

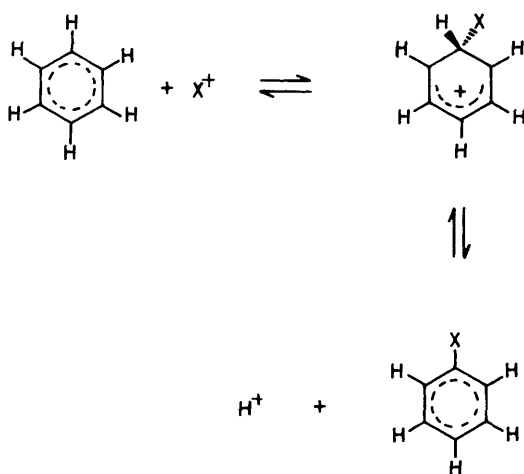
The Hydrolysis of 1,3,5-Tripyrrolidinobenzene

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In acidic solutions 1,3,5-tripyrrolidinobenzene (TPB) and methyl-TPB hydrolyse forming 3,5-dipyrrolidinophenol (DPP) and methyl-DPP, respectively. The reaction proceeds by two successive protonations on carbon atoms of the aromatic ring followed by hydrolysis. The reaction mechanism is described, and the protonation equilibria of TPB and DPP are determined.

σ -Complexes are known to be intermediates in electrophilic substitution reactions of benzene and its derivatives, as shown in Scheme 1. In the case of the protonation of 1,3,5-



Scheme 1. Electrophilic aromatic substitution

tripyrrolidinobenzene (TPB) the σ -complex is stable and the kinetics and thermodynamics of its formation have been previously studied in detail.¹ In this contribution we report upon the hydrolysis of TPB and methyl-TPB (Me-TPB) which proceeds *via* a two-fold protonation of the aromatic ring. The product of the hydrolysis is 3,5-dipyrrolidinophenol (DPP), which itself forms a σ -complex. The protonation and deprotonation of DPP leads to structures, which are analogous to those of TPB and TPBH_2^+ .

Experimental

The hydrolysis of TPB and Me-TPB is a relatively slow reaction with relaxation times longer than 60 s, and in this investigation the progress of the reaction was observed using a standard u.v.-vis. spectrophotometer. Since the compounds dissolve very slowly in water, 5×10^{-4} M-ethanolic solutions were prepared initially, to which a nine-fold volume of 10^{-5} M-hydrochloric acid was added. In these solutions TPB ($pK = 9.62$) and Me-TPB ($pK = 11.66$) exist in their monoprotonated forms. The hydrolysis reactions were started by mixing these solutions with equal volumes of aqueous solutions of HCl in the concentration range 4×10^{-3} – 4 mol dm^{-3} . Thus the solutions studied were 2.5×10^{-5} M-TPB or Me-TPB in 19:1 v/v water-ethanol mixtures. Further measurements were performed in 1:1 v/v water-ethanol mixtures. The solutions were thermostatted before mixing and the temperature was kept constant to $(25.0 \pm 0.1)^\circ\text{C}$ throughout all experiments. The temperature-

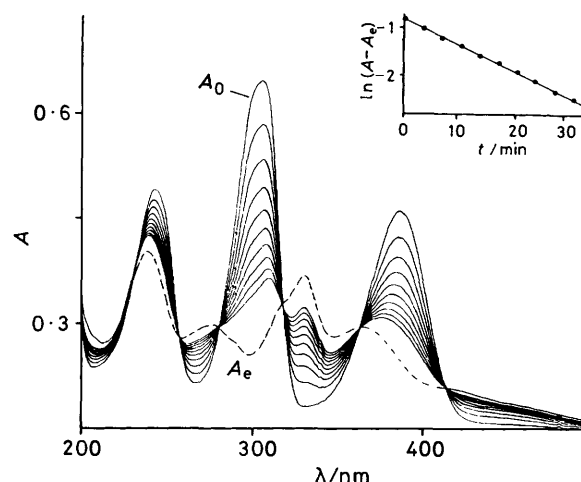


Figure 1. Absorption spectra taken during the hydrolysis of TPBH^+ in $3 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous HCl. The time lag between two consecutive spectra is 3.5 min. A_0 and A_e are the spectra recorded immediately after initiation of the reaction and at equilibrium, respectively. The insert shows $\ln(A - A_e)$ vs. time at 300 nm

jump relaxation method was used to study a fast intermediate protonation step.

