Acid–Base Reactions of N,N,N',N'-Tetramethyl-p-phenylenediamine with Carboxylic Acids in Benzene at 25°

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Abstract: The equilibrium constants of the reactions of the base N,N,N',N'-tetramethyl-p-phenylenediamine with various acids in benzene at 25° were studied spectrophotometrically. The ion-pair formation constants for the transfer of a single proton had the following values (l./mol): for trichloroacetic acid, 4.15×10^5; for picric acid, 1.33×10^5; for dichloroacetic acid, 1.6×10^4; for 2,5-dinitrobenzoic acid, 1.3×10^4; for 3,5-dinitrobenzoic acid, 4.3×10^3; for o-nitrobenzoic acid, 1.7×10^3; for monochloroacetic acid, 4.9×10^2, and for p-nitrobenzoic acid, 2.8×10^2. The order of decreasing acid strength is practically the same as that in water, except for 3,5-dinitrobenzoic acid. The chlorinated acetic acids showed the following homoconjugate ion-pair formation constants (l./mol): for trichloroacetic acid, 1.5×10^3, for dichloroacetic acid, 3×10^3, and for monochloracetic acid, 3.9×10^2. Only the latter acid showed an indication of further reaction to form a product of the type $BH^+(A \cdot 2\text{-}HA)^-$, with a formation constant of 35 l./mol. The addition of a second proton to N,N,N',N'-tetramethyl-p-phenylenediamine was studied for the chlorinated acetic acids only. The results are expressed in terms of correlating equations. The ratio of the concentration of the diprotonated to that of the monoprotonated base is given by 7.3×10^3 times the square of the monomer concentration of trichloroacetic acid. The log of the ratio is equal to $3.96 + 2.64$ times the log of the monomer concentration of dichloroacetic acid. The ratio is equal to twice the monomer concentration of monochloroacetic acid.

W urster's Blue is the univalent radical cation which is produced by the oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD). In water, the optimum pH for the oxidation[2] is very close to that of a solution of the monoprotonated reduced species (TMPDH⁺).[3] The opinion has been expressed that the oxidation of TMPD to the Blue (by chloranil, for example) will take place only in polar solvents.[4] The next article describes the production of the radical ion in benzene. Since the monoprotonated TMPDH⁺ had to be formed before oxidation would take place, it was necessary to evaluate the equilibrium constants of the reactions of TMPD with the various organic acids which were used in the study of Wurster's Blue. This paper is concerned with the calculation of the equilibrium constants of the various acid–base reactions in benzene at 25° between TMPD and the following acids: trichloroacetic (TCA), dichloroacetic (DCA), monochloroacetic (MCA), o-nitrobenzoic (ONBA), p-nitrobenzoic (PNBA), 3,5-dinitrobenzoic (3,5-DNBA), 2,5-dinitrobenzoic (2,5-DNBA), and picric (HPi).

Experimental Section

Reagents. TMPD dihydrochloride (Eastman) was neutralized with NaOH in water. The precipitated free base was extracted with ether, washed, and dried, and the solvent was removed by evaporation. The crude product was sublimed in vacuo immediately before use. ONBA (Eastman) was dissolved in ethanol, evaporated part way, and cooled; the small crop of crystals was discarded. Water was added to the filtrate to precipitate the acid; the latter was recrystallized from benzene and dried in vacuo. PNBA (Eastman) was recrystallized from an ethanol–water mixture and dried in vacuo. 3,5-DNBA (Eastman) was recrystallized twice from ethanol–water and dried in vacuo. 2,5-DNBA (Eastman) was recrystallized twice from benzene. HPi (Baker and Adamson) was recrystallized from benzene. The purification of the chlorinated acetic acids and of benzene has already been described.[5]

Apparatus and Procedures. All visible and uv measurements were made on a Cary Model 14 spectrophotometer which was equipped with a special cell holder through which water was pumped from a constant-temperature bath. The temperature of the water leaving the cell holder was 25.0 ± 0.1°. For most measurements, Beckmann 1-cm rectangular quartz cells equipped with ground-glass stoppers were used. For strongly absorbing solutions a 9-mm quartz block was placed inside the special cell described below. For very dilute solutions, Aminco 5- and 10-cm cylindrical cells were used. A special cell was constructed for carrying out titrations directly in the spectrophotometer. Its overall length was 12 in. At the bottom, there was a 1-cm rectangular quartz cell which was attached to Pyrex tubing by a graded seal. At the top, there was a ¹⁹/₃₈ standard-taper female joint. A little below the bottom of the joint a 1-in. long side arm was sealed at an angle of 45° to the main cell.

Stock solutions of acids and of TMPD were prepared by weighing directly into dry volumetric flasks and diluting to the mark with benzene. Dilutions were made with pipets or with a Manostat Digipet. Final dilutions were made at 25 ± 2°. Alternatively, measured amounts of the TMPD stock solution and benzene were placed in the special cell and small amounts of acid were added with shaking. A correction was made for the volume of added acid.

Results and Discussion

I. Spectra of TMPD, TMPDH⁺, and TMPDH₂²⁺. Figure 1 shows the spectra of 2×10^{-4} M TMPD in benzene containing different concentrations of TCA. It can be seen that the conversion of the free base to TMPDH⁺ is accompanied by the disappearance of the peak at 332 nm and the appearance of a new peak at 310 nm.

