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Spectroscopic Evidence of α,α-Dihydroxy Ketone in Biacetyl Aqueous Solutions

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From the analysis of emission, excitation, absorption, and ^{1}H NMR spectra of 2,3-butanedione (i.e., biacetyl), it has been established that about two thirds of the molecule in aqueous solutions exists as 3,3-dihydroxy-2-butanone (i.e., a hydrated form of biacetyl). For the first time, two different types of emission are discriminated: Emission is mostly due to the fluorescence spectrum of the monoketone upon irradiation of light with a shorter wavelength than 320 nm while it is due to the strong phosphorescence spectrum of biacetyl itself upon irradiation of light with a longer wavelength than 350 nm. The almost stoichiometric molecular rearrangement from the hydrated (monoketone) form in a water phase to the ordinary (diketone) form in a hydrocarbon phase has been found to take place.

The molecule, 2,3-butanedione (i.e., biacetyl; hereafter abbreviated as BA), has extensively been studied both on the energy decay dynamics[1-9] and on the electronic and molecular structures in the excited states.[10-14] Its substantially high phosphorescence quantum yield in fluid solutions still gives intriguing problems to molecular spectroscopists. The fundamental interpretations of the photochemical and photophysical processes were reviewed earlier.[15,16] Many optical studies thereof have so far been carried out in nonaqueous solvents or in the free molecule, on one hand. From the spectroscopic interest of cage effects, on the other hand, room temperature phosphorescence materials (including BA) in cyclodextrins and in micelles have recently come to attract attention;[17,18] the surrounding environments being water for these cases.

At an early stage of the ^{1}H NMR instrumental development, Greenzaid et al. observed the spectra of several aliphatic aldehydes and ketones in aqueous solutions and found that there, more or less, exists equilibrium between the hydration-dehydration reaction for each molecule.[19] Further, unusual absorption behavior was found for BA in water.[20-25] Substantial hydration was pointed out to occur in such solutions although several other photochemical processes were suggested.[22] Spectroscopically, no further developed optical study has been pursued from this point of view despite its importance: In fact, several authors seem to encounter similar problems recently.[17,18,23-25] Most all these works are thus likely to contain some erroneous conclusions because they did not necessarily take into account this molecular rearrangement reaction in the water phase.

The purpose of this paper is to give an additional piece of evidence for the equilibrium by means of the usual emission technique.

Experimental

The materials (i.e., BA, acetone, 3-hydroxy-2-propanone, 3-hydroxy-2-butanone, and 1,3-dihydroxy-2-propanone: all Tokyo Kasei GR grade reagents) were several times distilled in vacuo. The absorption and emission spectra were recorded on a Hitachi Absorption Spectrometer EPS-2 and on a Hitachi Fluorometer F-3000, respectively. The NMR spectra were measured on a 400 MHz Japan Electric NMR Spectrometer type JNM-GX400 using D_2O and C_6D_6 (both E. Merck reagents). The other solvents were all Dotite spectroscopic grade reagents. Dioxane (DX) and tetrahydrofuran (THF) were used immediately after the neat solvents were purged with nitrogen gas for several minutes.

Results and Discussion

Absorption Spectra. To our knowledge, there is not a suitable solvent which is miscible with water and is of an "inert" nature. As the next best choice, DX and THF were employed although these never fulfilled the latter requirement. In order to obtain reproducible (and thus reliable) spectral data, we measured the absorption spectra immediately after the sample solutions were prepared. Further, we paid a special caution to prevent the solutions from coming into contact with air under room light. The absorption spectra of BA at a constant concentration in THF-H_2O mixed solvents were measured with changing the molar fraction of H_2O. The results are partially shown in Fig. 1. An increase in absorption intensity around 260 nm with a decrease in H_2O concentration may largely be attributed to peroxides which still coexist in THF.

