hexadienyl-type radicals. We explained this solvent effect on the reaction switching in terms of the location of the lowest $n\pi^*$ and $\pi\pi^*$ triplet states. To classify the hydrogen donors that give cyclohexadienyl-type radicals, we propose a new criterion, the charge of hydrogen atom to be abstracted. The donors that give cyclohexadienyl-type radicals have negatively charged, hydride-type, hydrogens. On the other hand, the usual donors have positively charged hydrogens. They are separated into proton-type and CT-type donors according to established concepts. The established ideas such as the charge-transfer interaction and bond dissociation energy cannot explain the difference in the reactivities between tri-*n*-butyltin hydride and 1,4-cyclohexadiene.

Through the present study we have extended the studies on the photoreduction reactions of triplet carbonyls to a much wider field by exploring the intrinsic reactivity of the $\pi\pi^*$ triplet state which has been overlooked. Besides these physicochemical interests, synthetic aspects may also become useful in the photoreduction reactions of aromatic carbonyl compounds from their $\pi\pi^*$ triplet states.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 61740267) from the Ministry of Education, Science, and Culture. We thank Dr. Hiroshi Miyasaka and Professor Noboru Mataga, Osaka University, for the measurements of the picosecond time-resolved optical absorption spectra. We also thank the Institute for Molecular Science for the use of the HITAC M-680H computer and the library program GAUSSIAN82.

Protonation of 1,3,5-Triaminobenzenes in Aqueous Solutions. Thermodynamics and Kinetics of the Formation of Stable σ-Complexes

Wilhelm Knoche,* Wolfgang W. Schoeller, Reinhard Schomäcker, and Siegmund Vogel

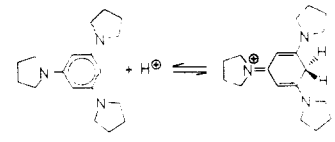
Contribution from the Fakultät für Chemie, Universität Bielefeld, Postfach 8640, 4800 Bielefeld 1, West Germany. *Received January 5, 1988*

Abstract: 1,3,5-Tripyrrolidinobenzene (pK_a = 9.62), 2-methyl-1,3,5-tripyrrolidinobenzene (pK_a = 12.75), 2-ethyl-1,3,5-tripyrrolidinobenzene (pK_a = 13.7), and 1,3,5-trimorpholinobenzene (pK_a = 2.45) bind protons to the aromatic ring leading to the formation of σ-complexes in basic and weakly acidic aqueous solutions. Equilibrium and kinetics of the formation of the σ-complexes have been studied. The data obtained correlate well with data quoted in the literature for σ-complexes in superacidic media.

Electrophilic aromatic substitutions belong to the most fundamental reactions in organic chemistry. They proceed via a two-step mechanism: in the first step an electrophile X^+ is added to the benzene ring and a σ-complex is formed, in which the cyclic π-conjunction is interrupted; in the second step, a proton leaves the σ-complex and the aromatic structure is restored.

This two-step mechanism is now generally accepted. It was originally derived from chemical isotope studies,[1] which yield an indirect proof for the existence of a σ-complex as an intermediate, but do not allow us to identify separately the reaction steps involved. The existence of a σ-complex has been proved by protonation studies in superacidic media.[2] Effenberger et al.[3] synthesized triaminobenzenes, which form stable σ-complexes. Their structures are now well characterized.[4] These complexes were isolated as perchlorate salts, and their UV and NMR spectra show clearly that protonation occurs at the aromatic ring and not at the nitrogen atoms. Scheme I shows one of the possible mesomeric forms of the σ-complex for 1,3,5-tripyrrolidinobenzene. Thus, the protonation of these aminobenzenes may be used as a model reaction for electrophilic aromatic substitutions, where equilibrium and kinetics of the formation of the σ-complex can be studied in detail.

Scheme I



In this contribution, results are reported for the triaminobenzenes 1,3,5-tripyrrolidinobenzene (TPB), 2-methyl-1,3,5-tripyrrolidinobenzene (MeTPB), 2-ethyl-1,3,5-tripyrrolidinobenzene (EtTPB), 1,3,5-trimorpholinobenzene (TMB), and 1,3,5-tripiperidinobenzene (TPiB). The structures of these components are given in Figure 1. For MeTPB and EtTPB only protonation of the alkyl-substituted carbon atom is observed.

Experimental Section

All reagents were of analytical grade except the substituted benzenes, which were prepared according to ref 3. For TPB, the progress of the protonation was observed spectrophotometrically at λ = 387 nm, for MeTPB, EtTPB, and TMB at λ = 400 nm, where the aromatic compounds do not absorb and the monoprotonated σ-complexes show absorption maxima. Stopped-flow and pressure-jump techniques were employed for the kinetic measurements. Slow reactions were followed with a standard UV/vis spectrophotometer. All kinetic experiments were performed under pseudo-first-order conditions; i.e., for the kinetic measurements, the optical absorbance is described by eq 1 with A_0 the amplitude of the relaxation effect, $\tau = k_{obs}^{-1}$, and A_e the absorbance at equilibrium. All results refer to 25 °C and the solvent 90:10 (v/v)

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

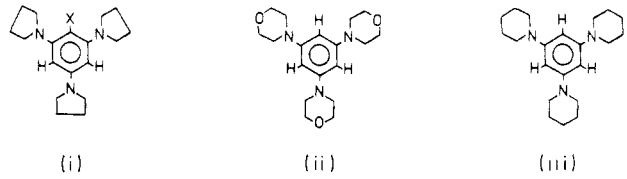
(1) Melander, L. *Isotope Effects on Reaction Rates*; Ronald: New York, 1960.