Figure 2 shows similar spectra of 2×10^{-3} M TMPD in benzene containing much higher concentrations of TCA. The band at 310 nm decreases with increasing acid concentration, and finally vanished in 7.3×10^{-2}

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(1) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Polytechnic Institute of Brooklyn in June 1968.

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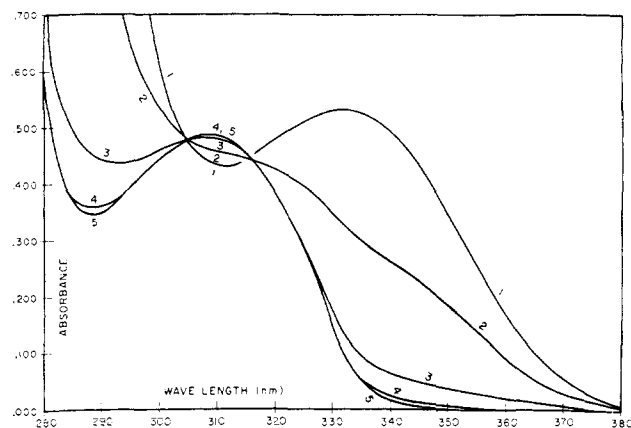(5) J. Steigman and W. Cronkright, Spectrochim. Acta, Part A, **26**, 1805 (1970).

Figure 1. Titration of 2×10^{-4} M TMPD with TCA in benzene at 25°. Absorbance plotted against wavelength in nm. TCA: Curve 1, none; 2, 10^{-4} M; 3, 2×10^{-4} M; 4, 3×10^{-4} M; 5, 10^{-3} M. Cell thickness, 1 cm.

Figure 2. Titration of 2.04×10^{-3} M TMPD with concentrated TCA in benzene at 25°. Absorbance plotted against wavelength in nm. TCA: Curve a, none; b, 1.88×10^{-3} M; c, 3.85×10^{-3} M; d, 7.65×10^{-1} M; e, 1.15×10^{-2} M; f, 1.53×10^{-2} M; g, 2.28×10^{-2} M; h, 3.76×10^{-2} M; i, 7.3×10^{-2} M. Cell thickness, 0.1 cm.

M TCA. These curves show the conversion of TM-PDH$^+$ to TMPDH$_2$$^{2+}$; the latter, which lacks unbonded n electrons, does not show any absorption bands in this region.

The assumption was made that the TMPDH$^+$ cation has the same spectrum in all species which contain it (ion pair, homoconjugate ion, etc.). If the added acid (for example, ONBA) had a spectrum which overlapped that of the monoprotonated cation, the further assumption was made that the two spectra were additive. In the case of the chlorinated acetic acids, no overlap was found. For the other acids, there was overlap by both the free acid and its anion.

The assumption that TMPDH$^+$ would exhibit the same spectrum in the presence of different acids requires justification. It is well known that acid–base reactions in benzene and similar aprotic solvents with low dielectric constants proceed by way of ion-pair formation, and that triple ions, quadrupoles, and higher aggregates may form as well.[6] In addition, solvation of anions by one or more molecules of acid (homoconjugate or heteroconjugate formation in Kolthoff's terminology) has been shown to exist in benzene.[7] These complex reactions, which are due to poor solvation of charged species by benzene, have their counterparts in the different spectra exhibited by indicator phenolic acids neutralized by different bases. Thus, Davis and her coworkers have shown that the phenolic indicators bromophthalein magenta E and B show markedly different spectra in benzene with various amines and other bases.[8,9] 2,4-Dinitrophenol behaves similarly.[10] However, the phenomenon is very much less marked in the case of neutral basic indicators. p-Tolyl di-n-propyl Nile Blue with excess 2,4,6-trinitro-m-cresol shows a peak at 633 nm, with a molar absorptivity of 62,500 and an isosbestic point near 556 nm. Trichloroacetic acid and diphenyl phosphate show peaks at 630 or 635 nm, with a molar absorptivity of about 57,500 and an isosbestic point near 553 nm.[11] In the work described here,

we have found that the spectra of TMPD in TCA, DCA, and MCA solutions in benzene are almost identical. Plots of the log of the absorbance of limiting acid solutions against wavelength from 300 to 330 nm are almost parallel.[12] In each case the maximum absorbance is found at 310 nm. Calculations of the molar absorptivities at 5-nm intervals from 300 to 330 nm show differences of 3% or less among the three acids. There is an additional demonstration that the spectra of the TMPDH$^+$ salts of the chlorinated acetic acids are very similar to each other. The determination of the concentrations of the free base and of TMPDH$^+$ required measurement of the absorbances of solutions at two wavelengths and the solution of simultaneous linear equations. For brevity we omitted the sum of the calculated concentrations of TMPD and TMPDH$^+$ in Tables II and IV. This sum can be compared with the stoichiometric concentration of TMPD in each solution. Among a total of 50 solutions divided among the three acids, there were 3 cases in which the difference was 10% or more, 10 cases in which the difference was 3–4%, and 37 solutions for which the difference was 2% or less. Table I gives the molar absorptivity indices of TMPD and of TMPDH$^+$ at the two wavelengths 310 and 340 nm.

