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THERMOCHEMICAL STUDIES ON THE PROTONATION OF 1,3,5-TRIAMINOBENZENE

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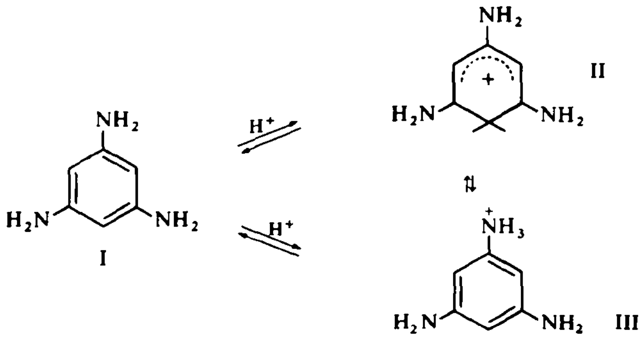
Abstract—The protonation of 1,3,5-triaminobenzene in a moderately acidic solution was found to occur both on the amino group and on the ring carbon atom. The equilibrium constants and the enthalpy and entropy changes for these two protonations were determined separately by analyzing the pH-dependence of the UV absorption intensity measured for the three-component equilibrium system. The enthalpy and entropy changes are as follows: $-14{\cdot}6 \pm 2{\cdot}5$ kcal/mol, $-28{\cdot}5 \pm 10$ cal/deg/mol for the protonation of the amino group; $-27{\cdot}2 \pm 0{\cdot}01$ kcal/mol, $15{\cdot}7 \pm 0{\cdot}2$ cal/deg/mol for the protonation on the ring carbon atom. The similar phenomenon was also observed for N,N-dimethyl-*m*-phenylenediamine.

INTRODUCTION

1,3,5-TRIAMINOBENZENE (TAB) (I) is known to be protonated at room temperature in moderately acidic solutions (pH $\sim 5{\cdot}5$)[1] on a ring carbon atom and to produce the triaminobenzenium ion (II). However, in a previous paper we found that a small amount of the amino-protonated species (III) coexists with II and that the ratio between them changes with temperature.[2] The spectra of TAB in acidic solutions at various temperatures show that the species III is dominant at lower temperatures while the species II increases its concentration on raising the temperature. This means that three components are in equilibrium in a moderately acidic solution.



The competition between the ring- and amino-protonations seems to be governed by their slight difference in stabilities. The species III is more stable than the species II, and the equilibrium constant for the amino-protonation depends on temperature more remarkably than that for the ring-protonation. The present investigation has

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been undertaken to analyze spectroscopically the equilibrium of the three-component system (I–III) and to estimate quantitatively the thermochemical values for the two different equilibria, discussed qualitatively in the previous paper.[2]

RESULTS AND DISCUSSION

Determination of the Equilibrium Constants

In the first place, we will consider the meaning of the inflection point of a sigmoid curve obtained by plotting the absorbance values of TAB solutions against their acidities. Let us denote the molar fractions of I, II and III by x, y, and y', respectively. If the equilibrium constants between I and II and between I and III are represented by K_1 and K_2, respectively, the following relations hold.

$$K_1 = y/(x[\mathrm{H}^+]) \qquad (1)$$

$$K_2 = y'/(x[\mathrm{H}^+]) \qquad (2)$$

$$x + y + y' = 1 \qquad (3)$$

The absorbance D of the system for $l$cm cell path-length at a given wavelength is represented by Eq 4.

$$D = Cl[\varepsilon_x - x[\mathrm{H}^+]\{K_1(\varepsilon_x - \varepsilon_y) + K_2(\varepsilon_x - \varepsilon_{y'})\}] \qquad (4)$$

where ε_x, ε_y and $\varepsilon_{y'}$ are the molar extinction coefficients of I, II and III, respectively, and C is the analytical concentration of TAB.

