Ionization and Dissociation of Picric Acid in 4-Methyl-2-pentanone Solutions at Various Water Concentration

Tatsuya Sekine* and Hirochika Naganawa
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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The spectrum of picric acid in 4-methyl-2-pentanone solutions which contained the acid and water at several concentrations was determined in the wavelength range from 330 to 500 nm and the data were statistically analyzed. It was concluded that picric acid molecules formed ion pairs together with four water molecules in these solutions and the ion pairs thus formed dissociated partially. Both of the ion pairs and dissociated picrate ions in these solutions had strong absorption in the visible range where no absorption was found with the acid molecules but the spectra of these two species were different. The formation and dissociation constants of the ion pairs were also calculated from the data and the role of water in these chemical reactions was considered.

In a previous paper,[1)] the dissociation of picric acid in water-saturated 4-methyl-2-pentanone was studied by a liquid-liquid distribution method and the results were compared with those of perchloric and nitric acid. It was concluded that picric acid in this medium was a weak acid ($\mathrm{p}K_\mathrm{a}$=4.7) which was weaker than perchloric acid ($\mathrm{p}K_\mathrm{a}$=3.5) but stronger than nitric acid ($\mathrm{p}K_\mathrm{a}$=6.0). An acid in the undissociated form in such organic solvents may be present in two different chemical forms; the acid molecule and the ion pair. However, it was not possible to know only from these liquid-liquid distribution data whether the undissociated picric acid was in one of these chemical forms or it was a mixture of both. In the present study, the spectrum of picric acid in 4-methyl-2-pentanone solutions was determined at various concentrations of the acid and water. The data were statistically analyzed and the spectrum of the ion pairs was estimated. Furthermore, the molar ratio of the two chemical forms of undissociated acid species was calculated. The formation constant of the ion pairs from the acid molecules as well as the dissociation constant of the ion pairs thus formed were determined at several water concentrations and the role of water for these reactions was considered.

Experimental

All the materials were of a reagent grade. A small amount of picric acid was stored in a reduced pressure desiccator. The 4-methyl-2-pentanone was distilled twice. All the procedures were carried out in a thermostated room at 298 K. A picric acid solution of water-saturated 4-methyl-2-pentanone was prepared by shaking the solvent with an aqueous solution which contained a certain amount of the acid. In order to prepare a picric acid solution of 4-methyl-2-pentanone at a certain acid concentration and a desired water concentration, a water-saturated solution containing the acid was mixed with a calculated amount of dry solvent in a stoppered polypropylene tube. Use of glass vessels was found to be unfavorable for the experiments. When glass vessels were used, the reproducibility of the data was poor but by use of polypropylene vessels, it was much improved. This is probably due to that a part of water and/or the acid are adsorbed on the surface of glass. The absorbance of the picric acid solutions which contained water was measured from 330 to 500 nm. The acid concentration was determined as follows. A portion of the solution was transferred into another tube and ten times volume of hexane was added in order to make the back extraction of the acid more easily. Then the solution was shaken with a 1×10^{-3} mol dm^{-3} aqueous sodium hydroxide solution and the optical absorption of the aqueous phase at 380 nm where the molar absorptivity was 1.34×10^4 was measured. The spectrum of tetrabutylammonium picrate of 4-methyl-2-pentanone solutions at different water concentrations was determined in a similar manner as previously reported.[2)] Quartz cells of 1 to 10 mm optical path were used for this spectrophotometry. The water concentration in the solution was determined by the Karl-Fischer titration. A spectrophotometer (Hitachi 556 type) which was connected with a personal computer (NEC 9801 VM type) through a 12 bit interface (Microscience Co. DAS-1898BPC type) was used throughout the experiments.