Table I. Peak Wavelengths (nm) and Molar Absorptivities of TMPD and TMPDH$^+$

Form	λ_{max}, nm	a_M, l. mol^{-1} cm^{-1}
TMPD	340	2.55×10^3
TMPD	310	2.10×10^3
TMPDH$^+$	340	0.05×10^3
TMPDH$^+$	310	2.40×10^3

II. Addition of the First Proton to TMPD by Various Acids. The formation constant of a simple ion pair BH$^+$A$^-$ in a reaction between a base B and an acid HA in benzene is described by

$$K_1 = \frac{[\text{BH}^+\text{A}^-]}{[\text{B}][\text{HA}]} \tag{1}$$

(6) An excellent review of both the early and most recent work in this field is found in M. M. Davis, National Bureau of Standards Monograph 105, U. S. Government Printing Office, Washington, D. C., 1968.
(7) Reference 6, pp 91–94.
(8) M. M. Davis and P. J. Schuhmann, *J. Res. Nat. Bur. Stand.*, **39**, 221 (1947).
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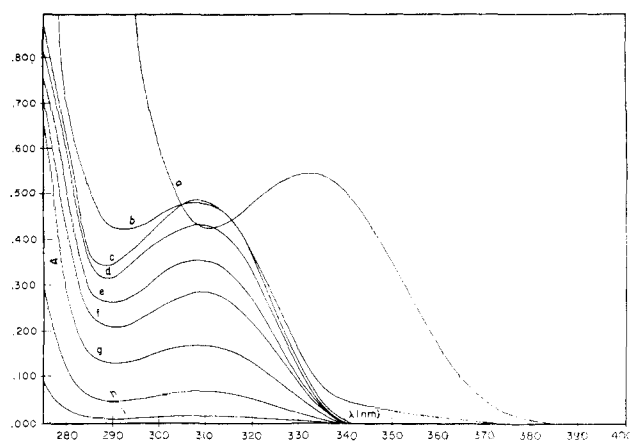(10) Reference 6, p 60.
(11) M. M. Davis and H. B. Hetzer, *Anal. Chem.*, **38**, 451 (1966).
(12) M. G. Mellon, "Analytical Absorption Spectroscopy," Wiley, New York, N. Y., 1950, p 102.

Table II. Spectrophotometric Data and Equilibrium Constants for TMPD and Chlorinated Acids in Benzene at 25°

$[\text{TMPD}]_0$, $M \times 10^6$	$[\text{HA}]_0$, $M \times 10^6$	Cell length, cm	A_{310}	A_{340}	$[\Sigma \text{BH}^+]$, $M \times 10^6$	$[\text{HA}]_M$, $M \times 10^6$	$\dfrac{[\Sigma \text{BH}^+]}{[\text{B}][\text{HA}]_M}$, l. mol^{-1}
			(a) TCA				
2.53	3.39	10	0.592	0.115	2.11	1.28	4.0 × 10⁶
20.2	20.0	1	0.432	0.065	18.1	1.90	4.3 × 10⁶
			(b) DCA				
4.33	5.12	5	0.509	0.392	1.58	3.40	1.53 × 10⁴
2.50	8.20	5	0.248	0.137	1.14	6.90	1.58 × 10⁴
4.83	10.2	5	0.534	0.268	2.65	7.10	1.81 × 10⁴
2.50	16.1	5	0.262	0.081	1.65	14.2	1.92 × 10⁴
5.0	20.5	5	0.605	0.145	4.11	15.1	2.57 × 10⁴
10.0	30.7	5	1.218	0.239	8.65	19.0	2.68 × 10⁴
9.8	10.2	1	0.221	0.137	4.58	5.10	1.70 × 10⁴
10.0	20.5	1	0.227	0.071	7.14	11.6	2.34 × 10⁴
24.7	20.5	1	0.565	0.315	12.9	5.80	1.88 × 10⁴
24.7	25.7	1	0.568	0.258	15.1	7.90	1.95 × 10⁴
10.0	30.7	1	0.232	0.047	8.19	19.5	2.50 × 10⁴
24.7	30.7	1	0.576	0.220	16.7	10.3	1.95 × 10⁴
24.7	51.0	1	0.589	0.110	21.1	22.0	2.46 × 10⁴
24.7	100.2	1	0.600	0.037	24.1	61.2	4.02 × 10⁴
238.0	185.0	0.1	0.551	0.250	146.0	9.40	1.62 × 10⁴
236.0	215.0	0.1	0.560	0.202	167.0	10.7	2.06 × 10⁴
234.0	250.0	0.1	0.554	0.157	180.0	15.9	1.95 × 10⁴
227.0	412.0	0.1	0.551	0.040	220.0	56.9	3.50 × 10⁴
232.0	301.0	0.1	0.554	0.114	195.0	25.7	1.85 × 10⁴
			(c) MCA				
16.0	40.0	1	0.350	0.344	2.80	36.0	590
16.0	80.0	1	0.359	0.289	5.10	69.0	660
16.0	81.0	1	0.357	0.281	5.00	70.0	630
16.0	120.0	1	0.361	0.241	6.90	101.0	730
16.0	160.0	1	0.368	0.212	8.20	132.0	750
16.0	162.0	1	0.371	0.214	8.20	133.0	740
16.0	304.0	1	0.383	0.132	11.6	233.0	990
16.0	405.0	1	0.384	0.098	12.8	299.0	1180
40.0	40.0	1	0.874	0.884	6.20	32.0	560
39.0	79.0	1	0.870	0.743	10.9	62.0	600
38.0	153.0	1	0.860	0.545	17.9	117.0	710
36.0	222.0	1	0.845	0.420	21.1	166.0	760
35.0	284.0	1	0.822	0.330	23.3	208.0	890
33.0	400.0	1	0.780	0.224	25.2	283.0	1060
31.0	501.0	1	0.738	0.172	25.3	345.0	1160
40.0	405.0	1	0.967	0.280	31.2	280.0	1060
40.0	608.0	1	0.970	0.133	34.8	397.0	1370
40.0	810.0	1	0.982	0.106	37.0	502.0	1620
40.0	102.0	1	0.980	0.183	37.8	604.0	1810
98.0	98.0	0.1	0.213	0.133	26.0	63.0	580
94.0	137.0	0.1	0.210	0.076	42.5	113.0	700
85.0	343.0	0.1	0.197	0.049	67.0	214.0	910
79.0	475.0	0.1	0.182	0.310	60.0	295.0	1120
193.0	190.0	0.1	0.429	0.273	73.0	90.0	680
191.0	236.0	0.1	0.430	0.250	87.0	110.0	740
189.0	279.0	0.1	0.425	0.197	93.0	134.0	720
185.0	364	0.1	0.420	0.154	109.0	177.0	820
181.0	445.0	0.1	0.416	0.124	122.0	217.0	970
177.0	522.0	0.1	0.411	0.104	131.0	255.0	1100
173.0	595.0	0.1	0.404	0.102	135.0	295.0	1220