The first and second derivatives of D are obtained from Eq 4 as follows:

$$\mathrm{d}D/\mathrm{d}[\mathrm{pH}] = 2{\cdot}303\, Cl\, x^2[\mathrm{H}^+]\{K_1(\varepsilon_x - \varepsilon_y) + K_2(\varepsilon_x - \varepsilon_{y'})\} \qquad (5)$$

$$\mathrm{d}^2D/\mathrm{d}[\mathrm{pH}]^2 = 2{\cdot}303^2\, Cl\, x^2[\mathrm{H}^+]\{K_1(\varepsilon_x - \varepsilon_y) + K_2(\varepsilon_x - \varepsilon_{y'})\}(1 - 2x) \qquad (6)$$

By plotting the D values at a fixed wavelength other than the isobestic point against the acidities (pHs) of solutions, a sigmoid curve is obtained. The inflection point of the curve is located at the pH value where the following conditions are satisfied.

$$\mathrm{d}D/\mathrm{d}[\mathrm{pH}] \neq 0, \quad \mathrm{d}^2D/\mathrm{d}[\mathrm{pH}]^2 = 0 \qquad (7)$$

Eqs 5 and 6 give the following unique solution at $x = 1/2$;

$$[\mathrm{H}^+]_{\frac{1}{2}} = 1/(K_1 + K_2) \qquad (8,$$

or

$$\mathrm{pH}_{\frac{1}{2}} = \log(K_1 + K_2) \qquad (9)$$

Thus the inflection point of the curve gives the combined value of K_1 and K_2. Hence the pK value of 5·50 ±0·03 obtained previously for the TAB $\rightleftarrows$ TABH$^+$ system at 25°[2] turns out to correspond to the p$(K_1 + K_2)$.

Next, we try to obtain the separate K_1 and K_2 values. As is shown below, the analysis is straightforward if ε_y is known at about 29,400 cm^{-1} where both ε_x and $\varepsilon_{y'}$ are negligibly small compared with ε_y.* Since the order of magnitude of ε_y is estimated to be 10^3, we can prepare a solution of TAB in which y is small enough to be neglected compared with $x(\fallingdotseq 1)$ but large enough to give fairly strong absorption ($D_a \fallingdotseq 1$) (see Table 1). By measuring the absorbance D_a at 29,400 cm^{-1} for the weakly acidic

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* Although the pure spectrum of III is not obtained, it is expected to be very similar to that of *m*-phenylenediamine.

solution satisfying the above condition, K_1 can be obtained from the following equation:

$$K_1 = D_a/(C_a\varepsilon_y[\mathrm{H}^+]_a) \quad ([\mathrm{H}^+]_a \ll (K_1 + K_2)^{-1}) \tag{10}$$

Here C_a and $[\mathrm{H}^+]_a$ represent the analytical concentrations of TAB and H^+ in the solution, respectively.

Next, let us turn to the K_2 value. We measure the absorbance (D_b) at 29,400 cm^{-1}, the solution containing TAB and H^+ with concentrations of C_b and $[\mathrm{H}^+]_b$, respectively. From the observed D_b value, we can obtain the x_b value by the aid of the following equation derived from Eqs 1 and 10;

$$x_b = D_bC_a[\mathrm{H}^+]_a/(D_aC_b[\mathrm{H}^+)_b] \tag{11}$$

Further from Eq 3

$$K_2 = (1 - x_b - D_b/\varepsilon_y)/(x_b[\mathrm{H}^+]_b) \tag{12}$$

From the combination of Eq 11 with Eq 12 K_2 can be evaluated.