All reagents were analytical grade obtained from Merck except for the pyrrolidinobenzenes. TPB and Me-TPB [prepared according to ref. (2)] were kindly provided by Prof. F. Effenberger, Universität Stuttgart. DPP was prepared by dissolving TPB (0.5 g) in acetonitrile (20 ml) and adding aqueous HCl (0.1M; 80 ml). When the solution had been shaken for 3 h, it was neutralized with Na_2CO_3 and the product was extracted three times with dichloromethane (30 ml). The extracts were dried (K_2SO_4) and the solvent was evaporated off to give a green solid, which was examined by u.v., n.m.r., and mass spectroscopy. The u.v. spectra had absorption bands in methanol at 238 nm (40 000) and at 373 nm (3 000), indicating the aromatic structure of DPP in this solvent. In water the absorption maxima were at 237 (20 000), 291 (16 400), and 371 nm (12 200), *i.e.* in water a non-aromatic structure exists. The numbers in brackets are the extinction coefficients in $\text{dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$. The spectra agree with those reported in the literature for DPP.³ The main peaks in the mass spectrum were at 232 (molecular weight of DPP), 178 (DPP - 2 HCN), and 205 (DPP - HCN).

Results

Figure 1 shows spectra of an aqueous solution of TPB at different times during the hydrolysis reaction which was initiated by the addition of HCl. At all wavelengths an

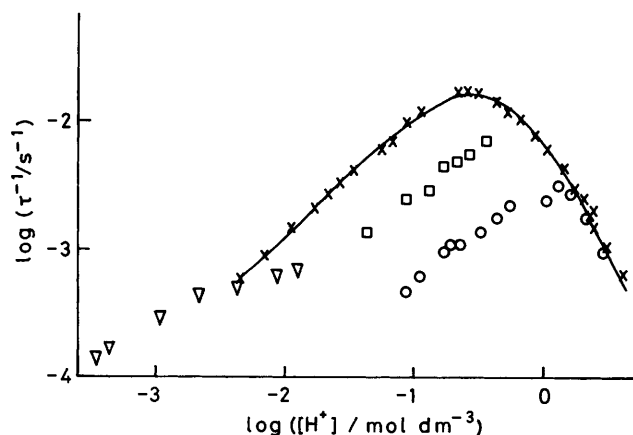


Figure 2. Log $1/\tau$ vs. log $[H^+]$ for the hydrolysis of TPB in 19:1 v/v water-ethanol (\times); TPB in 1:1 v/v water-ethanol (\circ); Me-TPB in 19:1 v/v water-ethanol (∇); Me-TPB in 1:1 v/v water-ethanol (\square). The curve is drawn according to eqn. (2)

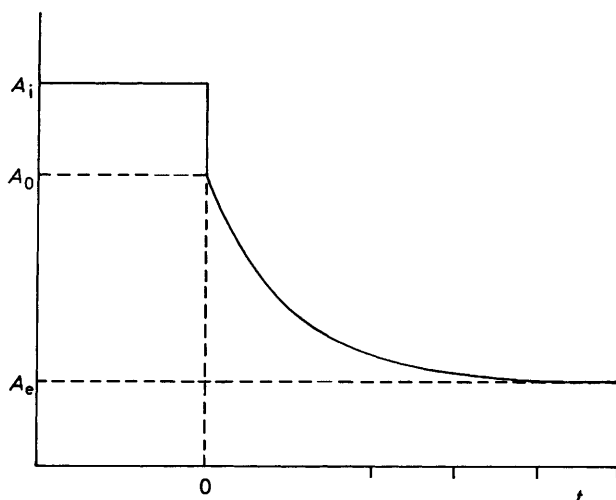


Figure 3. Absorbance at 300 nm vs. time (schematically) when at $t = 0$ a solution of $TPBH^+$ is mixed with aqueous HCl

exponential change in the absorption with the same rate is observed, *i.e.* the absorption at constant wavelength can be expressed by equation (1a)

$$A = A_e + (A_0 - A_e) \exp(-t/\tau) \quad (1a)$$

This means a single (though possibly multistep) first-order reaction is observed and the rate law is given by equation (1b)

$$dA/dt = -k_{\text{obs}}(A - A_e) \quad (1b)$$

with $k_{\text{obs.}} = 1/\tau$. The absorption values A_0 and A_e are extrapolated by equation (1a) to the start of the reaction ($t = 0$) and to equilibrium ($t \gg \tau$), respectively, $k_{\text{obs.}}$ is the observed rate constant, and τ is the relaxation time. The term $1/\tau$ is determined by the slope of the plot of $\ln(A - A_e)$ vs. t (see the insert to Figure 1). The correlation coefficients of these plots were better than 0.999 for $t < 3\tau$ at all measurements. The absorption at equilibrium, A_e , and thus the final product of the hydrolysis does not depend on the pH of the solutions studied.