If there is a reaction between BH^+A^- and additional HA to form the homoconjugate ion pair $\text{BH}^+(\text{AHA}^-)$, the corresponding constant, K_2, is given by

$$K_2 = \frac{[\text{BH}^+(\text{AHA}^-)]}{[\text{BH}^+\text{A}^-][\text{HA}]} \qquad (2)$$

The following mass balance equations apply

$$[\text{B}] = [\text{B}]_0 - [\text{BH}^+\text{A}^-] - [\text{BH}^+(\text{AHA})^-] \qquad (3)$$

$$[\text{HA}] = [\text{HA}]_0 - [\text{BH}^+\text{A}^-] - 2[\text{BH}^+(\text{AHA})^-] \qquad (4)$$

In these equations, $[\text{B}]_0$ and $[\text{HA}]_0$ represent the initial stoichiometric concentrations of base and of acid.

Combining eq 2, 3, and 4 gives

$$[\text{HA}] = [\text{HA}]_0 - [\text{BH}^+\text{A}^-](1 + 2K_2[\text{HA}]) \qquad (5)$$

It is not possible to measure $[\text{BH}^+\text{A}^-]$ directly; rather, the quantity

$$\Sigma[\text{BH}^+] = \Sigma[\text{BH}^+] + [\text{BH}^+\text{A}^-] + [\text{BH}^+(\text{AHA})^-] \qquad (6)$$

is estimated from the spectrophotometric measurements. It can be shown that the following equations apply

$$\frac{[\text{BH}^+\text{A}^-] + [\text{BH}^+(\text{AHA})^-]}{[\text{B}]} =$$
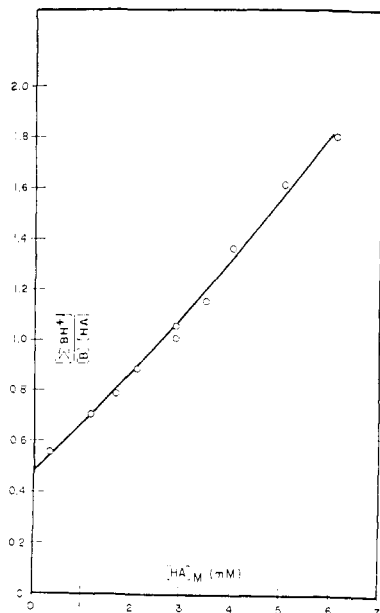
$$K_1[\text{HA}] + K_1K_2[\text{HA}]^2 \qquad (7)$$

Figure 3. Plot of the ratio $\Sigma[BH^-]/[B][HA]_M$ against $[HA]_M$: 4×10^{-4} M TMPD in benzene containing various concentrations of MCA. Solid curve calculated from eq 13. Data are in Table IIc.

$$\frac{[BH^-A^-] + [BH^+(AHA)^-]}{[B][HA]} = K_1 + K_1K_2[HA] \quad (8)$$

That is, a plot of $\Sigma[BH^+]/[B][HA]$ against $[HA]$ yields a straight line, with intercept K_1 and slope K_1K_2. The concentration of acid which enters into eq 8 is the concentration of the monomeric species. For this a correction must be made for the fraction of the acid which is dimerized. The corrected concentration is called $[HA]_M$

$$[HA]_M = \frac{-1 + \sqrt{1 + 8[HA]K_D}}{4K_D} \quad (9)$$

Here [HA] is the uncorrected concentration of free acid (monomer and dimer) and K_D is the dimerization constant of the acid. The following values of K_D (l. mol^{-1}) were used: for MCA, 48; for DCA, 27; and for TCA, 6.7.[5] A plot of $\Sigma[BH^+]/[B][HA]_M$ against $[HA]_M$ should yield a straight line, whose intercept is K_1, and whose slope is K_1K_2. A computer program called CARDS was used for this purpose.[13] Starting with the experimental data, an assumed value for K_2 was inserted, and calculations were made of $\Sigma[BH^+]$, [B], and $[HA]_M$. Analysis of the results and the estimation of a new value for K_2 was then done by hand.