(2) (a) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelley, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034. (b) Köhler, H.; Scheibe, A. *Z. Anorg. Allg. Chem.* **1956**, *285*, 221. (c) Yamaoka, T.; Hosoya, H.; Nagakura, S. *Tetrahedron* **1970**, *26*, 4125. (d) Kresge, A. J.; Chiang, Y.; Hakka, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 6167.

(3) Effenberger, F.; Mack, K. E.; Nagel, K.; Niess, R. *Chem. Ber.* **1977**, *110*, 165.

(4) Effenberger, F.; Reisinger, F.; Schönwälder, K. H.; Bäuerle, P.; Stezowski, J. J.; Jogun, K. H.; Schöllkopf, K.; Stohrer, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 882.

0002-7863/88/1510-7484$01.50/0



(i) (ii) (iii)

Figure 1. Structures of (i) TPB (X = H), MeTPB (X = CH_3), EtTPB (X = C_2H_5), (ii) TMB, and (iii) TPiB.

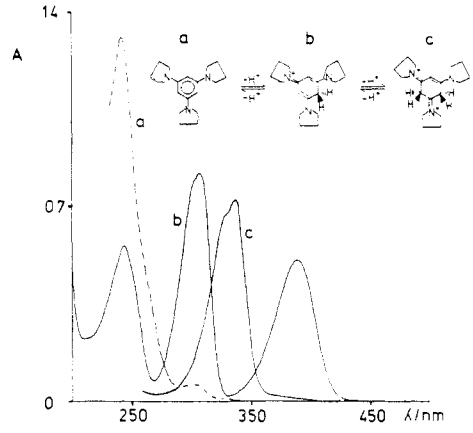


Figure 2. Spectra of (a) TPB at pH 12.5; (b) $TPBH^+$ at pH 7.0; and (c) $TPBH_2^{2+}$ at pH 0.5.

water/ethanol, if not indicated otherwise. Ethanol was added in order to improve the dissolution of the substituted benzenes. The concentration of the triaminobenzenes was 10^{-5}–3×10^{-5} mol dm^{-3}. Measurements were performed in the range 10–40 °C in order to obtain reaction enthalpies and activation parameters. Reaction volumes have been calculated from relaxation amplitudes and from the pressure dependence of the absorbance between 1 and 100 MPa.

Results

1,3,5-Tripyrrolidinobenzene. The rate of protonation was measured between pH 0.3 and 10.5. The conditions of the experiments and the observed relaxation times are summarized in Table I for 25 °C. The acidity constants of TPB are[5,6] given in eq 2 and 3. The index C indicates that the protons are bound

$$K_{1,C} = \frac{[TPB][H^+]}{[TPBH^+]} = 10^{-9.62} \text{ mol dm}^{-3} \quad (2)$$

$$K_{2,C} = \frac{[TPBH^+][H^+]f_I^2}{[TPBH_2^{2+}]f_{II}} = 0.16 \text{ mol dm}^{-3} \quad (3)$$

to carbon atoms. f_I and f_{II} are activity coefficients of mono- and divalent ions, respectively. They are estimated according to[7] eq 4. The spectra of the different protonated TPB species are shown in Figure 2. They indicate that both protons are bound to the aromatic ring system.

$$-\log f_z = 0.5z^2[I^{0.5}/(1 + I^{0.5}) - 0.3I] \quad (4)$$

The pressure-jump technique was applied in the range 9.5 < pH < 10.5, i.e. at pH close to $pK_{1,C}$. At higher pH the relaxation amplitude is too small, at lower pH the reaction was not studied with this technique, since unbuffered solutions were used in order to avoid catalysis by the buffer.

In the range 5.5 < pH < 9.3, phosphate or ammonium buffer had to be added to the solution. The stopped-flow technique was applied, mixing equal volumes of (i) 6×10^{-5} M TPB at pH 11 and (ii) buffer of appropriate concentration. pH and spectra of the solutions were measured immediately after completion of the reaction. Figure 3 shows how the buffer catalyzes the reaction. The reaction rates were extrapolated to zero buffer concentration,

(5) Vogel, S.; Knoche, W.; Schoeller, W. W. *J. Chem. Soc., Perkin Trans. 2* **1986**, 769.
(6) Knoche, W.; Vogel, S. *J. Chem. Soc., Perkin Trans. 2*, in press.
(7) Davies, C. W. J. *Ion Association*; Butterworth: London, 1962.

Table I. Relaxation Times for the Protonation of TPB at 25 °C (Concentration of TPB 3×10^{-5} mol dm^{-3})

pH	$\tau \times 10^3$, s	comments
10.49	167 ± 5	
10.33	219 ± 5	
10.23	259 ± 6	
10.10	370 ± 5	
10.04	363 ± 7	
9.94	460 ± 10	
9.84	539 ± 8	pressure
9.77	567 ± 5	jump
9.73	600 ± 8	
9.64	600 ± 10	
9.62	640 ± 10	
9.48	725 ± 15	
9.41	810 ± 10	
9.05	950 ± 20	
9.33	810 ± 50	
9.11	900 ± 50	
8.90	940 ± 50	
8.65	1010 ± 60	stopped-flow
8.34	980 ± 50	I = 0.1 mol dm^{-3}
8.10	930 ± 50	τ extrapolated to zero
7.43	480 ± 50	buffer concn
6.86	190 ± 20	
6.40	77 ± 6	
5.50	10 ± 2	
4.0	<2	
$[H^+]$	$\tau \times 10^3$, s	comments
0.001	50 ± 10	
0.002	106 ± 20	$[H^+]$, concn of HCl
0.005	123 ± 20	
0.011	135 ± 20	
0.023	270 ± 100	
0.050	630 ± 100	
0.0095	270 ± 40	
0.0245	460 ± 60	
0.050	610 ± 100	
0.15	850 ± 120	I = 0.45 mol dm^{-3}
0.25	960 ± 150	
0.35	1050 ± 150	
0.45	1200 ± 180	
0.05	370 ± 40	I = 0.05 mol dm^{-3}
0.05	440 ± 50	I = 0.10 mol dm^{-3}
0.05	490 ± 60	I = 0.20 mol dm^{-3}
0.05	550 ± 60	I = 0.30 mol dm^{-3}
0.05	610 ± 70	I = 0.40 mol dm^{-3}

