined by the analysis based on Eqs (21) and (22), with the result ϵ_{eb}(369 mμ = 6600. Application of this ϵ value to the vibrational peak in the relative absorption spectra for the free or hydrogen-bonded species in isooctane, benzene and toluene led to the respective absolute spectra, two examples of which are shown in Fig. 8.

Effects of other basic substances. Some basic substances other than triethylamine have also been investigated. Pyridine has essentially the same effect as triethylamine on both the reaction rate and the equilibrium. On the other hand, dioxan produces no appreciable change in the reaction rate, but it has a definite effect on the equilibrium. Thus, on changing the solvent from a hydrocarbon to dioxan, the keto–enol equilibrium was found to be displaced to the side of the enol form. (The equilibrium in dioxan was reached by addition of a small amount ($\sim 10^{-4}$ mol/l.) of triethylamine.) This can be interpreted as due to a stabilization of the enol form caused by the formation of a hydrogen-bond between anthranol and dioxan.

EXPERIMENTAL

Materials. Anthrone was carefully purified by chromatography using a column of activated silica gel, which was recommended by Funakubo and Nagai,[13] with isooctane–toluene mixtures of varying ratios as the developer and benzene as the eluent. The resulting soln of anthrone was evaporated on a water bath in a stream of N_2. Anthranol was prepared by the method of Nukada and Basho;[1] the pure anthranol was obtained only as a soln in toluene because of its instability.

Isooctane (2,2,4-trimethylpentane) obtained from Enjay Company Inc., U.S.A., was purified by being passed through a freshly activated silica gel column. Benzene and dioxan (extra-pure grade) were fractionally crystallized several times, refluxed with P_2O_5, and then distilled.[14] Toluene was dried over P_2O_5 and fractionally distilled. Et_3N was treated with activated alumina and then fractionally distilled.[14] Spectro-grade pyridine was used without further purification.

Apparatus. Absorption spectra were obtained at controlled temps with a Hitachi spectrophotometer of type EPU-2A or EPS-2, silica cells of 10 mm and 100 mm path lengths being used. Fluorescence and excitation spectra were measured at room temp with the type EPU-2A spectrophotometer in combination with a Hitachi fluorescence accessory of type G-3.

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