Data Analysis

In a 4-methyl-2-pentanone solution, picric acid may be present in three forms; an acid molecule ($\mathrm{Hpic(H_2O)}_p$), an ion pair ($\mathrm{H^+pic^-(H_2O)}_q$), and a picrate ion ($\mathrm{pic^-(H_2O)}_r$) which has released a proton ($\mathrm{H^+(H_2O)}_s$). Each of the value of p, q, r, and s in the above chemical formulas could be different when the water concentration is different but these values can not be determined in the present study. Thus the total concentration of picric acid in the solution may be written as;

$$[\mathrm{Acid}]_\mathrm{total} = \sum[\mathrm{Hpic(H_2O)}_p] + \sum[\mathrm{H^+pic^-(H_2O)}_q] + \sum[\mathrm{pic^-(H_2O)}_r] \quad (1)$$

The water concentration experimentally determined is the sum of the associated and unassociated water with the acid. However, since the water concentration in the present study (0.5 to 0.8 mol dm^{-3}) is in a large excess to the acid, the concentration of total water could be regarded as that of the unassociated water. The ionization of acid is caused by the water in the medium. If the number of water molecules which are necessary for the formation of an ion pair from an acid molecule is always the same even when the water concentration in the medium is different, the following statistical treatments are possible. Under such conditions, each of p, q, r, and s could be treated as a fixed value in the equations in order to make a simpler expression. The equilibrium for the formation of ion pairs from the acid molecules may generally be written as;

$$\mathrm{Hpic(H_2O)}_p + n\,\mathrm{H_2O} \rightleftarrows \mathrm{H^+pic^-(H_2O)}_q$$

$$K_{\mathrm{ip}} = \frac{[\mathrm{H^+pic^-(H_2O)}_q]}{[\mathrm{Hpic(H_2O)}_p]\,[\mathrm{H_2O}]^n} \qquad (2)$$

Part of the ion pairs may undergo dissociation. The equilibrium can be written as;

$$\mathrm{H^+pic^-(H_2O)}_q \rightleftarrows \mathrm{H^+(H_2O)}_s + \mathrm{pic^-(H_2O)}_r$$

$$K_{\mathrm{dis}} = \frac{[\mathrm{H^+(H_2O)}_s]\,[\mathrm{pic^-(H_2O)}_r]}{[\mathrm{H^+pic^-(H_2O)}_q]} \qquad (3)$$

Since several properties of the medium such as the dielectric constant etc. could be different when the water concentration is different, the value of dissociation constant of the ion pairs may be affected by the change in the concentration of water.

The overall acid dissociation constant in the medium may be written as;

$$K_{\mathrm{a}} = \frac{[\mathrm{H^+(H_2O)}_s]\,[\mathrm{pic^-(H_2O)}_r]}{[\mathrm{Hpic(H_2O)}_p] + [\mathrm{H^+pic^-(H_2O)}_q]} \qquad (4)$$

This can also be rewritten as;

$$K_{\mathrm{a}} = \frac{K_{\mathrm{dis}}\,K_{\mathrm{ip}}[\mathrm{H_2O}]^n}{1 + K_{\mathrm{ip}}\,[\mathrm{H_2O}]^n} \qquad (5)$$

The absorbance of the solution, A, may be written as;

$$A = \varepsilon_{\mathrm{mol}}[\mathrm{Hpic(H_2O)}_p] + \varepsilon_{\mathrm{ip}}[\mathrm{H^+pic^-(H_2O)}_q] + \varepsilon_{\mathrm{ion}}[\mathrm{pic^-(H_2O)}_r] \qquad (6)$$

where $\varepsilon_{\mathrm{mol}}$, $\varepsilon_{\mathrm{ip}}$, and $\varepsilon_{\mathrm{ion}}$ is the molar absorptivity of acid molecules, ion pairs, and dissociated picrate ions, respectively, at a certain wavelength.