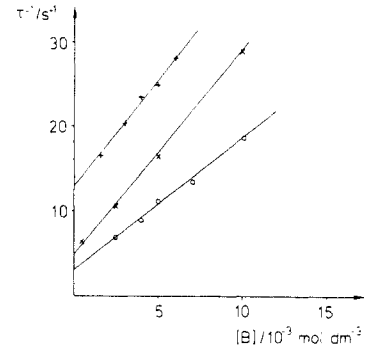
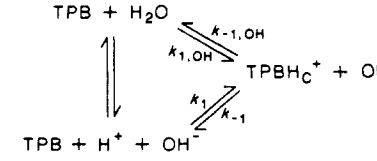


Figure 3. Dependence of the relaxation time on the concentration of phosphate buffer: (+) pH 6.40; (×) pH 6.86; (○) pH 7.43.

and only the extrapolated values are included in Table I.

Between pH 6.3 and 10.5 both H^+ and OH^- are involved in the reaction, therefore the reaction scheme has to be written as eq 5. The neutralization reaction $H^+ + OH^- \rightleftharpoons H_2O$ is too fast



(5)

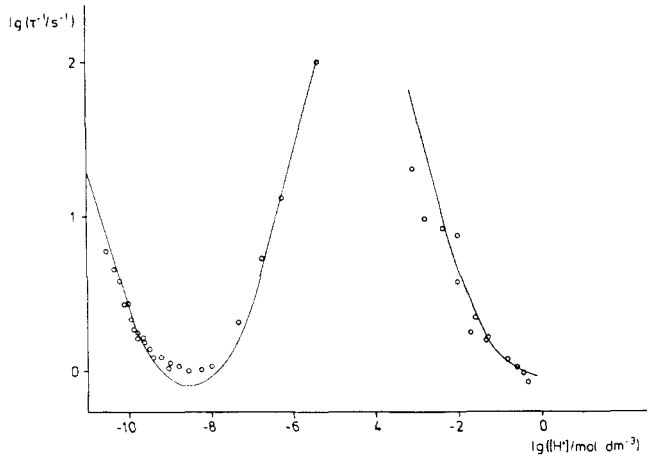


Figure 4. Double logarithmic plot of the reciprocal relaxation time vs proton concentration for the protonation of TPB. The curve is calculated according to eq 6 and 12 in the range $-10.5 < \log c_H < -5.5$ and $\log c_H > -3.5$, respectively.

to be observable with the techniques applied, and a single relaxation effect is expected for (5), with the relaxation time given by eq 6a for unbuffered solutions and by eq 6b for buffered solutions. The derivation of eq 6a, 6b, and 11 is given in the

$$1/\tau = k_{1,OH} + k_{-1,OH}f_I^2\left([OH^-] + \frac{[TPBH^+][OH^-]}{[H^+] + [OH^-]}\right) + k_{-1} + k_1\left([H^+] + \frac{[TPB][H^+]}{[H^+] + [OH^-]}\right) \quad (6a)$$

$$1/\tau = k_{1,OH} + k_{-1,OH}f_I^2[OH^-] + k_{-1} + k_1[H^+] \quad (6b)$$

Appendix. For pH >9.5 we observe a linear dependence of the relaxation time on $[OH^-] + [TPBH^+]$, from which $k_{1,OH} = 0.62 \pm 0.04\ s^{-1}$ and $k_{-1,OH} = (24 \pm 3) \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ are obtained.

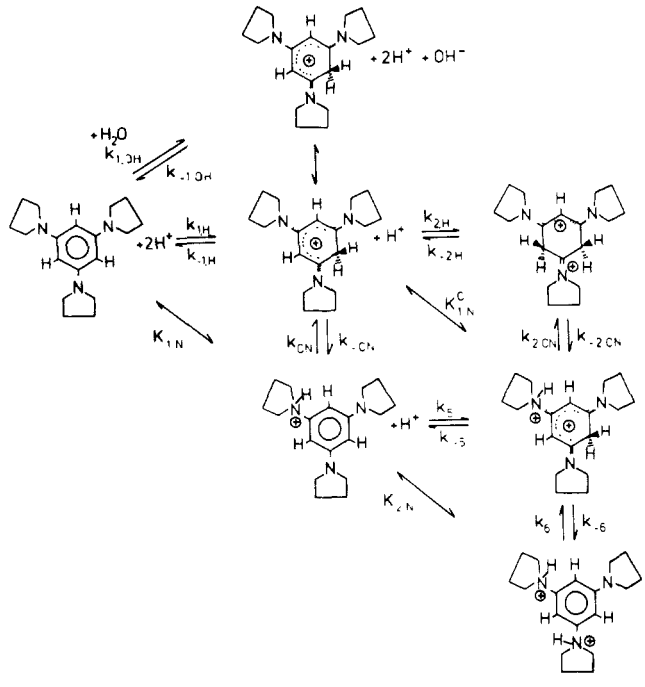
Activity corrections may be neglected since these measurements were performed at ionic strengths below 10^{-3} mol dm^{-3}. The rate constants are related to the dissociation constant by eq 7 where $K_W = 10^{-14.20}$ mol^2 dm^{-6} is the ion product of water in 90:10 (v/v) water/ethanol.[8] Details of these measurements in basic solutions are given in ref 5.