III. TMPD and the Chlorinated Acetic Acids. (a) TCA. The reaction in benzene between TMPD and TCA is quite extensive, even when the reactant concentrations are below 10^{-4} M. Table IIa presents the spectrophotometric data and the calculated ion-pair formation constants for approximately 10^{-4} and 10^{-5} M reagent solutions. The predominant reaction is simple ion-pair formation. The following paper deals in part with the calculation of K_2, the homoconjugate ion-pair formation constant. It has the value 1.5×10^3 l. mol^{-1}. The average value of K_1 (from Table II) is 4.15×10^5 l. mol^{-1}.

(13) From the Ph.D. thesis of W. Cronkright.

(b) DCA. Solutions with stoichiometric concentrations of TMPD between 2×10^{-5} and 2.5×10^{-3} M and DCA concentrations from 5×10^{-5} to 4×10^{-3} M were examined. The spectrophotometric data and the calculated concentrations of the different chemical species in the various solutions are shown in Table IIb. Appreciable concentrations of both ion pairs and homoconjugate ion pairs were found in all cases.

With the iterative technique described earlier, values of $[HA]_M$ were calculated, using an approximate value of K_2. Plots of $\Sigma[BH^+]/[B][HA]_M$ against $[HA]_M$ gave a straight line whose slope was K_1K_2 and whose intercept was K_1. The best fit was obtained with least squares. The new value of K_2 was then used to calculate a new value of $[HA]_M$, and the data were again plotted. When the least-squares analysis produced no further change in the values of the two constants, it was assumed that the final values had been obtained. In these calculations, the data drawn from 2×10^{-3} M solutions of TMPD were omitted, since the concentration of monomeric DCA represented a small difference between two much larger numbers. The final values of K_1 and K_2 are 1.6×10^4 and 3×10^3 l. mol^{-1}, respectively.

(c) MCA. Solutions with stoichiometric MCA concentrations between 4×10^{-4} and 10^{-2} M and with TMPD concentrations between 1.6×10^{-4} and 2×10^{-3} M were examined. This system was the most complex of the three. It was necessary to assume the existence of ion pairs, homoconjugate ion pairs, and homoconjugate ion pairs with two acid molecules, i.e., BH^+-$(A(HA)_2)^-$. Such species are believed to exist in benzene.[14] The following equations apply, in addition to those developed earlier

$$K_3 = \frac{[BH^+(A \cdot 2HA)^-]}{[BH^-(AHA)^-][HA]_M} \quad (10)$$

$$\frac{\Sigma[BH^+]}{[B]} =$$

$$K_1[HA]_M + K_1K_2[HA]_M{}^2 + K_1K_2K_3[HA]_M{}^3 \quad (11)$$

$$\frac{\Sigma[BH^-]}{[B][HA]_M} = K_1 + K_1K_2[HA]_M + K_1K_2K_3[HA]_M{}^2 \quad (12)$$

$$[HA] = [HA]_0 -$$

$$\frac{\Sigma[BH^+](1 + 2K_2[HA]_M + 3K_2K_3[HA]_M{}^2)}{(1 + K_2[HA]_M + K_2K_3[HA]_M{}^2)} \quad (13)$$

The most meaningful data were obtained from solutions with initial TMPD concentrations equal to 4×10^{-4} M, since the spectrophotometric measurements were accurate, and at the same time the ratio $\Sigma[BH^+]/[B]$ was not lowered too much by extensive homoconjugate ion-pair formation. The constant obtained from these solutions was then used at other concentrations in order to calculate $[HA]_M$ and K_3. The intercept and the first and second regression coefficients were obtained by least squares from the data given by eq 13. For this purpose, a package IBM computer program (STATPK) was used.[13] A satisfactory fit was obtained for the second-degree polynomial equation. The data and the calculated concentrations of different species are shown in Table IIc. Figure 3 shows the results of these cal-

(14) S. Bruckenstein and A. Saito, *J. Amer. Chem. Soc.*, **87**, 698 (1965).

culations giving the data points and the fitted curve. The best values were: $K_1 = 4.9 \times 10^2$, $K_2 = 3.9 \times 10^2$, and $K_3 = 35$ l. mol^{-1}.

IV. Reactions of TMPD with Other Acids. The reactions in benzene of TMPD with 2,5-DNBA, 3,5-DNBA, ONBA, PNBA, and HPi were also examined. This was a more limited investigation because of the relatively low solubilities of some of the acids, spectrophotometric interference from them or their anions, and a lack of precise information about their acid dimerization constants.

The molar absorptivity of TMPD in benzene was determined at 350 nm. Between 10^{-4} and 5×10^{-4} M, it was 1.82×10^3 l. mol^{-1} cm^{-1}. Although this point is on a steeply rising part of the spectrum, it was possible to locate it by very slow scanning. The cation TMPDH$^+$ shows no absorption at this wavelength. The spectra of the various nitrated benzoic acids were measured to get the acid correction at 350 nm, and excess diethylamine (DEA) was added to get the absorptivity of the anionic form. It was felt that since in general there is only a small difference in spectrum between an acid and its anion, any difference in anion spectra between DEA and TMPD solutions would also be small. This was not true of picric acid; there was interference at 350 nm. Accordingly, the absorptivity of TMPDH$^+$Pi$^-$ was determined at 410 nm in excess TMPD, as was that of picric acid itself, and the equilibrium constant was calculated from absorbances measured at that wavelength. The molar absorptivity of TMPDH$^+$Pi$^-$ at 410 nm was 7.21×10^3 l. mol^{-1} cm^{-1}, and that of picric acid was 50 l. mol^{-1} cm^{-1}. Table III gives the molar absorptivities of the nitrated benzoic