From Eqs. 1 to 6, the following equation is obtained;

$$A = \frac{1}{2}K_{\mathrm{a}}\left(\sqrt{1 + 4K_{\mathrm{a}}^{-1}[\mathrm{Acid}]_{\mathrm{total}}} - 1\right) \times \left\{\frac{1}{2}\,\varepsilon_{\mathrm{u}}\left(\sqrt{1 + 4K_{\mathrm{a}}^{-1}[\mathrm{Acid}]_{\mathrm{total}}} - 1\right) + \varepsilon_{\mathrm{ion}}\right\} \qquad (7)$$

where ε_{u} is the molar absorptivity of the acid in the undissociated form which can be written as;

$$\varepsilon_{\mathrm{u}} = \frac{\varepsilon_{\mathrm{ip}}\,K_{\mathrm{ip}}[\mathrm{H_2O}]^n + \varepsilon_{\mathrm{mol}}}{1 + K_{\mathrm{ip}}\,[\mathrm{H_2O}]^n} \qquad (8)$$

When the water concentration is different, the value of ε_{u} should not be the same as seen from this equation.

In the present study, the spectra of solutions were determined at various acid and water concentrations and the data were analyzed by a successive approximation method using a least squares computer program.

Results

In the present study, the spectra of the following 98 sample solutions were measured. The water concentration was 0.801 (water saturated), 0.751, 0.701, 0.651, 0.601, 0.551, and 0.501 mol dm^{-3} and the total picric acid concentration was 14 different values from 5×10^{-6}