Estimation of ε_y

The ε_y value can be estimated by the method described below. From Eq 12 the following relation can be obtained;

$$\varepsilon_y = D/[C\{1 - x(1 + K_2[\mathrm{H}^+])\}] \tag{13}$$

At the inflection point of the D-pH curve ($x = 1/2$, $[\mathrm{H}^+] = 1/(K_1 + K_2)$), ε_y is equal to $2D(K_1 + K_2)/(CK_1)$. We find that the higher the temperature, the smaller the value of K_2/K_1 is, and that at room temperature it is much less than unity. Therefore, ε_y may be approximated as $2D/C$; D and C being taken from the inflection point of the D-pH curve.* According to this method, ε_y at 29,400 cm^{-1} was estimated to be $(3{\cdot}5 \pm 0{\cdot}3) \times 10^3$.†

Temperature Dependence of the Equilibrium Constants and the Estimation of the Thermochemical Quantities

By the aid of Eqs 10–12 and the ε_y value, K_1 and K_2 were obtained at three different temperatures, 6°, 14° and 24°. The ε_y values at 6° and 14° were assumed to be equal to that obtained at 24°. The obtained equilibrium constants are summarized in Tables 1 and 2. The plots of log K_1 and log K_2 against $1/T$(T: the absolute temperature) show straight lines as shown in Fig 1. The enthalpy (ΔH) and entropy (ΔS) changes were estimated from the slopes of these lines and their intercepts on the ordinate. The results are summarized in Table 3. Tables 1–3 show that, at lower temperatures species III is dominant, and that species II increases its concentration with increase of temperature. This explains the experimental facts[2] that the peak at 29,400 cm^{-1} due to II increases its intensity at higher temperatures but the peak at 34,200 cm^{-1} due to III exhibits the opposite tendency.

These two types of protonation were also observed spectroscopically for other systems. Fig 2 shows that, for aqueous solutions of N,N-dimethyl-*m*-phenylenediamine, the absorption spectrum (curve 2) observed at pH 4·05 is different from that of the neutral molecule (curve 1) and agrees well with that of aniline (curve 3). This

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* If $[\mathrm{H}^+]$ is large enough to diminish x to zero but small enough to suppress the second protonation and, again, if K_2 is much smaller than K_1, ε_y may be approximated as D/C.

† Although the error amounts to 10 per cent, several thermochemical quantities can be obtained more accurately.

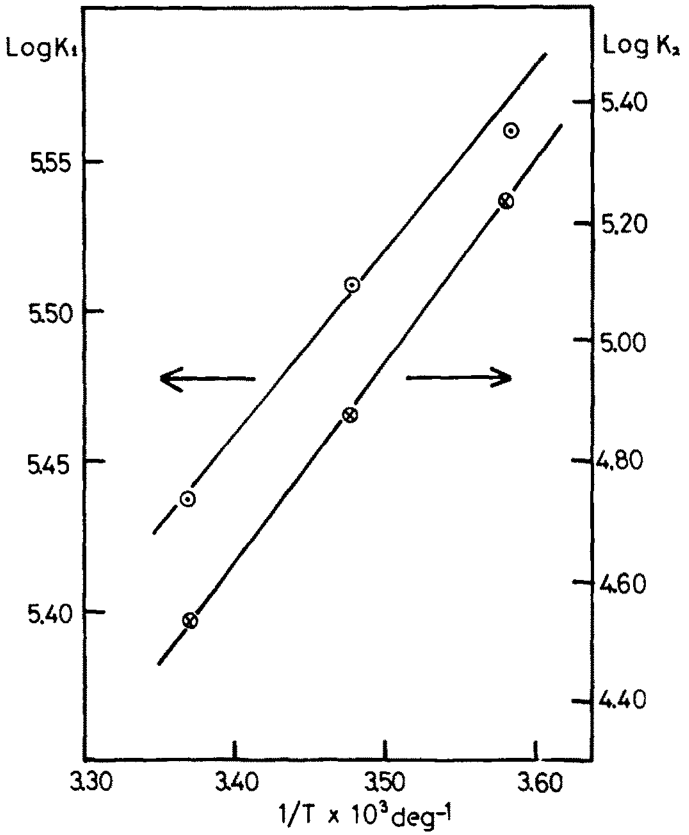
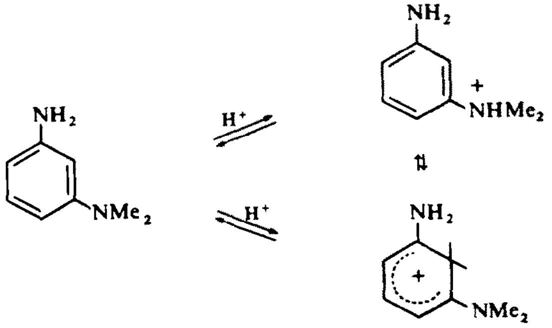