$$k_{-1,OH}/k_{1,OH} = K_{1,C}/K_W \quad (7)$$

From the linear dependence of $1/\tau$ on $[H^+]$ between pH 5.5 and 7.5, we obtain $k_1 = (2.4 \pm 0.3) \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$, and with the value of $K_{1,C}$, we evaluate $k_{-1} = (5.8 \pm 0.8) \times 10^{-3}\ s^{-1}$; i.e. in eq 6 k_{-1} is negligibly small compared to $k_{1,OH}$. In Figure 4 log τ^{-1} is plotted vs log c_H, and between pH 5.5 and 10.5 the curve is calculated according to eq 6. The general agreement between experimental points and theoretical curve indicates that (5) correctly describes the reaction mechanism. The deviation of +20% at the minimum reaction rate may be due to an error in the extrapolation to zero buffer concentration.

At pH 4.5 the reaction proceeds too fast to be measured with the stopped-flow technique, but below pH 3.5 a strong decrease of the reaction rate is observed. This is due to the fact that at low pH protons do not only bind to the aromatic ring but also to nitrogen atoms. In order to differentiate between different protonations, we indicate binding of protons to carbon by $TPBH_C^+$ and $TPBH_CH_C^{2+}$ and binding to nitrogen by $TPBH_N^+$ and $TPBH_NH_N^{2+}$. Binding to nitrogen was already postulated at the investigation of the hydrolysis of TPB.[6] The binding to nitrogen is much faster than the binding to carbon.[9] That means, the equilibrium between TPB, $TPBH_N^+$, and $TPBH_NH_N^{2+}$ is established before the protonation at carbon atoms proceeds, when in a stopped-flow experiment a solution containing TPB at pH 11 is mixed with aqueous HCl.

Scheme II



Furthermore, at pH <1.2 we have to consider that two protons may be bound to carbon atoms of TPB (see eq 3). This leads to the reaction in Scheme II. The rate-determining steps (binding of protons to carbon atoms) are indicated by two arrows (⇌), whereas the fast protonation steps are indicated by the double arrows (↔). Finally, for the calculation of the relaxation time, we have to consider that TPB may react with H_2O with the rate constant $k_{1,OH}$. Thus, the rate law of the reaction is given by eq 8. The indices refer to Scheme II. The backward reactions need

$$-d([TPB] + [TPBH_N^+] + [TPBH_NH_N^{2+}])/dt = k_{1,OH}[TPB] + k_{1,H}[TPB][H^+] + k_{CN}[TPBH_N^+] + k_5\frac{f_I^2}{f_{II}}[TPBH_N^+][H^+] + k_6[TPBH_NH_N^{2+}] \quad (8)$$

not be considered, since in acidic solutions the protonation is virtually irreversible. The reactions between TPB, $TPBH_N^+$, and $TPBH_NH_N^{2+}$ are fast compared to the rate-limiting steps, and therefore $[TPBH_N^+]$ and $[TPBH_NH_N^{2+}]$ may be expressed by [TPB] and the dissociation constants given in eq 9 and 10. The proton concentration is large compared to that of TPB, and therefore it virtually does not change during the progress of the reaction.

$$K_{1,N} = [TPB][H^+]/[TPBH_N^+] \quad (9)$$

$$K_{2,N} = [TPBH_N^+][H^+]f_I^2/[TPBH_NH_N^{2+}]f_{II} \quad (10)$$

Taking this into account and summarizing eq 8–10 leads to the expression given in eq 11 for the relaxation time. $k_{1,OH}$ is known

$$\frac{1}{\tau} = [k_{1,OH} + [H^+](k_{1,H} + k_{CN}K_{1,N}^{-1}) + [H^+]^2(k_5K_{1,N}^{-1} + k_6K_{1,N}^{-1}K_{2,N}^{-1})f_I^2f_{II}^{-1}]/[1 + [H^+]K_{1,N}^{-1} + [H^+]^2K_{1,N}^{-1}K_{2,N}^{-1}f_I^2f_{II}^{-1}] \quad (11)$$

from the relaxation measurements at pH >9.0. Comparing eq 11 with eq 6b shows that $k_{1,H} + k_{CN}K_{1,N}^{-1} = k_1$; i.e., $TPBH_C^+$ may be formed either by direct protonation of TPB or by an intramolecular proton transfer from $TPBH_N^+$. For low pH, where $[H^+]^2 \gg K_{1,N}K_{2,N}$, eq 11 may be reduced to eq 12. For pH <3.5

$$1/\tau = (k_{1,H} + k_{CN}K_{1,N}^{-1})K_{1,N}K_{2,N}f_{II}/[H^+]f_I^2 + k_5K_{2N} + k_6 \quad (12)$$

(8) Gutbezahl, B.; Grunwald, E. *J. Am. Chem. Soc.* **1953**, *75*, 565.
(9) Eigen, M. *Angew. Chem.* **1963**, *75*, 489; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

Table II. Kinetic and Thermodynamic Parameters of the Reaction XTPB + $H^+ \rightarrow$ $XTPBH^+$ at 25 °C