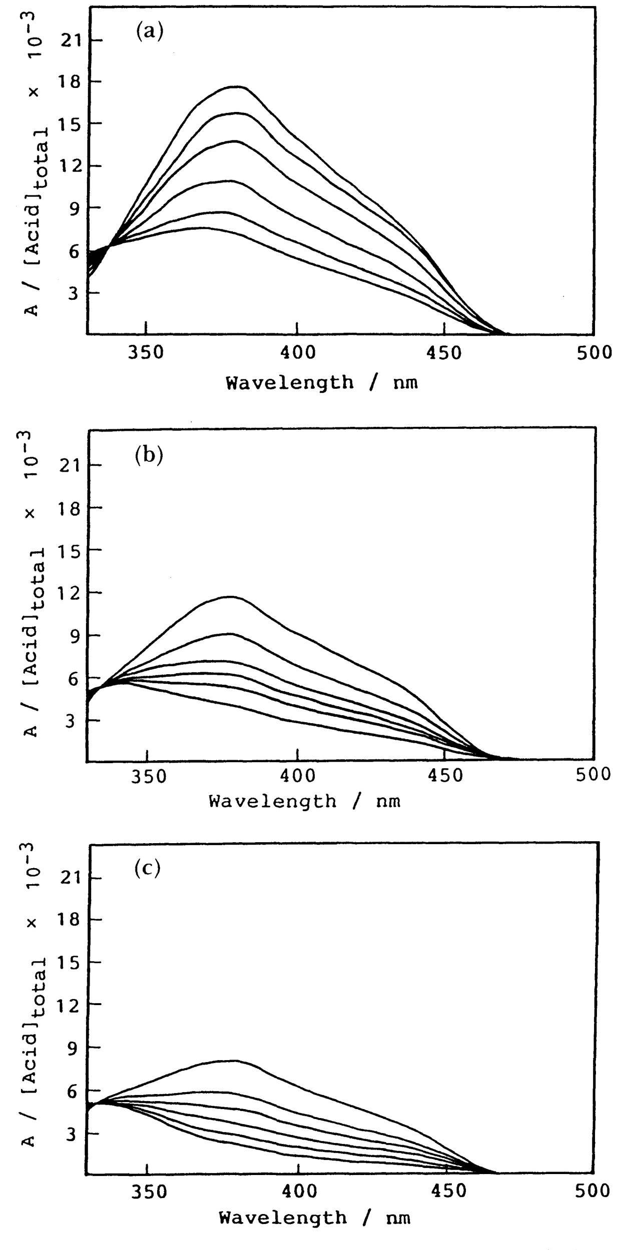

Fig. 1. Examples of spectra of picric acid in 4-methyl-2-pentanone which contained water. The total acid concentration, $[\mathrm{Acid}]_{\mathrm{total}}$, for each curve in the figures is from the top to the bottom in the right side. (a) $[\mathrm{H_2O}]_{\mathrm{total}}$ is 0.801 mol dm^{-3} (water saturated) and $[\mathrm{Acid}]_{\mathrm{total}}$ is 4.77×10^{-6}, 1.45×10^{-5}, 2.90×10^{-5}, 8.25×10^{-5}, 2.03×10^{-4}, and 3.45×10^{-4} mol dm^{-3}. (b) $[\mathrm{H_2O}]_{\mathrm{total}}$ is 0.651 mol dm^{-3} and $[\mathrm{Acid}]_{\mathrm{total}}$ is 1.96×10^{-5}, 4.94×10^{-5}, 1.10×10^{-4}, 1.60×10^{-4}, 2.50×10^{-4}, and 6.02×10^{-4} mol dm^{-3}. (c) $[\mathrm{H_2O}]_{\mathrm{total}}$ is 0.501 mol dm^{-3} and $[\mathrm{Acid}]_{\mathrm{total}}$ is 2.10×10^{-5}, 5.25×10^{-5}, 9.39×10^{-5}, 1.84×10^{-4}, 3.29×10^{-4}, and 8.05×10^{-4} mol dm^{-3}.

to 1×10^{-3} mol dm^{-3} for each water concentration. Figures 1(a) to 1(c) give the spectra obtained when the water concentration was 0.801, 0.651, and 0.501 mol dm^{-3} as examples of the experimental data.

The absorbance of the 14 solutions of the same water concentration but different $[\mathrm{Acid}]_{\mathrm{total}}$ was measured from 330 to 500 nm at an interval of 1 nm. Since the absorbance due to the solvent could not be canceled out when the wavelength was lower than 330 nm, no optical data were obtained in this lower wavelength range. From these data, the value of ε_u was determined on the basis of Eq. 7 for each wavelength to give the best-fit with the optical data at a certain given value of K_a. By repeating these procedures, a value of K_a which was common for the data of all the wavelengths and a value of ε_u for each wavelength (total 171 values of ε_u in the above wavelength range) were calculated for each given water concentration. Table 1 lists the values of K_a for the seven water concentrations thus obtained. The spectra of the undissociated species were calculated as shown in Fig. 2. When the water concentration in the medium was very low, for example, such as 5×10^{-3} mol dm^{-3}, no absorption due to the ion pairs and/or due to the dissociated picrate ions was found in the visible range and the spectrum from 330 to 500 nm was essentially similar to that of picric acid in cyclohexane obtained by separate experiments. For this reason, it was concluded that only the spectrum of the acid molecules was observed under such conditions. This spectrum is also given in Fig. 2. It was found that the spectrum of 1×10^{-5} mol dm^{-3} of tetrabutylammonium picrate in 4-methyl-2-pentanone was not affected by water in the concentration range of the present study. The salt could be regarded to dissociate nearly completely at this concentration at least in the water-saturated medium.[2] From these, it could be assumed that the molar absorptivity of the dissociated picrate ions, $\varepsilon_{\mathrm{ion}}$, is not affected by water under the conditions of the present study.

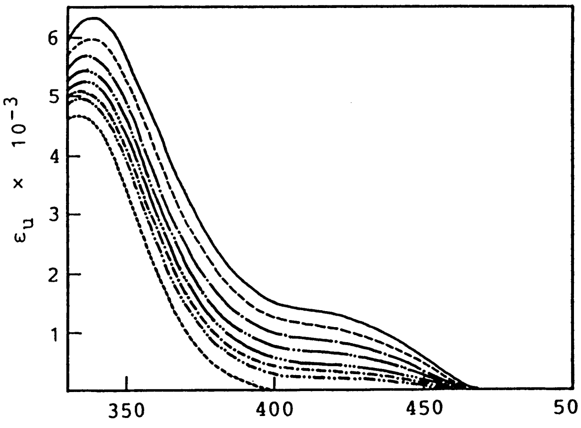

Fig. 2. Calculated spectrum of picric acid in the undissociated form when the $[\mathrm{H_2O}]_{\mathrm{total}}$ is different. The $[\mathrm{H_2O}]_{\mathrm{total}}$ is 0.801, 0.751, 0.701, 0.651, 0.601, 0.551, 0.501, and 5.0×10^{-3} mol dm^{-3} from the top to the bottom.