Figure 2 summarizes the results of the kinetic measurements. The hydrolysis of TPB in 19:1 v/v water-ethanol shows a maximum rate at $[H^+] = 0.2 \text{ mol dm}^{-3}$. The curve through the experimental data is calculated by equation (2).

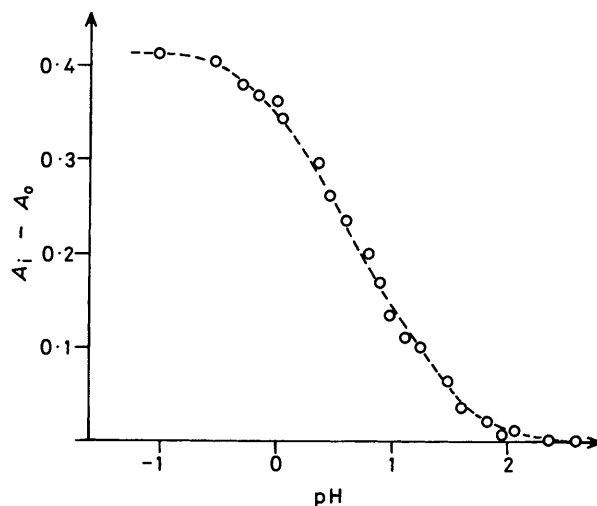


Figure 4. The fast change in absorbance $A_i - A_0$ vs. pH at constant concentration of TPB, $\lambda = 300 \text{ nm}$. The curve is calculated with $K_2 = 0.16 \text{ mol dm}^{-3}$ [see equation (5)]

$$1/\tau = a[H^+] + b[H^+]^{-2} \quad (2)$$

In 1:1 v/v water-ethanol the same dependence of the reaction rate on proton concentration is obtained with a maximum at $[H^+] \approx 1 \text{ mol dm}^{-3}$. For solutions of Me-TPB in 1:1 v/v water-ethanol the reaction rate increases linearly with the proton concentration for $[H^+] < 0.4 \text{ mol dm}^{-3}$. In 19:1 v/v water-ethanol a linear dependence is observed only for $[H^+] < 2 \times 10^{-3} \text{ mol dm}^{-3}$ whereas at higher proton concentration the reaction rate changes only slightly. For Me-TPB the measurements cannot be extended to lower pH values, since there the reaction amplitude is too small ($A_0 - A_e < 0.005$). Therefore an expected decrease of the reaction rate at high proton concentration cannot be detected.

Figure 3 shows schematically the change in absorbance during an experiment. The term A_0 , extrapolated according to equation (1), may differ significantly from the absorbance A_i calculated for a $2.5 \times 10^{-5} \text{ M}$ solution of TPB in its mono-protonated form (for which the dilution factor was taken into account). Therefore it has to be assumed that a second fast reaction occurs at the mixing of a solution of $TPBH^+$ with aqueous HCl prior to the hydrolysis. The rate of the change from A_i to A_0 cannot be resolved by stopped-flow measurements, therefore the chemical reaction involved has a relaxation time shorter than 3 ms. The reversibility of this fast step was verified by acidifying a solution of $TPBH^+$ to pH = 0 and neutralizing it immediately afterwards. The spectrum of the solution does not change by this treatment (except for the dilution factor). The term $(A_i - A_0)$ depends on the final proton concentration as shown in Figure 4. The pH dependence fits a protonation equilibrium, *i.e.* in this fast and reversible reaction $TPBH^+$ is further protonated according to Scheme 2 and in

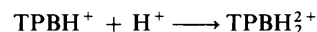


Figure 4 the curve through the experimental data is calculated with the dissociation constant $K_2 = 0.16 \text{ mol dm}^{-3}$ for this reaction.