FIG 1. The plots of log K_1 and K_2 against $1/T$.

means that protonation occurs on the dimethylamino group.* However, the solution with the higher concentration of the amine ($\sim 10^{-2}$ M/l) shows the absorption peak at 28,570 cm^{-1}. The electronic spectra of the substituted benzenium ions and their derivatives have a characteristic absorption peak in the region of 25,000 cm^{-1} $\sim$29,000 cm^{-1}.[2-4] Hanazaki and Nagakura[5] calculated the electronic structures of



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* The spectrum of the protonated species is more similar in the peak position to that of aniline than that of dimethylaniline. Therefore we assumed that the protonation probably occurs on the dimethylamino group, however this is not conclusive.

methyl derivatives of the benzenium ion by the SCF MO CI method and showed that the peak position of this band is rather insensitive to substituents. These facts show that the peak at 28,570 cm^{-1} should be ascribed to the substituted benzenium ion produced by the ring protonation of N,N-dimethyl-*m*-phenylenediamine. The ring protonation occurs by the following equilibrium scheme, although only to a small extent at room-temperature.

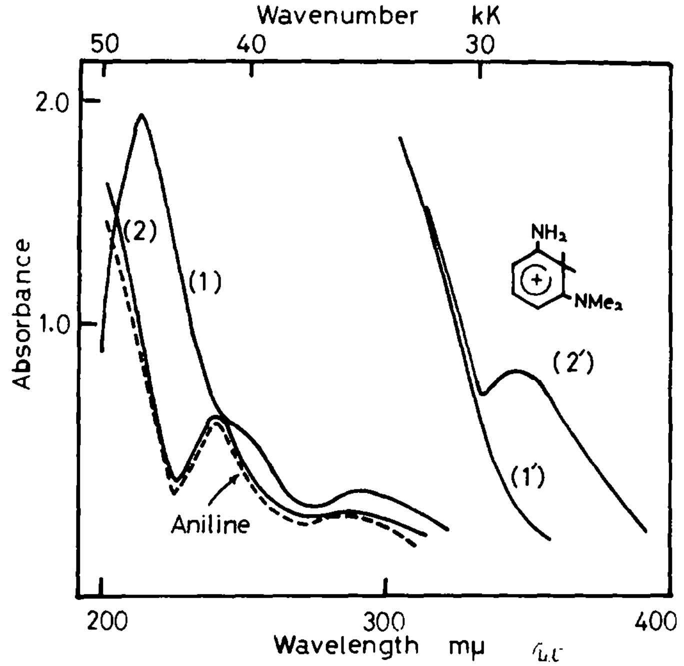


FIG 2. The spectra of N,N-dimethyl-*m*-phenylenediamine in aqueous solutions of pH 6·80 and 4·50. The concentration of N,N-dimethyl-*m*-phenylenediamine is ~ 10^{-5} mol/l for curves (1) and (2), and ~ 10^{-2} mol/l for curves (1′) and (2′). The pH of the solution is 6·80 for curves (1) and (1′) and 4·50 for curves (2) and (2′).