The above results indicate that water is indispensable for the formation of ion pairs in the medium. From the values of ε_u, the value of n and of K_{ip} were calculated on the basis of Eq. 8 by the successive approximation method. After trials, the number of water molecules which were necessary to form the ion pairs from acid molecules in 4-methyl-2-pentanone, n in Eq. 2, was found to be 4.0. The value of K_{ip} is found to be $10^{-0.35}$ as given in Table 1. Furthermore, the value of K_{dis} at each water concentration was determined by introducing a set of values of K_a, K_{ip}, and n into Eq. 5 as listed in Table 1. Figure 3 gives the spectra of the three chemical species of picric acid. The spectrum of ion pairs was obtained by the above calculation but that of acid molecules and of dissociated picrate ions were obtained by separate experiments under conditions where only one of these species was found in the solution.

Table 1. Summary of the Values Obtained by Analysis of Data

$[\mathrm{H_2O}]_{\mathrm{total}}$	$\log K_a$	$\log K_{\mathrm{ip}}$[a]	$\log K_{\mathrm{dis}}$	n[b]	R[c]
0.801	−4.51	−0.35	−3.70	4.0	0.156
0.751	−4.61	−0.35	−3.71	4.0	0.125
0.701	−4.73	−0.35	−3.72	4.0	0.098
0.651	−4.87	−0.35	−3.74	4.0	0.075
0.601	−5.01	−0.35	−3.75	4.0	0.056
0.551	−5.15	−0.35	−3.75	4.0	0.040
0.501	−5.33	−0.35	−3.77	4.0	0.028

a) In the successive approximation procedures of data analysis, K_{ip} in Eq. 2 was assumed to be constant even when the water concentration was different. The range of error for this value obtained is ±0.07. b) The number of water molecules which are necessary to form an ion pair from one acid molecule. The range of error for this value obtained is ±0.14. c) The molar ratio of ion pairs to the acid in the undissociated form; $R=[\mathrm{H^+pic^-}]/([\mathrm{Hpic}]+[\mathrm{H^+pic^-}])$.

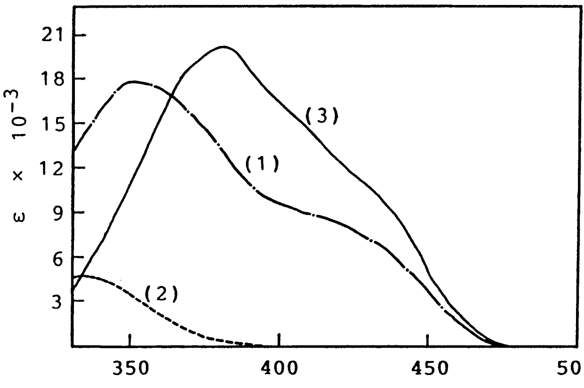

Fig. 3. Absorption spectrum of (1) ion pairs obtained by calculation and that of (2) acid molecules and (3) dissociated picrate ions obtained by separate experiments. The solvent is 4-methyl-2-pentanone containing water.