The hydrolysis reaction is slow at high proton concentration, as can be seen in Figure 2. Thus the spectrum of the intermediate $TPBH_2^{2+}$ could be measured immediately after mixing equal volumes of a solution of $TPBH^+$ and of aqueous 4M-HCl. The spectrum is shown in Figure 5 together with spectra of TPB and $TPBH^+$. The spectrum of $TPBH_2^{2+}$ differs completely from the

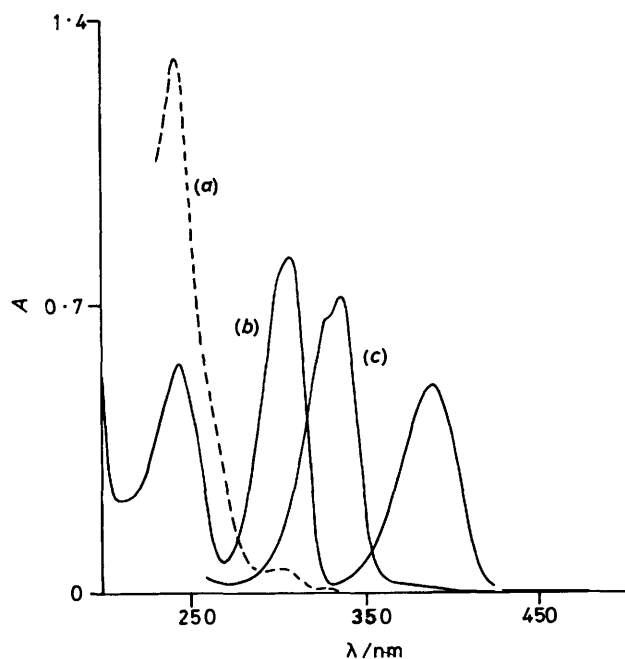


Figure 5. Absorption spectra in 19:1 v/v water-ethanol solutions of (a) TPB at pH 12.5; (b) TPBH⁺ at pH 7.0; (c) TPBH₂²⁺ at pH -0.5

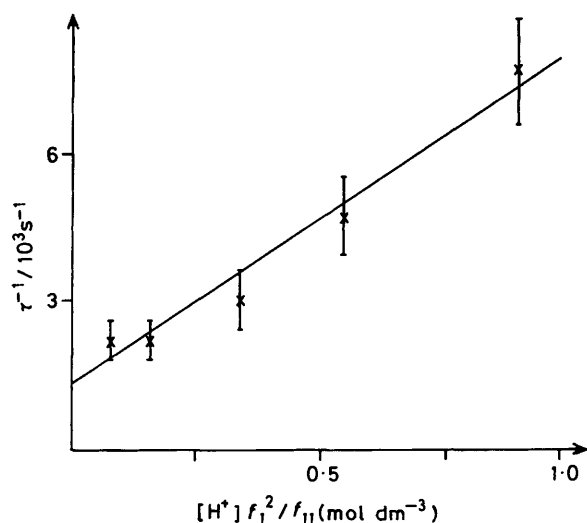


Figure 6. Reciprocal relaxation time vs. proton concentration for the second protonation of TPB at 25 °C [see equation (8)]

other spectra, therefore it can be assumed that the second proton is also bound to a carbon atom of the central ring. The shorter λ_{\max} value of the absorption of the doubly protonated species is consistent with two C-protonations giving rise to a less conjugated system than if there were one C- and one N-protonation.

For C-acids the rate of protonation/deprotonation is not diffusion-controlled, and in several cases for this reaction relaxation times longer than 10^{-5} s were observed.⁴ Therefore the temperature-jump technique was used to investigate this protonation. Since for relaxation measurements the concentrations of product and educt have to be similar, these measurements are restricted to proton concentrations between 0.05 and 0.5 mol dm⁻³ (since $K_2 = 0.16$ mol dm⁻³) at which the