Table III. Molar Absorptivities of Nitrated Acids and Their Anions in Benzene

Acid	$[HA]_0$, $M \times 10^4$	$[DEA]_0$, $M \times 10^4$	A_{350}	a_M (HA)	a_M (A$^-$)
2,5-DNBA	8.0		0.404	505	
	8.0	300	0.482		602
	8.0	600	0.490		612
3,5-DNBA	40.0		0.660	165	
	40.0		0.665	166	
	37.5	94	0.707		189
ONBA	20.0		0.476	238	
	20.0	300	0.608		304
PNBA	16.0		0.263	164	
	16.0	300	0.359		224

acids and their diethylammonium salts. All measurements were made in 1-cm cells.

The following equation, which is readily derived, was used for the determination of the TMPD concentration in the presence of the different nitrated benzoic acids

$$[TMPD] = $$

$$\frac{A_{350} - a_{HA}[HA]_0 - (a_{A^-} - a_{HA})[TMPD]_0}{1820 + a_{HA} - a_{A^-}} \quad (14)$$

In this equation, A_{350} is the measured absorbance at 350 nm, a_{HA} and a_{A^-} are the molar absorptivities of an acid and of all forms of its anion, 1820 is the molar absorptivity of TMPD, and the other symbols have their customary meaning. For the picrate solutions, use
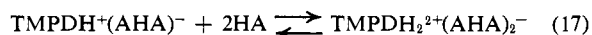
was made of

$$[TMPDH^+Pi^-] = \frac{A_{410} + 50[HPi]_0}{7160} \quad (15)$$

The acid–base constants were calculated on the following basis.

$$K = \frac{\Sigma[BH^+]}{[B]([HA]_0 - \Sigma[BH^+])} \quad (16)$$

The results are shown in Table IV. The data for picric acid are not included. The constant calculated from the ratio $[BH^+Pi^-]/[B][HPi]$ had these values: 1.20×10^5, 1.55×10^5, 1.23×10^5, and 1.34×10^5, for solutions with a fixed initial concentration of TMPD (1.60×10^{-5} M) and varying HPi initial concentrations (1.60×10^{-5}–3.20×10^{-5} M).

V. Addition of a Second Proton to TMPD. This reaction was studied only in solutions of the three chloroacetic acids because of solubility limitations encountered with the other acids or their salts. The concentration of the diprotonated cation, TMPDH$_2^{2+}$, was calculated from the decrease in the absorbance of the monoprotonated cation, TMPDH$^+$. It was assumed that a given type of ion pair would form a species similar to itself on further protonation; $e.g.$

$$TMPDH^+(AHA)^- + 2HA \rightleftharpoons TMPDH_2^{2+}(AHA)_2^- \quad (17)$$

with an equilibrium constant, K_4

$$K_4 = \frac{[TMPDH_2^{2+}(AHA)_2^-]}{[TMPDH^+(AHA)^-][HA]^2} \quad (18)$$

If the monoprotonated species was TMPDH$^+$-(A·2HA)$^-$, further protonation was assumed to yield TMPDH$_2^{2+}$(A·2HA)$_2^-$. In addition, it was assumed that only these two diprotonated species existed, with no mixed particles of the type TMPDH$_2^{2+}$(AHA)$^-$·(A·2HA)$^-$. The constant for the formation of PDH$^+$(A·2HA)$^-$ is K_3 (see eq 10).

$$K_3 = \frac{[TMPDH^+(A·2HA)^-]}{[TMPDH^+(AHA)^-][HA]} \quad (19)$$

The constant for the analogous reaction with TMPDH$_2^{2+}$ is K_5.

$$K_5 = \frac{[TMPDH_2^{2+}(A·2HA)_2^-]}{[TMPDH_2^{2+}(AHA)_2^-][HA]^2} \quad (20)$$

The overall ratio of diprotonated species to monoprotonated species is called R.

$$R = \frac{K_4[HA]^2 + K_4K_5[HA]^4}{1 + K_3[HA]} \quad (21)$$

(a) TCA. Solutions with two stoichiometric concentrations of TMPD, 5×10^{-4} and 2×10^{-3} M, were prepared with different initial concentrations of excess TCA. The data are shown in Table Va.

Analysis of the TCA data showed that homoconjugate ion pairs were formed. The assumption was made that the only monoprotonated species present was BH$^+$(AHA)$^-$ and that the only diprotonated species was BH$_2^{2+}$(AHA)$_2^-$. It followed that

$$[HA]_T = [HA]_0 - 2\Sigma[BH^+] - 4\Sigma[BH_2^{2+}] \quad (22)$$

Equation 9 was then used to calculate $[HA]_M$, the con-

Table IV. Spectrophotometric Data and Equilibrium Constants for Nitrated Benzoic Acids and TMPD in Benzene at 25°