Discussion

In the previous paper,[1)] the dissociation constant of picric acid in water-saturated 4-methyl-2-pentanone was determined by a liquid–liquid distribution method to be $10^{-4.7}$. This value is approximately similar to that in the water-saturated medium obtained by the spectrophotometry in the present study, $10^{-4.51}$. The water concentration in the solvent was the same throughout the experiments and no spectrophotometric measurements were made in this previous liquid-liquid distribution study. For this reason, the chemical form of the undissociated acid and the role of water for the acid dissociation could not be concluded. However, the following conclusions can be drawn from the results in the present study. (i) Since the spectrum of picric acid in this solvent at lower water concentrations is quite similar to that in cyclohexane, all the acid should be in the form of acid molecule under these conditions. Thus the change in the spectrum by the change in the water concentration in 4-methyl-2-pentanone can well be explained in terms of ion-pair formation from one acid molecule with four water molecules and that of the dissociation of ion pairs thus formed. In other words, water is an essential base which has an electron donating oxygen atom and causes the ion-pair formation. However, 4-methyl-2-pentanone should be a too weak base for this. (ii) Since the value of K_{dis} was not affected very much by the change in the water concentration as is seen from Table 1, the change in the physical properties of the medium should be only slight in the concentration range of water of the present study. (iii) The overall acid dissociation constant, K_a in Eq. 4, is dependent on the water concentration but the dissociation constant of the ion pairs, K_{dis} in Eq. 3, is only slightly dependent on it. Thus the dependence of the overall acid dissociation constant on the water concentration is an apparent effect. This is because although the ionization of the acid is caused by water, K_a in Eq. 4 does not contain the term of water concentration. The effect of water can be normalized by Eq. 5. (iv) The value of K_{dis} in water-saturated solvent ($10^{-3.70}$) is similar to that of the dissociation constant of sodium and potassium salt of this acid ($10^{-3.60}$ for sodium salt and $10^{-3.61}$ for potassium salt) in the same medium as reported in the previous paper.[2)] This indicates that the degree of dissociation of the ion pairs is rather similar to that of sodium or potassium salt of this acid in the same medium. Furthermore, the spectrum of the ion pairs in Fig. 3 is quite similar to that of the ion pairs of sodium or potassium picrate in water-saturated 4-methyl-2-pentanone.[2)] Both of the spectrum of lithium picrate in the ion-pair form and in the dissociated ion form in 2-butanone previously reported by Gilkerson and Roberts[3)] are quite similar to that of picric acid in the corresponding chemical form obtained in the present study. (v) Since four water molecules should hydrate a proton when the acid is ionized, the cation, $H_9O_4^+$, may be formed in such a medium like in aqueous solutions[4,5)]. This cation could be present in the dissociated form or in the ion-pair form with a picrate ion in 4-methyl-2-pentanone.

Iwachido, Oosawa, and Tôei studied the dissociation of picric acid in 4-methyl-2-pentanone, 2-butanone, and acetone by spectrophotometry and by vapor-pressure osmometric method.[6)] In this previous paper, the dissociation equilibrium in the following equation was considered.

$$\mathrm{HA}_{x(\mathrm{H_2O})} + n\mathrm{H_2O} \rightleftarrows \mathrm{H}^{+}_{y(\mathrm{H_2O})} + \mathrm{A}^{-}_{z(\mathrm{H_2O})}$$

From Fig. 1 in this previous paper, the pK_a in water-saturated 4-methyl-2-pentanone can be read as $10^{-4.3}$. Furthermore, the hydration number of proton was concluded to be 4.0 in this previous study. However, as seen from Fig. 2 in the present study, the spectrum of the undissociated acid, which is the cumulative spectrum of both the acid molecules and ion pairs, is dependent on the water concentration. This is due to the difference in the proportion of the ion pair species in the undissociated acid when the water concentration is different. Thus when the acid dissociation is determined by spectrophotometry and when the formation of ion pairs is not taken into account, the fraction of ion pairs is not involved in the fraction of the undissociated acid but it is involved in the fraction of the dissociated picrate ions. This should cause an overestimation of the acid dissociation. Furthermore, as seen from Fig. 3, the spectra of ion pairs and dissociated picrate ions are different and this causes an error in the estimation of the dissociation constant when the wavelength to be used for the data analysis is different. Table 1 also gives the calculated molar ratio of the ion pairs to the undissociated acid at each water concentration. This ratio should be independent from the acid concentration when the water concentration is the same as seen from Eq. 2. When ion pairs are formed, a careful correction for this species should be made for the determination of the acid dissociation constant by spectrophotometry. Such a correction should not be necessary when the medium is high dielectric as water or it is low dielectric as cyclohexane. This is because in the former, the formation of ion pairs is negligible and in the latter, the dissociation of the ion pairs is negligible. However, in a moderately dielectric medium as in 4-methyl-2-pentanone (dielectric constant=13.1, dry solvent at 293 K), consideration on the effect for the optical absorption due to the ion pairs is important under certain conditions. This should be necessary in order to make a reasonable estimation of the dissociation equilibrium of the acid.

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