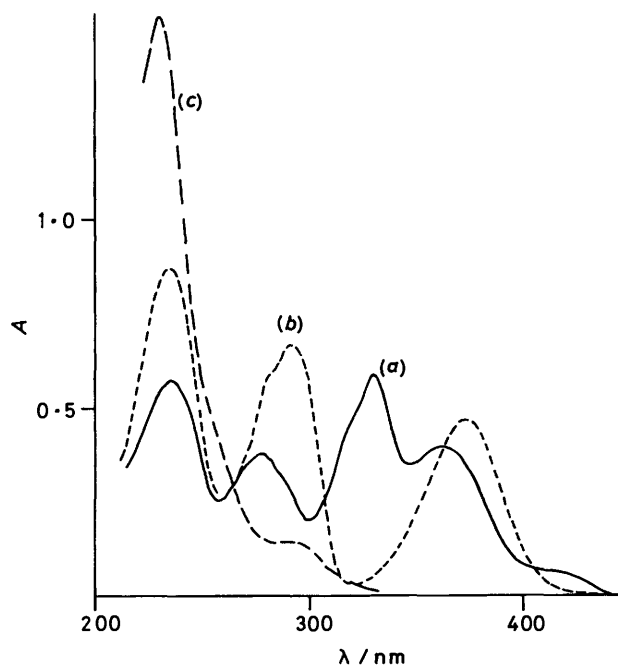


Figure 7. Absorption spectra in 19:1 v/v water-ethanol solutions of (a) DPPH⁺ at pH 3.9; (b) DPP at pH 8.8; (c) DPP_{dep}⁻ at pH 11.9

hydrolysis proceeds with highest rate. Therefore the temperature-jump experiments had to be performed within 60 s after preparing the reaction solution. Only under these conditions were relaxation effects observed with relaxation times which depend on the proton concentration as shown in Figure 6.

In order to identify the hydrolysis product of TPBH⁺, we recorded the spectra of 3,5-dipyrrolidinophenol (DPP) at various pH values. Two protonation equilibria were obtained with $\log K_{+1} = -5.3$ for the protonation of and $\log K_{-1} = -11.3$ for the deprotonation of DPP. The spectra of the three differently protonated species are shown in Figure 7. A comparison of the spectra with the spectrum at equilibrium in Figure 1 indicates that DPPH⁺ is the product of the hydrolysis of TPBH⁺.

Discussion

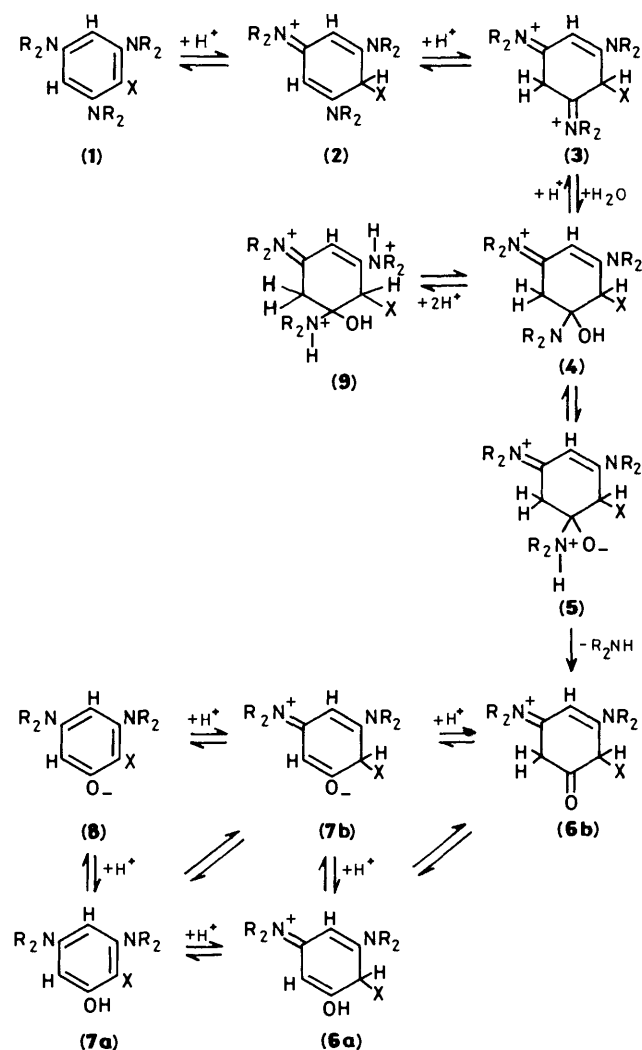
Most measurements concerning TPB were taken in 19:1 v/v water-ethanol, and therefore these data are used for the discussion of the reaction mechanism. All experimental results obtained for the hydrolysis of TPB are consistent with the reaction scheme shown in Scheme 2. In the following equations the different species are indicated by the numbers in Scheme 2, i.e. for DPP the experimentally determined dissociation constants are given as $K_{6,7}$ and $K_{7,8}$ instead of K_{+1} and K_{-1} , respectively.