First we consider a chemical equilibrium between the hydration-dehydration reaction as follows:

$$BA + n\,H_2O \leftrightarrow BA[H_2O]_n. \quad (1)$$

Then we obtain a stoichiometric equation by using an analytical method[26,27] as follows:

$$\frac{1}{\varepsilon - \varepsilon_A} = \frac{1}{(\varepsilon'_A - \varepsilon_A)KC^n} + \frac{1}{\varepsilon'_A - \varepsilon_A} \quad (2)$$

where ε'_A and ε_A are the molar extinction coefficients of the hydrated (monoketone) form and the diketone form of BA, respectively; ε an apparent absorption

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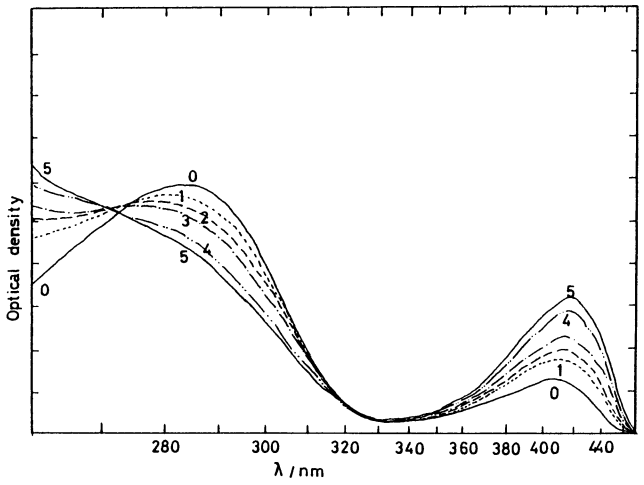

Fig. 1. Absorption spectra of BA in H_2O–THF mixed solvents at 25 °C. BA concentration is fixed at 2.6×10^{-2} mol dm^{-3}. H_2O concentrations (in mol dm^{-3} units) are: (0)55, (1)38.5, (2)33, (3)27.5, (4)16.5, and (5)11.

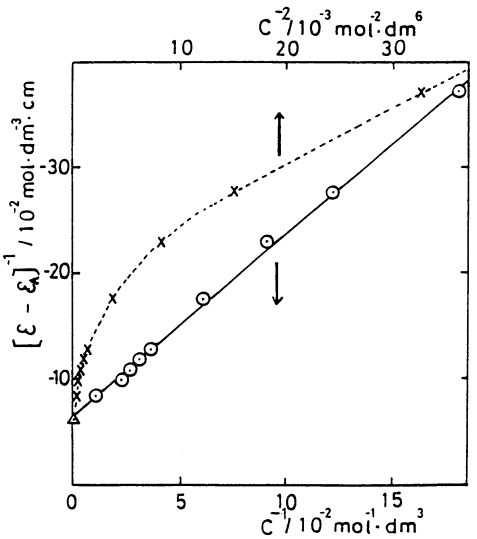

Fig. 2. Plots of $(\varepsilon-\varepsilon_A)^{-1}$ against C^{-n} (C: H_2O concentrations; and n=1,2) at 410 nm. For ○, n=1; for ×, n=2; and for △, see text.

coefficient of the system as a function of wavelengths; and C the total concentration of water. Plots of $(\varepsilon-\varepsilon_A)^{-1}$ against C^{-n} may give a straight line as far as Eq. 1 holds. In Fig. 2, $(\varepsilon-\varepsilon_A)^{-1}$ at 410 nm was plotted against C^{-1} and C^{-2}. It should be noted that a linear relation was obtained for case n=1, but not for n=2 (and also not for n=0.5). The hydration number n is thus 1. From the slope and the intercept of the straight line in Fig. 2, the values of K and ε'_A were estimated to be 3.61×10^{-2} dm^3 mol^{-1} and ca. 0 dm^3 mol^{-1} cm^{-1}, respectively. As shown in Table 1, the obtained K value is close to that evaluated by Bell et al. for another solvent system at 25 °C under the assumption that the 420 nm absorption system is completely due to the $S_1(n\pi^*)\leftarrow S_0$ transition of the ordinary diketone form of

Table 1. Equibrium Constant K at 25 °C

Solvent system[a]	Means[b]	$K/10^{-2}$ dm^3 mol^{-1}	α[c]
H_2O-DX	Abs.	3.8±0.5	0.48±0.07
H_2O-THF	Abs.	3.7±0.5	0.49±0.08
H_2O-EtOH	Abs.	1.9±1.0	0.95±0.4
D_2O	NMR	3.4±0.3	0.53±0.05
H_2O[d]	NMR	(3.6)[e]	0.500
H_2O-DX[f]	Abs.	(6.0)[e]	0.299

a) DX: dioxane; THF: tetrahydrofuran; EtOH: ethanol. b) Abs.: absorption. c) Molecular ratio: [unhydrate]/[hydrate]. d) Taken from Ref. 19. e) Calculated from the reported α-value by using 55.4 mol dm^{-3} for pure water at 25 °C. f) Taken from Ref. 21.