TABLE 1. THE EVALUATED K_1 VALUES AT THREE DIFFERENT TEMPERATURES, 6°, 14° AND 24°

Temp (°C)	$[H^+]_e$(mol/l)	C_e(mol/l)	D_e	K_1[a]	pK_1[a]
6	$2{\cdot}40 \times 10^{-8}$	$4{\cdot}23 \times 10^{-2}$	1·30	$3{\cdot}66 \times 10^5$ ±0·3	−5·56 ±0·04
14	$2{\cdot}82 \times 10^{-8}$	$4{\cdot}23 \times 10^{-2}$	1·36	$3{\cdot}26 \times 10^5$ ±0·2	−5·51 ±0·03
24	$3{\cdot}55 \times 10^{-8}$	$4{\cdot}23 \times 10^{-2}$	1·44	$2{\cdot}74 \times 10^5$ ±0·2	−5·44 ±0·03

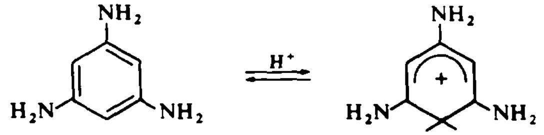
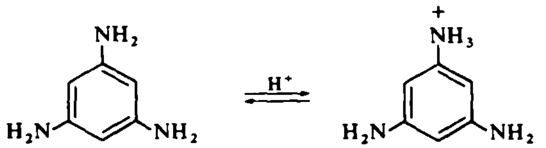
[a] The probable errors in these quantities were estimated by changing ε_y within ±10%, namely in the range of $3{\cdot}8 \times 10^3 \sim 3{\cdot}2 \times 10^3$.

TABLE 2. THE EVALUATED K_2 AND K_3 VALUES AT THREE DIFFERENT TEMPERATURES, 6°, 14° AND 24°

Temp (°C)	$[H^+]_b$ mol/l	C_b mol/l	D_b	x	y^a	y'^a	K_2^a	pK_2^a	$K_3 = (y'/y)^a$
6	$7·59 \times 10^{-6}$	$5·80 \times 10^{-4}$	1·10	0·195	0·542 ±0·04	0·265 ±0·04	$1·78 \times 10^5$ ±0·3	−5·25 ±0·08	0·49 ±0·13
14	$5·13 \times 10^{-6}$	$5·88 \times 10^{-4}$	1·12	0·325	0·544 ±0·04	0·131 ±0·04	$7·81 \times 10^4$ ±2·4	−4·89 ±0·15	0·24 ±0·08
24	$1·35 \times 10^{-5}$	$5·71 \times 10^{-4}$	1·42	0·193	0·711 ±0·05	0·096 ±0·05	$3·71 \times 10^4$ ±2·1	−4·57 ±0·35	0·13 ±0·10

[a] The probable errors in these quantities were estimated by changing ε_y within ±10%, namely in the range of $3·8 \times 10^3 \sim 3·2 \times 10^3$.

TABLE 3. THE VALUES FOR THE ENTHALPY AND ENTROPY CHANGES FOR THE TWO EQUILIBRIA, I ⇌ III AND I ⇌ II

	Equilibrium	ΔH(kcal/mol)	ΔS(cal/deg/mol)
(I)		−27·2 ±0·01	15·7 ±0·2
(II)		−14·6 ±2·5	−28·5 ±10

EXPERIMENTAL

Materials. TAB was prepared and purified by the same method as described previously.[2] N,N-dimethyl-*m*-phenylenediamine was prepared by catalytically reducing N,N-dimethyl-*m*-nitrobenzene (4 g) in Et_2O (50 ml) with Pd-C. After the calculated volume of H_2 had been absorbed, the soln was filtered and dried over $CaCl_2$. White crystals of the amine precipitated on cooling the filtrate with dry ice–acetone.

Measurements. A Cary model 14 recording spectrophotometer and a Hitachi model 124 recording spectrophotometer were used for the measurements of UV spectra. The temp control of the sample soln was carried out using a Coolnics circulator model CTE-1B supplied by Yamato Co., Ltd. Unless otherwise stated, the measurements were made at a constant temp, 25 ±0·5°. The pH of the soln was determined with a Hitachi–Horiba Type N5 pH meter.

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