First we will discuss the equilibria and kinetics of the protonation of TPB and DPP. The protonation of TPB (1) gives a stable σ -complex TPBH⁺ (2) with a dissociation constant¹

$$K_1 = \frac{c_1 c_H}{c_2} = 2.5 \cdot 10^{-10} \text{ mol dm}^{-3} \quad (3)$$

In basic solutions the reaction proceeds via





Scheme 2. Reaction scheme of the protonation and the hydrolysis of TPB ($X = H$) and Me-TPB ($X = CH_3$). There are further mesomeric forms for the non-aromatic species

and the rate law of this reaction is

$$\frac{dc_1}{dt} = -k_{1,OH}c_1 + k_{-1,OH}c_2c_{OH}f_1^2 \quad (4b)$$

The rate constants have been determined¹ to be $k_{1,OH} = 0.62 \text{ s}^{-1}$ and $k_{-1,OH} = 24\,300 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. (K_1 is the ratio of the rate constants multiplied by the ionic product of water.) According to Figure 4, at the second protonation, a short-lived intermediate $TPBH_2^+$ (3) is formed with the dissociation constant

$$K_2 = \frac{c_2c_Hf_1^2}{c_3f_{II}} = 0.16 \text{ mol dm}^{-3} \quad (5)$$

The activity coefficients f_I for monovalent and f_{II} for divalent ions are estimated by the extended Debye-Hückel equation

$$\log f_z = -0.5z^2 \left(\frac{I^{0.5}}{1 + I^{0.5}} - 0.3I \right) \quad (6)$$

Figure 5 shows the spectra of a different protonated TPB. The unprotonated TPB has an absorption maximum at 244 nm due

to the aromatic ring. The spectrum of the monoprotonated σ -complex $TPBH^+$ shows three absorption maxima at 245, 306, and 387 nm. A completely different spectrum is observed for the double-protonated form $TPBH_2^+$, indicating that the second proton is not bound to nitrogen but to a carbon atom of the ring. This indicates structure (3), in which the conjugated system between two pyrrolidino groups corresponds to the cyanine system $N^+=CH-CH=CH-N$, which generally shows an absorption maximum at about 320 nm.⁵

Since both the first protonation and the hydrolysis are slow compared with the second protonation, the rate law for the second protonation can be written separately

$$\frac{dc_3}{dt} = k_2c_2c_Hf_I^2f_{II}^{-1} - k_{-2}c_3 \quad (7)$$

Activity coefficients must be included since the activated complex has a charge of +2. Equation (7) leads to the following expression for the relaxation time

$$1/\tau = k_{-2} + k_2c_Hf_I^2f_{II}^{-1} \quad (8)$$

taking into account that $c_2 \ll c_H$. From intercept and slope of the straight line in Figure 6 we obtain $k_{-2} = (1.3 \pm 0.2) 10^3 \text{ s}^{-1}$ and $k_2 = (6.6 \pm 1.0) 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The equilibrium constant is given as the ratio of the rate constants, $K_2 = (0.20 \pm 0.05) \text{ mol dm}^{-3}$, a value which agrees with the spectroscopically determined $K_2 = 0.16 \text{ mol dm}^{-3}$. Thus rate and equilibrium constants are known for the two protonation steps of TPB.

The spectrophotometric pH-titration of 3,5-dipyrrolidino-phenol (7a,b) yields the dissociation constants for the deprotonation and the protonation of DPP,

$$K_{7,8} = \frac{c_8c_H}{c_7}f_I^2 = 10^{-5.3} \text{ mol dm}^{-3} \quad (9)$$

and

$$K_{6,7} = \frac{c_7c_H}{c_6} = 10^{-11.3} \text{ mol dm}^{-3} \quad (10)$$

with $c_7 = c_{7a} + c_{7b}$ and $c_6 = c_{6a} + c_{6b}$. [In Figure 7 species (8) is called DPP_{dep}^- .]