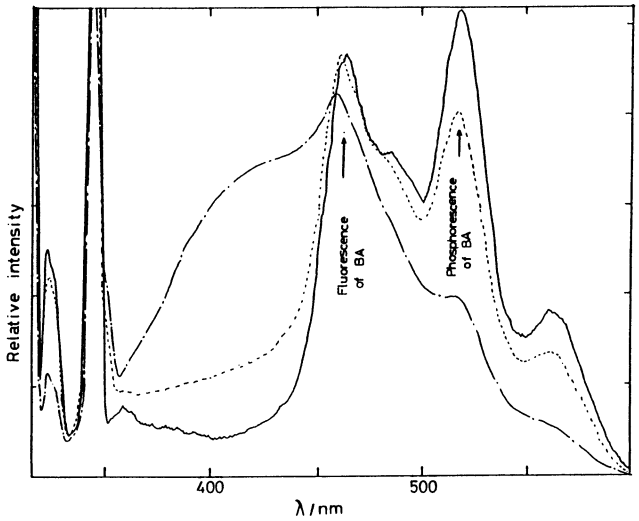

Fig. 3. Emission spectra of ca. 10^{-3} mol dm^{-3} BA in H_2O–THF mixed solvents at 20 °C. Water concentrations are: (——), 0 vol%; (----), 5 vol%; and (-·-·-), 10 vol%. Several sharp bands in the 330—350 nm range are due to Raman lines of the solvents. λ_{exc}=313 nm; slit widths (in light wavelength units): 1.5 nm.

BA.[21] The present (more general) treatment confirms that Bell and McDougall's assumption is almost acceptable because of the obtained $\varepsilon'_A\approx 0$ in the 380—430 nm range. The same method was applied to the 270—320 nm absorption system. However, no reliable correlation was obtained for n=1 (and n=2).

Emission Spectra. When BA in aqueous solutions is irradiated with light monochromated at 313 nm, a broad emission spectrum appears around 420 nm, near the absorption maximum of the $S_1(n\pi^*)\leftarrow S_0$ absorption of BA (see also Fig. 1). This band shows an increase in intensity with an increase in water concentration (see Fig. 3) while no such an anomalous emission was observed for ca. 10^{-3} mol dm^{-3} BA in nonaqueous solvents such as toluene, methylcyclohexane, and hexane. With a further increase in water concentration, the intensity of the 420 nm band comes to surpass those of the three bands at 457 nm (fluorescence of BA), at 512 nm (phosphorescence of BA), and at 560 nm (phosphorescence of BA). Such an example (in ca. 100% H_2O) is shown in Fig. 4 (see the solid line

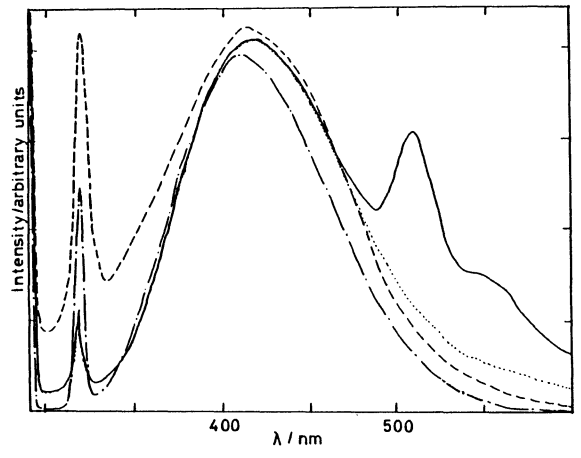

Fig. 4. Emission spectra of ca. 10^{-3} mol dm^{-3} ketones in aqueous solutions at 20 °C. λ_{exc}=313 nm. Slit widths: 1.5 nm. (——) and (-----): BA in the absence and existence of oxygen, respectively; (---): 3-hydroxy-2-propanone; and (-·-·-): 3-hydroxy-2-butanone (acetoin). Bands around 320 nm are attributed to Raman lines of H_2O.