$[\text{TMPD}]_0$, $M \times 10^5$	$[\text{HA}]_0$, $M \times 10^5$	A_{350}	$[\Sigma\text{BH}^+]$, $M \times 10^5$	$[\text{HA}]_0 - [\Sigma\text{BH}^+]$, $M \times 10^5$	$\dfrac{[\Sigma\text{BH}^+]}{[\text{B}]([\text{HA}]_0 - [\Sigma\text{BH}^+])}$
(a) 2,5-DNBA					
9.76	4.76	0.150	4.40	0.36	15.4×10^3
9.52	19.0	0.159	6.40	12.6	15.2×10^3
9.30	27.9	0.189	7.10	20.8	15.4×10^3
19.4	19.0	0.270	10.4	8.60	13.5×10^3
19.0	27.9	0.269	12.7	15.2	13.2×10^3
18.5	36.4	0.284	13.8	22.6	12.8×10^3
18.1	44.4	0.305	14.5	29.9	13.4×10^3
36.9	36.3	0.473	22.2	14.1	10.7×10^3
33.9	66.7	0.480	27.6	39.1	11.2×10^3
(b) 3,5-DNBA					
9.75	9.75	0.154	2.20	7.50	4×10^3
9.52	19.0	0.137	3.80	15.2	4.4×10^3
9.09	36.4	0.133	5.20	31.2	4.2×10^3
8.33	66.6	0.154	6.10	60.5	4.5×10^3
38.1	19.0	0.539	10.5	8.50	4.5×10^3
36.4	36.4	0.437	16.0	20.4	3.8×10^3
34.8	52.2	0.374	19.4	32.8	3.8×10^3
33.3	66.7	0.334	21.4	45.3	4.0×10^3
30.8	92.2	0.296	23.3	68.9	4.5×10^3
28.6	114.0	0.298	23.0	91.2	4.5×10^3
26.6	133.0	0.308	22.3	111.0	4.6×10^3
(c) ONBA					
39.4	19.6	0.651	6.4	13.2	1.5×10^3
38.6	38.4	0.596	11.2	27.2	1.5×10^3
37.7	64.1	0.554	16.2	47.9	1.6×10^3
36.5	91.0	0.531	19.9	71.1	1.7×10^3
34.4	143.0	0.542	24.2	119.0	2.0×10^3
(d) PNBA					
50.0	80.0	0.885	8.4	71.6	2.82×10^2
50.0	160.0	0.910	14.5	146.0	2.81×10^2

Table V. Spectrophotometric Data on TMPD Diprotonation by Chlorinated Acids in Benzene at 25°

$[\text{TMPD}]_0$, $M \times 10^4$	$[\text{HA}]_0$, $M \times 10^3$	A_{310}	$[\text{BH}^+]$, $M \times 10^4$	$[\text{BH}_2^{2+}]$, $M \times 10^5$	$[\text{HA}]_M$, $M \times 10^3$
(a) TCA					
4.71	2.38	1.116^a	4.65	0.6	1.40
4.50	4.55	0.988	4.11	3.9	3.42
4.30	6.52	0.854	3.56	7.4	5.17
4.12	8.33	0.735	3.06	10.6	6.72
3.96	10.0	0.630	2.62	13.4	8.10
3.67	13.0	0.483	2.01	16.6	10.5
3.41	15.5	0.383	1.60	18.1	12.5
3.89	17.7	0.311	1.30	18.9	14.1
2.91	20.6	0.247	1.03	18.8	16.3
4.83	1.22	1.176^b	4.89		0.34
18.8	2.38	0.451	18.8		0.06
18.0	4.55	0.426	17.8	1.0	0.89
17.2	6.51	0.386	16.1	11.0	2.75
16.5	8.34	0.346	14.4	20.0	4.40
15.2	11.5	0.265	11.0	42.0	7.00
14.1	14.3	0.208	8.70	54.0	9.29
13.2	16.7	0.166	6.90	63.0	11.2
12.4	18.7	0.131	5.45	69.0	12.7
11.6	20.6	0.109	4.54	71.0	14.3
(b) DCA					
3.88	20.5	0.867^b	3.61	2.7	11.9
3.88	10.3	0.914	3.80	0.8	6.85
3.88	50.0	0.690	2.87	10.1	22.3
3.88	100.0	0.444	1.85	20.3	34.5
3.88	150.0	0.307	1.28	26.0	44.0
3.88	200.0	0.209	0.87	30.1	52.1
7.75	300.0	0.252	1.05	67.0	65.4
7.75	400.0	0.145	0.60	71.5	76.9
7.81	150.5	0.622	2.59	52.2	43.8
7.75	251.0	0.310	1.29	64.6	59.1
(c) MCA					
2.56	60.0	0.589^a	2.46	1.0	20.3
2.56	100.0	0.582	2.42	1.4	27.4
2.56	150.0	0.577	2.40	1.6	34.6
2.56	200.0	0.571	2.38	1.8	40.6

[a] Values measured in 1-cm cells. [b] Values measured in 0.1-cm cells.

Table VI. Formation Constants of TMPDH$^+$ by Various Acids in Benzene at 25°, and Correlating Equations for Diprotonation

Acid	K_a, H$_2$O^a	BH$^+$A$^-$ (K_1), l. mol^{-1}	BH$^+$(AHA)$^-$ (K_2), l. mol^{-1}	BH$^+$(A·2HA)$^-$ (K_3), l. mol^{-1}
TCA	2.2×10^{-1}	$4.15 \times 10^5 \pm 0.10$	1.5×10^3	
HPi	1.96×10^{-1}	$1.33 \times 10^5 \pm 0.14$		
DCA	5×10^{-2}	$1.6 \times 10^4 \pm 0.08$	$3 \times 10^3 \pm 0.3$	
2,5-DNBA	2.39×10^{-3}	$1.3 \times 10^4 \pm 0.16$		
3,5-DNBA	1.50×10^{-3}	$4.3 \times 10^3 \pm 0.1$		
ONBA	6.1×10^{-3}	$1.47 \times 10^3 \pm 0.17$		
MCA	1.4×10^{-3}	$4.9 \times 10^2 \pm 0.2$	$3.9 \times 10^2 \pm 0.7$	35 ± 18
PNBA	3.6×10^{-4}	2.8×10^2		