Information about the electronic structures of these compounds is obtained from the spectra of DPP at different pHs as shown in Figure 7. At pH 11.9 the spectrum of DPP_{dep}^- is observed, where the absorption maximum at 233 nm indicates an aromatic structure, species (8), in Scheme 2. At pH 8.8 the spectrum of DPP shows the three absorption bands of a σ -complex, which are already known from $TPBH^+$, indicating that DPP has structure (7b) in agreement with n.m.r. data.³ The spectrum of DPP in methanol shows that in this solvent the aromatic structure is preferred, which may also exist in the mixed solvents used, and is therefore given as (7a) in Scheme 2. At pH 3.8 the spectrum of $DPPH^+$ shows both the three absorption bands of a σ -complex and the absorption at 334 nm due to a cyanine system. Correspondingly, the two structures (6a) and (6b) are proposed for $DPPH^+$. The equilibrium between these species (which may be regarded as a keto-enol equilibrium) can be roughly estimated in the following way: the absorption at 334 nm decreases and the absorptions at 245, 306, and 387 nm increase (*i.e.* the concentration of the cyanine compound decreases and that of the σ -complex increases) when ethanol is added to the solution of $DPPH^+$, and in solutions containing more than 50 vol % ethanol only the spectrum of a σ -complex is observed. Thus the equilibrium constant can be estimated:

Table. Equilibrium and rate constants at 25 °C

	$K_1/\text{mol dm}^{-3}$	$K_2/\text{mol dm}^{-3}$	$k_{3,4}/\text{s}^{-1}$
TPB-10% EtOH	$(2.5 \pm 0.3) 10^{-10}$	0.16 ± 0.02	0.050 ± 0.010
TPB-50% EtOH	$(3.2 \pm 0.8) 10^{-10}$	1.9 ± 0.5	0.016 ± 0.003
Me-TPB-10% EtOH	$(2.0 \pm 0.2) 10^{-13}$	0.017 ± 0.002	0.075 ± 0.015
Me-TPB-50% EtOH	$(2.5 \pm 0.6) 10^{-13}$	0.5 ± 0.1	0.015 ± 0.002

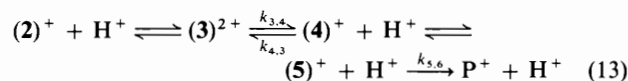
$$K_T = c_{6a}/c_{6b} \approx 2 \quad (11)$$

assuming that the absorption coefficients do not strongly depend on the composition of the solvent. The equilibrium between species (7a) and (7b) has been studied in different solvents, and in water the σ -complex (7b) is strongly favoured.³

So far equilibria and kinetics of the protonation of TPB and of the protonation and deprotonation of DPP have been discussed. We will now consider the hydrolysis of TPBH^+ to DPPH^+ . The reaction mechanism shown in Scheme 2 is proposed for this process, similar to the mechanism of the hydrolysis of enamines⁶ and azomethines.⁷ For the derivation of the rate law we summarize the concentrations of all products of the hydrolysis by

$$c_P = c_6 + c_7 + c_8 \quad (12)$$

The unprotonated TPB (1) need not be considered, since hydrolysis occurs only in acidic solution. Thus the reaction scheme may be reduced to



where the numbers refer to the structures in Scheme 2. The rate law is given by

$$\frac{dc_P}{dt} = k_{5,6}c_5 \quad (14)$$

The reaction (4) to (5) consists of a proton transfer from an oxygen to a nitrogen atom. This reaction is very fast,⁴ and equilibrium is established between (4) and (5) in the time range of the hydrolysis. Therefore, c_5 can be expressed as

$$c_5 = K_{4,5}c_4 \quad (15)$$

The protonation-deprotonation between (2) and (3) is also fast compared with the hydrolysis, and we can write

$$c_2 = \frac{c_3 f_{II} K_2}{c_H f_I^2} \quad (16)$$

Species (4) and (5) have not been observed spectrophotometrically, therefore we assume that they are intermediates at low concentration, and a quasi-stationary condition is used for ($c_4 + c_5$). This means

$$\frac{dc_P}{dt} = -\frac{d(c_2 + c_3)}{dt} \quad (17)$$

and therefore

$$k_{5,6}c_5 = k_{3,4}c_3 - k_{4,3}c_4 c_H f_I^2 f_{II}^{-1} \quad (18)$$

Summarizing equations (14)–(18) leads to the differential equation

$$-\frac{dc_3}{dt} = \frac{1}{\tau} c_3 \quad (19)$$

where

$$\frac{1}{\tau} = \frac{k_{5,6}K_{4,5}k_{3,4}c_H f_I^2}{(k_{4,3}c_H f_I^2 f_{II}^{-1} + k_{5,6}K_{4,5})(K_2 f_{II} + c_H f_I^2)} \quad (20)$$