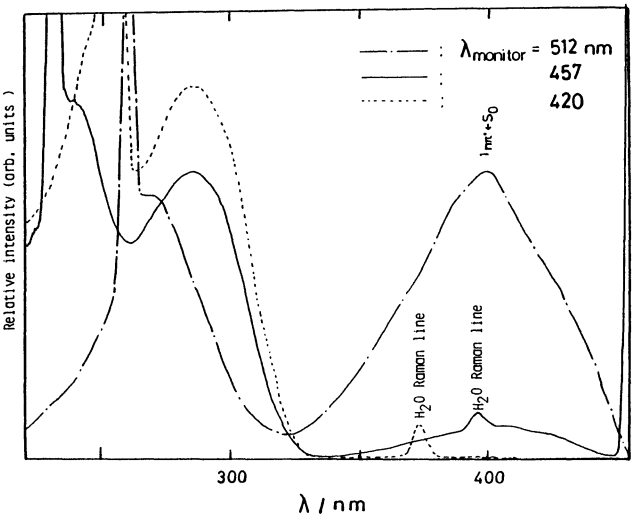

Fig. 5. Excitation spectra of ca. 10^{-3} mol dm^{-3} BA in aqueous solutions at 20 °C. Slit widths: 1.5 nm. Note that 2nd order excitation light appears with large intensity below 260 nm since no light filter was employed.

curves). For comparison, fluorescence spectra of the four monoketones (i.e., 3-hydroxy-2-propanone (hydroxyacetone), 3-hydroxy-2-butanone (acetoin), 1,3-dihydroxy-2-propanone (dihydroxyacetone), and acetone) were measured at 20 °C in aqueous solutions. Excitation light was all the same. For space saving, the spectra of the former two are shown in Fig. 4. A similarity between the 420 nm emission spectrum of BA in aqueous solutions and the fluorescence spectrum of each monoketone strongly suggests that the former is due to the monoketone species (namely, the hydrated form of BA, $CH_3C(OH)_2CO\text{-}CH_3$). Several other optical properties (such as band width, emission quantum yield, Stokes shift, etc.) resemble the general optical features of monoketones.[28,29]

Excitation Spectra. In order to identify this additional species more clearly, we observed several excitation spectra of BA in aqueous solutions at various wavelengths of the emission spectra monitored. Only three spectra are shown in Fig. 5. Obviously, there are big differences in the spectral locations and in the intensity distribution patterns when emission is monitored at 512 nm (the peak wavelength of the normal phosphorescence) and at 420 nm (that of the anomalous fluorescence): In between is the remainder which was measured at $\lambda_{monitored}$=457 nm (the peak wavelength of the normal fluorescence spectrum of BA). The different spectral dependence is a manifestation that there are chemically different emitting species: one with an absorption maximum at 400 nm and another with that at 285 nm.

Further, we studied the emission, absorption, and excitation spectra of the four monoketones, loc. cit., in aqueous solutions at 20 °C. Although small spectral shifts of the absorption maxima were found from molecule to molecule, these emission spectra were very

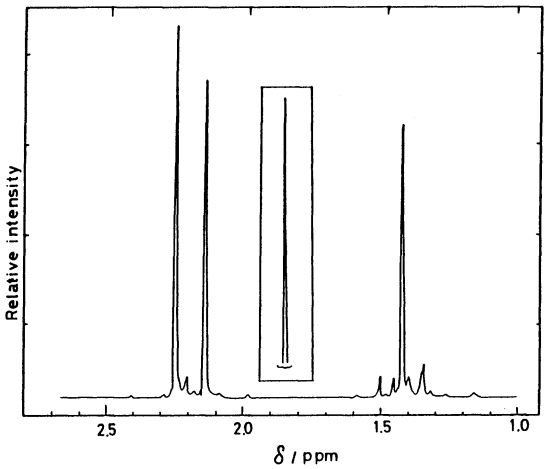

Fig. 6. 400 MHz ^{1}H NMR spectra of 1.5×10^{-2} mol dm^{-3} BA in D_2O at 20 °C. The inserted shows only one peak obtained from BA in C_6D_6.

similar to each other (vide supra). It was confirmed that each excitation spectrum showed a close correlation to the corresponding absorption spectrum. All these results lead us to the conclusion that the 420 nm emission in BA aqueous solutions is due to the hydrated form of BA.