	TPB	MeTPB
log $K_{1,C}$, mol dm^{-3}	−9.60 ± 0.04	−12.75 ± 0.10
$\Delta H_1°$, kJ mol^{-1}	−50 ± 6	−50 ± 6
$\Delta S_1°$, J mol^{-1} K^{-1}	20 ± 10	80 ± 10
$\Delta V_1°$, cm^3 mol^{-1}	2 ± 2	1 ± 3
$k_{1,OH}$, s^{-1}	0.62 ± 0.08	(5.2 ± 0.5) × 10^{-3}
$k_{-1,OH}$, dm^3 mol^{-1} s^{-1}	(2.4 ± 0.3) × 10^4	0.16 ± 0.02
$\Delta H_{1,OH}^{\ddagger}$, kJ mol^{-1}	46 ± 3	57 ± 5
$\Delta S_{1,OH}^{\ddagger}$, J mol^{-1} K^{-1}	−95 ± 10	−100 ± 10
$k_{1,H} + k_{CN}/K_{1,N}$, dm^3 mol^{-1} s^{-1}	(2.4 ± 0.3) × 10^7	
$k_{2,H} + k_{2,CN}/K_{1,N}^C$, dm^3 mol^{-1} s^{-1}	(6.6 ± 1.6) × 10^3	
$K_{1,N}K_{2,N}$, mol^2 dm^{-6}	2 × 10^{-9}	

in Figure 4 the curve through the experimental data is calculated according to eq 12 with $k_5K_{2,N} + k_6 = 0.9$ s^{-1} and $K_{1,N}K_{2,N} = 2 \times 10^{-9}$ mol^2 dm^{-6} by using $k_{1,H} + k_{CN}K_{1,N}^{-1} = 2.4 \times 10^7$ dm^3 mol^{-1} s^{-1}, as determined earlier.

In this low pH range the measurements were performed at an ionic strength between 0.1 and 0.45 mol dm^{-3} where both the activity corrections introduced in eq 12 and the estimation of the activity coefficients by eq 4 represent only a very rough approximation. This explains the deviations between experimental data and the theoretical curve. However, in principle, the consideration of the activity coefficients is correct, as can be seen in Table I from the data for constant [H^+] = 0.05 mol dm^{-3} at various ionic strengths: An increase in $f_I^2 f_{II}^{-1}$ is expected when the ionic strength is increased, and correspondingly an increase of the relaxation time is observed.

$\Delta H_1°$ and $\Delta V_1°$ have been determined by measuring the absorbance of a solution of TPB as function of temperature and pressure, respectively (detailed data are available as supplementary material). The measurements have to be performed in basic solutions, since p$K_{1,C}$ = 9.6, and therefore the reaction enthalpy $\Delta H_b°$ = 8 ± 2 kJ mol^{-1}, reaction entropy $\Delta S_b°$ = −60 ± 8 eu, and reaction volume $\Delta V_b°$ = −19 ± 2 cm^3 mol^{-1} are obtained for reaction 13. The corresponding parameters for reaction 14 are calculated by eq 15 with $\Delta H_W°$ = −56 kJ mol^{-1}, $\Delta S_W°$ = 80 eu, and $\Delta V_W°$ = 21 cm^3 mol^{-1} for the neutralization reaction 16. The

$$TPB + H_2O \rightarrow TPBH_C^+ + OH^- \quad (13)$$

$$TPB + H^+ \rightarrow TPBH^+ \quad (14)$$

$$\Delta X_1° = \Delta X_b° + \Delta X_W° \quad (15)$$

$$H^+ + OH^- \rightarrow H_2O \quad (16)$$

kinetics of the second protonation have been studied previously[6] in solutions containing 0.05–0.5 M HCl. At this high proton concentration TPB hydrolyzes with a half-life time of about 100 s. Temperature-jump experiments have been performed within the first half-life after preparing the solutions, and relaxation times of 10^{-4}–10^{-3} s are observed (detailed data are available as supplementary material). The rate constant $k_2 = 6.6 \times 10^3$ dm^3 mol^{-1} s^{-1} has been determined, which according to Scheme II corresponds to eq 17. All kinetic and thermodynamic constants obtained for the protonation of TPB are summarized in Table II.

$$k_2 = k_{2,H} + k_{2,CN}/K_{1,N}^C \quad (17)$$

2-Methyl-1,3,5-tripyrrolidinobenzene and 2-Ethyl-1,3,5-tripyrrolidinobenzene. The protonation of MeTPB was studied by measurements analogous to those performed with TPB. The pH range of the investigation is restricted, since MeTPB hydrolyzes quickly below pH 4.[6] The equilibrium constant $K_{1,C} = 10^{-12.75}$ mol dm^{-3} was obtained from spectrophotometric measurements. The results of the kinetic measurements are summarized in Figure 5 (detailed data are available as supplementary material). At pH >12.5 a linear dependence of τ^{-1} on [OH^-] is observed, yielding the rate constants $k_{1,OH} = 5.2 \times 10^{-3}$ s^{-1} and $k_{-1,OH} = 0.16$ dm^3 mol^{-1} s^{-1}. According to eq 7, they agree with the previously obtained value of $K_{1,C}$. Between pH 12 and 10 the reaction rate reaches a minimum; it increases again at lower pH due to the direct reaction of MeTPB with H^+. However, k_1 and k_{-1} cannot be evaluated since the reciprocal relaxation time does not depend linearly on [H^+]. According to eq 11, this has to be attributed to the contribution of $[H^+]/K_{1,N}$ in the denominator on the right-hand side of the equation, which could be neglected in the case of TPB for pH <5.5. That means $K_{1,N}$ is much smaller for MeTPB than for TPB, but a numerical evaluation of the kinetic data is not possible for MeTPB below pH 11. The kinetic and thermodynamic parameters obtained are included in Table II.

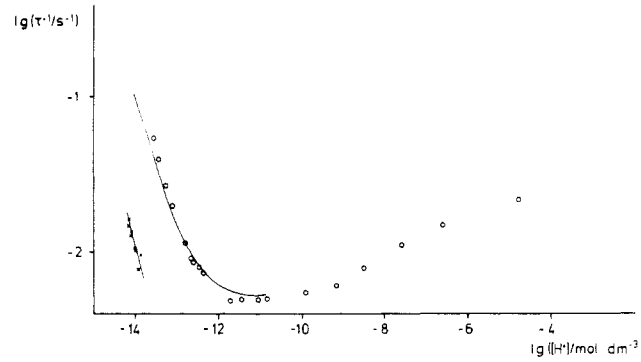


Figure 5. Double logarithmic plot of the reciprocal relaxation time vs proton concentration for the protonation of (○) MeTPB and (×) EtTPB.