At low proton concentrations this equation can be reduced to

$$\frac{1}{\tau} = k_{3,4}K_2^{-1} c_H f_I^2 f_{II}^{-1} \quad (21a)$$

i.e. in this range, the reaction step (3) \rightleftharpoons (4) is rate determining. Equation (21a) predicts that $1/\tau$ is proportional to c_H , which agrees with the experimental finding of a slope of 1 in the plot of $\log 1/\tau$ vs. $\log c_H$ in Figure 2. This yields $k_{3,4}/K_2 = 0.30 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and with $K_2 = 0.16 \text{ mol dm}^{-3}$, $k_{3,4} = (5.0 \pm 1.0) 10^{-2} \text{ s}^{-1}$. At high proton concentration equation (20) yields

$$\frac{1}{\tau} = \frac{k_{5,6}K_{3,4}K_{4,5}f_{II}}{c_H f_I^2} \quad (21b)$$

i.e. reaction step (5) \rightleftharpoons (6) becomes rate determining and $1/\tau$ should be proportional to $1/c_H$. However, in this range a slope of -2 is observed in Figure 2. To account for this dependence, an intermediate (9) must be assumed where TPB is protonated three times (and therefore has a charge of +3). Since the intermediate is in fast equilibrium with species (4), the second and third protonations must occur at a nitrogen atom, which indicates that the intermediate cannot be obtained by a further protonation of species (3). Owing to the high concentration of the intermediate (9), the quasi-stationary assumption (17) is not allowed. Instead of equation (18) we should use the equilibrium conditions

$$c_9 = c_4 c_H^2 K_{4,9} f_{III}^3 f_{II}^{-1} \quad (22)$$

and

$$c_3 = c_4 c_H K_{3,4}^{-1} f_{II}^2 f_{III}^{-1} \quad (23)$$

The relaxation time then is given by

$$\frac{1}{\tau} = \frac{k_{5,6}K_{4,5}K_{3,4}}{K_2 + c_H f_I^2 f_{II}^{-1} + K_{3,4}K_{4,9}c_H f_I^3 f_{II}^{-1}} \quad (24)$$

For very high proton concentrations this equation yields

$$\frac{1}{\tau} = \frac{k_{5,6}K_{4,5}f_{III}}{K_{4,9}c_H^2 f_I^3} \quad (25)$$

in agreement with the experimental results in Figure 2. However, these results were obtained at ionic strengths larger than 0.5 mol dm^{-3} . In this range, activity coefficients are not known with sufficient accuracy and their introduction into rate equations becomes dubious. Therefore a definite discrimination between equations (21b) and (25) is not possible.

The measurements in 50:50 v/v water-ethanol mixtures were performed in order to study the influence of the solvent and to

determine whether ethanol is directly involved in the hydrolysis reaction (e.g. as catalyst). As can be seen in Figure 2 the dependence of the reaction rate on proton concentration is similar for both solvents, and therefore it can be assumed that the reaction mechanism is not changed. Some constants are summarized in the Table. The increase in the dissociation constant K_2 and the decrease in the rate constant $k_{3,4}$ at the increase of the ethanol concentration may be attributed to the change in dielectric constant and therefore the preference of the less polar structures in 50% ethanol. This means the solvent ethanol plays no major role at the hydrolysis of TPB.

Similar measurements were carried out with Me-TPB. The results shown in Figure 2 and the constants listed in the Table indicate that the hydrolysis of Me-TPB obviously follows the same reaction mechanism as TPB. The largest influence of the substituent is observed in the value of the dissociation constant K_1 , which has been attributed to stereoelectronic effects.⁸ Our results are not sufficient to discuss the influence of the substituent on reaction rates and equilibria.

In summary it can be stated that the hydrolysis of TPB and Me-TPB follows Scheme 2 indicating (a) a double protonation on the aromatic ring is necessary prior to the hydrolysis; (b) a triprotonated complex is likely as an intermediate since triprotonation has also been observed for 1,3,5-trimorpholino-benzene and 1,3,5-tripiperidinobenzene;⁹ (c) DPPH^+ is the

primary product of the hydrolysis. Several equilibrium constants involved in the hydrolysis reaction can be determined, namely K_1 [equation (3)], K_2 [equation (5)], $K_{7,8}$ [equation (9)], $K_{6,7}$ [equation (10)], and K_T [equation (11)].

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