^{1}H NMR Spectra. The ^{1}H chemical shifts and integrated intensities of BA were measured for two solvent systems: D_2O and C_6D_6. The concentration of BA was of ca. 10^{-2} mol dm^{-3} for each case. The results are shown in Fig. 6. Three prominent peaks were observed in D_2O solutions while only one prominent peak in C_6D_6 solutions. Without doubt, the strong single peak at δ 1.86 in C_6D_6 solutions is due to the six equivalent protons of $C^1H_3COCOC^1H_3$. The relative integrated intensity ratio among the three prominent

peaks in D_2O solutions was approximately 1.8 (for the peak at δ 2.25): 1.0 (for the peak at δ 2.14): 1.0 (for the peak at δ 1.42). That the integrated intensities of the latter two peaks are almost equal to each other allows the assignment to be the same as proposed by Greenzaid et al.:[19] the peak at δ 2.25 as the six equivalent protons in the ordinary diketone form of BA; and the peak at 2.14 ppm as the three equivalent protones of C^1H_3CO- and the peak at δ 1.42 as the three remainder (i.e., $C^1H_3C(OD)_2$-) in the hydrated form. Many small peaks are due to several impurities produced photochemically during the experimental procedure.

Greenzaid et al. found that the molecular ratio of the dehydrated to the hydrated form of BA in H_2O was 0.50,[19] a little bit smaller value with reference to 0.54 for our BA-D_2O system. This small difference is, however, within the experimental errors ($\pm$0.05).

Reversibility of the Molecular Rearrangement and Equilibrium Constants. Another important aspect is that the hydration-dehydration reaction takes place in equilibrium on going from one phase to another. We confirmed this by measuring the ^1H NMR spectra of BA first in aqueous solution (phase 1), secondly in C_6D_6 solution (phase 2) after extraction of the BA from the phase 1 solution by fresh perdeuterated benzene, and lastly in D_2O solution (phase 3) after extraction of the BA from the C_6D_6 (phase 2) solution by fresh heavy water. Apart from the contaminated ^1HDO signal at δ 4.74 in D_2O and at δ 1.60 in C_6D_6 solution, the triplet to singlet and the singlet to triplet signal pattern changes were well reproduced. This means that the BA molecule exists extensively as the hydrated form in the water phase while they are almost completely as the ordinary diketone form in the benzene phase.

This equilibrated molecular rearrangement was also confirmed by measuring emission and excitation spectra of two-phases-forming (i.e., unmiscible) H_2O-methylcyclohexane (MCH) solution systems. The chemical treatments are the same as mentioned above, but for a system of H_2O and MCH instead that of D_2O and C_6D_6. Both the emission and excitation spectra are almost completely ascribed to the ordinary diketone form of BA in the MCH phases while those are due to the both forms in the water phases.

The equilibrium constants obtained for the hydration-dehydration reaction of BA in several aqueous solvent systems are briefly summarized in Table 1 together with the data reported previously by other investigators.[19,21] Apart from some differences in the K-values, all the data establish that there occurs an extensive hydration reaction of BA in such aqueous solutions. An interesting issue may arise on this molecuar rearrangement and on the decay dynamics of BA around an interface of oil-water as well as around those of micelle-water and cyclodextrin-water. This reversibility in the molecular rearrangement strongly suggests that there is a possibility of BA (as well as benzil[30]) to become a new probing reagent for studies of such hydrophobic/hydrophilic macromolecular phenomena. At least, this polymorphous nature of BA should fully be taken into account on the discussion of the dynamics and structures in micelles,[17,18] in cyclodextrins,[18] and in water-contained organic solvents.[23,24]

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30) Benzil is well-known to emiss both phosphorescence and fluorescencence with remarkable emission yields in fluid solutions (e.g., see Ref. 31). Very recently, we have studied absorption spectra of benzil in various solvents. In contrast to the results obtained thereof (Ref. 32), no anomalous absorption intensification of BA was observed in hydrogen donating solvents. The environmental intensification scheme of BA thus seems to be close to the cases of acetone and cyclopentanone (Ref. 33). Reversely, no evidence of the reactions of hydration and methylation has not been obtained for benzil.

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