Table III. pK Values of Triaminobenzenes at 25 °C [pK = −log K (mol dm^{-3})]

	TPB	MeTPB	EtTPB	TMB	TPiB
−log $K_{1,C}$	9.62	12.75	13.7	2.45	
−log $K_{1,N}$				3.40	6.30
−log $K_{2,C}$	0.80	1.77			
−log $K_{2,N}$				1.07	3.50
−log $K_{3,N}$				−1.0	0.2

Table IV. Rate Constants of C-Protonations of Triaminobenzenes at 25 °C

	TPB	MeTPB	EtTPB	TMB
$k_{1,OH}$, s^{-1}	0.62	5.2 × 10^{-3}	5.5 × 10^{-3}	
$k_{-1,OH}$, dm^3 mol^{-1} s^{-1}	2.4 × 10^4	0.16	1.9 × 10^{-2}	
$k_{1,H}$, dm^3 mol^{-1} s^{-1}	2.4 × 10^7			2.8 × 10^3
$k_{-1,H}$, s^{-1}	5.8 × 10^{-3}			1.1
k_2, dm^3 mol^{-1} s^{-1}	6.6 × 10^3			
k_{-2}, s^{-1}	1.3 × 10^3			

The most striking result is the decrease in the dissociation constant $K_{1,C}$, i.e. the increase in the stability of $MeTPBH^+$ as compared to $TPBH^+$, which is due to the difference in the reaction entropies. A further small increase in stability is observed for $EtTPBH^+$, $K_{1,C} = 10^{-13.7}$ mol dm^{-3}. The kinetic measurements could be performed only in a narrow pH range, since EtTPB is unstable in aqueous solutions. The results of the kinetic measurements are included in Figure 5; rate and equilibrium constants are given in Tables III and IV.

1,3,5-Trimorpholinobenzene and 1,3,5-Tripiperidinobenzene. For TMB the first protonation occurs only partially at the aromatic ring and predominantly at a nitrogen atom. Equilibrium measurements yield the overall dissociation constant given in eq 18.

$$K_1 = \frac{[TMB][H^+]}{[TMBH_C^+] + [TMBH_N^+]} = 3.6 \times 10^{-4} \text{ mol dm}^{-3} \quad (18)$$

The equilibrium constant between the two monoprotonated species is given by eq 19. K_{CN} has been calculated from the relaxation

$$K_{CN} = [TMBH_C^+]/[TMBH_N^+] = 0.11 \quad (19)$$

amplitude (A_0 in eq 1) of stopped-flow measurements by electrical conductance to detect the progress of reaction.[10] With this

(10) Knoche, W.; Sachs, W.; Vogel, S. *Bull. Soc. Chim. Fr.* **1988**, 377.

Scheme III

technique A_0 depends on concentrations, equivalent conductivities, K_1, and K_{CN}. Thus, K_{CN} may be obtained from the experimental value of A_0, since K_1 has been determined (eq 18) and the equivalent conductivities of the ions are known or can be estimated with sufficient accuracy.

The kinetics of the protonations were studied with the pressure-jump technique, and the rate constant $k_{1,H} + k_{CN}/K_{1,N} = 1.1\ s^{-1}$ was obtained. Further protons bind to nitrogen atoms of TMB, and the second and third dissociation constants were determined spectrophotometrically. In the case of TPiB proton binding has been observed only to nitrogen atoms, and three dissociation constants were determined. Details of the measurements with TMB and TPiB are given in ref 10. The equilibrium and rate constants obtained are summarized in Tables III and IV, respectively.

Discussion

There are two important aspects that emerge from our investigations. First, C-protonation versus N-protonation is strongly dependent on the amino components attached to the benzene ring. 1,3,5-Tripyrrolidinobenzene and 1,3,5-tripiperidinobenzene represent two limiting cases: in the former C-protonation is strongly favored, while in the latter one observes only N-protonation. This is mainly due to the change in the carbon pK_a, since it may be assumed that the nitrogen pK_a depends only weakly on the substituents.

The effect of activating the benzene ring by the various amino groups may be compared with the corresponding effect on a double bond, i.e. the influence of the amino substituents on the properties of enamines. There it is known that pyrrolidinoenamines are much more reactive toward electrophiles than piperidinoenamines.[11] The stronger activation of a double bond via conjugation by a pyrrolidine than that by a piperidine is also seen in the photoelectron spectra and the electrochemical redox potentials of these compounds.[12] The pyrrolidinoenamines are in general more electron-rich than the piperidinoenamines. Consequently, they have the lower ionization potential. Recent investigations[13] on enamines have attributed this effect to conformational differences between the five-membered ring and the six-membered ring system. The former is more amenable to form an exocyclic double bond, which is a prerequisite for the shift of electron density from the nitrogen atom into the olefinic double bond (see Scheme III). This interpretation is also in accord with the classical experiments of H. C. Brown et al.,[14] which reveal that in cycloalkanes the stability of an sp^2 center depends on ring size. In the case at hand, three amino groups are donating electrons into the ring system. Hence, the difference in reactivity exerted by a pyrrolidino group versus that by a piperidino group is strongly enhanced. The trimorpholinobenzene is a borderline case between tripyrrolidino- and tripiperidinobenzene.

Another factor should be mentioned here: The various amino substituents introduce mutual steric strain when they are attached to the benzene ring. This strain is larger in a coplanar than in a twisted orientation of the substituents with respect to the π-system. Furthermore, the strain is enhanced for TMB and TPiB as compared to the smaller TPB. The mutual position between benzene ring and substituents influences the strength of C-protonation.

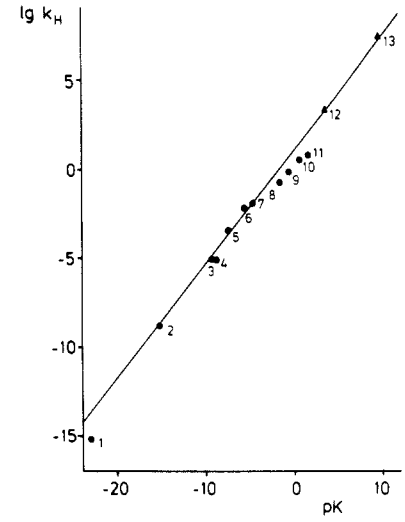


Figure 6. Brønsted relation for the protonation of aromatic compounds (log k_H vs $pK = -\log K_{1,C}$): (●) data taken from ref 15, (▲) our results. Key: 1, benzene; 2, anisole; 3, 1,3-dimethoxy-2-methylbenzene; 4, 1,3-dimethoxybenzene (4-position); 5, 1,3-dihydroxy-2-methylbenzene; 6, 1,3,5-trimethoxybenzene; 7, 1,3,5-triethoxybenzene; 8, azulene; 9, guiazulene-2-sulfonate; 10, 4,6,8-trimethylazulene; 11, guiazulene; 12, 1,3,5-trimorpholinobenzene; 13, 1,3,5-tripyrrolidinobenzene.

Second, there is an unexpectedly large difference in the dissociation constant $K_{1,C}$ and the rate constants $k_{1,OH}$ and $k_{-1,OH}$ for TPB and MeTPB (see Table II). These large shifts cannot be explained by purely electronic considerations, and Effenberger[4] points to the steric differences between the σ-complexes $TPBH^+$ and $MeTPBH^+$. $TPBH^+$ is planar whereas $MeTPBH^+$ is nonplanar with the methyl group in quasi-axial position and a proton in equatorial position. Since the leaving group (and because of the principle of microreversibility, therefore also the entering group) has to be in quasi-axial position, energy is needed to convert the stable $MeTPBH^+$ to the acidic intermediate, where a proton is in quasi-axial position and the methyl group is in equatorial positions. This explains the differences in the rate constants. However, the large change in the dissociation constant is not due to a difference in energy but to a difference in entropy. This is evident from the consideration of the proton-transfer reaction

$$TPBH^+ + MeTPB \rightarrow TPB + MeTPBH^+$$

with the thermodynamic parameters

$$\Delta V^\circ = -1 \pm 3\ cm^3\ mol^{-1}$$

$$\Delta H^\circ = 0 \pm 5\ kJ\ mol^{-1}$$

$$\Delta S^\circ = 60 \pm 20\ J\ mol^{-1}\ K^{-1}$$

The increase in entropy may indicate that solvation plays an important role; i.e., the solvation shell of $MeTPBH^+$ is less tight than that of $TPBH^+$, and therefore the solvating water molecules are less ordered.

Finally, our results should be compared with data obtained for the formation of other protonated σ-complexes. For this purpose, Figure 6 shows a simple Brønsted plot summarizing our measurements and data given by Kresge.[15] There is an excellent linear dependence of log k_H on pK_a for all substituted benzenes with slope $d(\log k_H)/d(pK_a) = 0.64$. The values of benzene itself do not fit well to the straight line, which may be due to the fact that they are obtained by a long extrapolation from concentrated to dilute acid solutions. The points for the azulenes are slightly below the straight line, which indicates that steric effects influence weakly

(11) Hickmott, P. W. *Tetrahedron* **1982**, *98*, 1975, 3363, and references cited therein.
(12) Schoeller, W. W.; Niemann, J.; Rademacher, P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 369.
(13) Muller, K.; Previdoli, F.; Desilvestro, H. *Helv. Chim. Acta* **1981**, *64*, 2497.
(14) Brown, H. C.; Brewster, J. H.; Shechter, H. *J. Am. Chem. Soc.* **1964**, *76*, 467.
(15) Kresge, A. J.; Mylonakis, S. G.; Sato, Y.; Vitullo, V. P. *J. Am. Chem. Soc.* **1971**, *93*, 6181.
(16) Bernasconi, C., Ed. *Investigations of Rates and Mechanisms of Reactions, Techniques of Chemistry*, 4th ed.; Wiley: New York, 1986; Vol. VI, Part II.

the rate of σ-complex formation.

The good correlation between the data obtained for TPB and the data obtained in superacidic media proves that the study of the protonation of TPB may provide a detailed insight into the mechanism of σ-complex formation. Since for TPB the measurements are performed in dilute solutions, the influence of the solvent and the influence of substituents can be studied separately. To this purpose, further measurements are in progress.

Acknowledgment. We thank Prof. F. Effenberger, Universität Stuttgart, for providing the substituted benzenes and Prof. A. J. Kresge, University of Toronto, for valuable discussion.

Appendix

Relaxation Times. The rate law for reaction 5 is given in eq A1. From this equation the relaxation time is calculated in the usual way;[16] i.e. the actual concentration [A] is replaced by the time-independent equilibrium concentration [$\bar{A}$] and the "deviation" x_A, where $x_A \ll [\bar{A}]$.

$$d[TPBH_C^+]/dt = k_{1,OH}[TPB] - k_{-1,OH}f_\pm^2[TPBH_C^+][OH^-] + k_1[TPB][H^+] - k_{-1}[TPB_C^+] \quad (A1)$$

For reaction 5 we have due to the conservation of mass

$$x_{TPB} = -x_{TPBH,C} \quad (A2)$$

The law of electroneutrality requires

$$x_H + x_{TPBH,C} = x_{OH} \quad (A3)$$

Equation A3 is valid for unbuffered solutions, where only H_2O and no other base or acid reacts with TPB. Finally, the neutralization reaction $H^+ + OH^- \rightleftarrows H_2O$ is fast compared to the protonation of TPB, and therefore this dissociation equilibrium is always established, which means that eq A4 applies. Combining eq A1–A4 leads to eq A5 with $1/\tau$ given by eq 6a.

$$\overline{[OH^-]}x_H = -\overline{[H^+]}x_{OH} \quad (A4)$$

$$dx_{TPBH,C}/dt = -(1/\tau)x_{TPBH,C} \quad (A5)$$

In buffered solution eq A3 is not appropriate, since the buffer ions contribute to the electroneutrality. However, since the solutions are buffered, we may apply eq A6. Combining eq A1, A2, and A6 leads to eq A5 with $1/\tau$ given by eq 6b.

$$x_H = x_{OH} = 0 \quad (A6)$$

In order to derive eq 11 we start with eq 8 and insert the deviation x_i. Equation 8 is applied only in the range pH <3.5, and therefore the proton concentration is large compared to that of TPB. That means the solutions are buffered and the reaction proceeds under pseudo-first-order conditions; i.e., we may assume eq A7 applies. This leads to eq A8. The reactions leading to

$$x_H = 0 \quad (A7)$$

the equilibria 9 and 10 are fast compared to reaction 8; i.e., with eq A7 we have eq A9 and A10. Inserting eq A9 and A10 into eq A8 leads to eq A11 with $1/\tau$ given by eq 11.

$$-d(x_{TPB} + x_{TPBH,N} + x_{TPBHH,NN})/dt = k_{1,OH}x_{TPB} + k_{1,H}\overline{[H^+]}x_{TPB} + k_{CN}x_{TPBH,N} + k_5f_I^2f_{II}^{-1}\overline{[H^+]}x_{TPB,N} + k_6x_{TPBHH,NN} \quad (A8)$$

$$x_{TPB} = (\overline{[TPB]}/\overline{[TPBH_N^+]})x_{TPBH,N} \quad (A9)$$

$$x_{TPBHH,NN} = (\overline{[TPBH_NH_N^{2+}]}/\overline{[TPBH_N^+]})x_{TPBH,N} \quad (A10)$$

$$-dx_{TPBH,N}/dt = (1/\tau)x_{TPBH,N} \quad (A11)$$

Registry No. MeTPB, 20758-47-8; EtTPB, 20758-48-9; TMB, 16857-97-9; TPiB, 16857-95-7; TPB, 16857-93-5; TPB^+, 103979-21-1; TPB^{2+}, 116054-41-2.

Supplementary Material Available: Tables of relaxation times measured for solutions of TPB, MeTPB, and EtTPB and equilibrium constants (6 pages). Ordering information is given on any current masthead page.

Radical-Anionic Nature of the Transition State in the Michael Addition Reaction[1]

Zeev Gross and Shmaryahu Hoz*

Contribution from the Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel 52100.
Received January 12, 1988. Revised Manuscript Received June 10, 1988

Abstract: The kinetics of the addition of CN^- to a series of para mono- and disubstituted 1,1-diaryl-2-nitroethylene was studied in water and DMSO. log k correlates with σ^0 better than with σ with a ρ value of 0.24 in water and 1.16 in DMSO. The points for the mono- and dimethoxy derivatives (**1** and **3**) in water deviate positively from the Hammett type line. When a Yukawa–Tsuno type equation is used, a linear plot that includes the *p*-MeO derivatives is obtained with $R = -0.5$. Contrary to expectations, the ρ value in DMSO is ca. 5-fold larger than that in water and the data points for the *p*-MeO substituents do not deviate from the Hammett type correlation. In the reaction of the *p*-dinitro derivative **9** in DMSO, 10% of a product rising from nucleophilic attack at the other terminus of the double bond (α to the nitro group) was observed. These unusual results are rationalized by using current theories, which assign the transition state a significant contribution of charge-transfer configurations (configurations B and C). The relative and absolute contribution of each of the configurations to the transition state is responsible for the observed phenomena.

Nucleophilic additions to highly activated systems are of prime importance from both synthetic and mechanistic points of view. The common feature of these activated compounds, which include aromatics substituted by electron-withdrawing groups,[2] carbonium ions,[3] carbonyl derivatives,[4] and activated olefins,[5] is that they all posses low LUMOs (LL). Several years ago we suggested that, at the transition state of their reaction with nucleophiles, these

(1) Nucleophilic Attacks on Low LUMO Compound. 5. Part 4: Reference 8.

(2) Miller, J. *Aromatic Nucelophilic Substitution*; Elsevier: Amsterdam, The Netherlands, 1968. Bernasconi, C. F. *MTP Int. Rev. Sci.:Org. Chem., Ser. One* **1973**, *3*, 33. Barlin, G. B. *Aromt. Heteraromat. Chem.* **1974**, *2*, 271.

(3) Ritchie, C. D. *Pure Appl. Chem.* **1978**, *50*, 1281.

(4) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. Bender, M. L. *Mechanism of Homogeneous Catalysis from Proton to Proteins*, Wiley: New York, 1971. Patai, S., Ed. *The Chemistry of the Carbonyl Group*; Wiley: London, 1972; Vol. 1. Zabicky, J., Ed. *The Chemistry of the Carbonyl Group*; Wiley: London, 1972; Vol. 2. Cordes, E. H. Bull, H. G. *Chem. Rev.* **1974**, *74*, 581. Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1.

0002-7863/88/1510-7489$01.50/0