Correlating Equations for Addition of Second Proton to TMPD

TCA	$R = \dfrac{[BH_2{}^{2+}]}{[BH^+]} = 7.5 \times 10^3[HA]_M{}^2$
DCA	$\log R = 3.96 + 2.64 \log [HA]_M$
MCA	$R = 2.1[HA]_M$

^{a} G. Kortum, W. Vogel, and K. Andrussow, Ed., "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961.

centration of free monomeric acid, from [HA]$_T$. The ratio R of $\Sigma[BH_2{}^{2+}]$ to $\Sigma[BH^+]$ was plotted against [HA]$_M{}^2$. The plot is shown in Figure 4. It can be seen that this is a straight line passing through the origin. The slope of the curve is K_4. A least-squares calculation yielded the value 7.5×10^3 l.^{2} mol^{-2}.

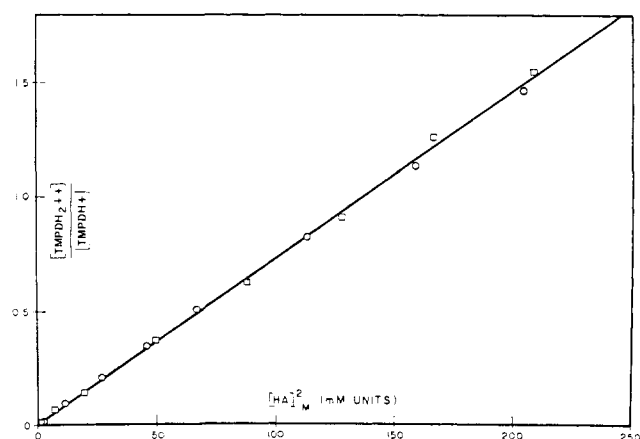formed. This relationship is

$$\log R = 3.96 + 2.64 \log [HA]_M \qquad (24)$$

In the figure, $\log R$ was plotted against [HA]$_M$, the latter expressed in millimoles per liter for convenience.
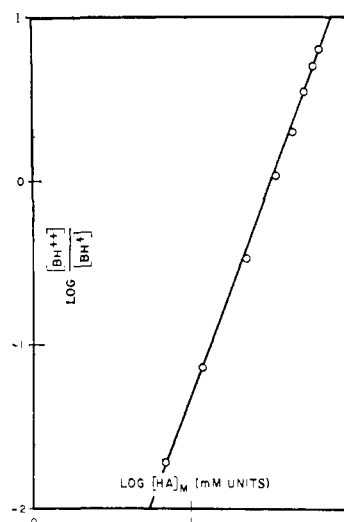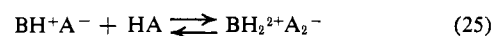

Figure 4. Formation of TMPDH$_2{}^{2+}$ by TCA. Plot of the ratio [TMPDH$_2{}^{2+}$]/[TMPDH+] against [HA]^2_M in mmol/l. Data points are in Table Va: O, 5×10^{-4} M[TMPD]; □, 2×10^{-3} M[TMPD].

Figure 5. Plot of log [BH$_2{}^{2+}$]/[BH$^+$] against log [DCA]$_M$, the latter in mmol/l. Data points are in Table Vb.

(b) DCA. The data are shown in Table Vb. A plot of R against [HA]$_M{}^2$ was not linear, showing that this acid undergoes more complex protonation reactions than TCA. The reaction for the diprotonation of the base can be written in the following generalized way

$$BH^+(A \cdot nHA)^- + (1 + n)HA \rightleftharpoons BH_2{}^{2+}(A \cdot nHA)_2{}^- \qquad (23)$$

in which n represents the number of acid molecules which are hydrogen bonded to the anion. Figure 5 shows a plot of log K vs. log [HA]$_M$. The slope gives $(1 + n)$, the number of HA molecules required by the stoichiometry of eq 23. This value was 2.64, meaning that on the average 1.64 molecules of DCA were hydrogen bonded to the dichloroacetate anion over the stoichiometric acid range 2.05×10^{-2}–2.51×10^{-1} M.

An empirical relationship between R and [HA]$_M$ was found from Figure 5, yielding the region of acid concentration in which the diprotonated species was

(c) MCA. In benzene, MCA is so weak (with respect to diprotonation) that the spectrum of TMPDH$^+$ showed virtually no change from 6×10^{-2} M acid to 2×10^{-1} M acid. The data are shown in Table Vc. Since the absorbance change was so small, an apparent formation constant was calculated from it without regard for homoconjugate ion-pair formation.

$$BH^+A^- + HA \rightleftharpoons BH_2{}^{2+}A_2{}^- \qquad (25)$$

$$K = \frac{[BH_2{}^{2+}A_2{}^-]}{[BH^+A^-][HA]_M} \qquad (26)$$

The average value of K was 2.1 l. mol^{-1} or $R = 2.1[HA]_M$.

Table VI gives a summary of all the results. The acids are listed in the decreasing order of effectiveness of monoprotonation of the base in benzene. With the ex-

ception of 3,5-DNBA, this is also the order of their acidity constants in water, although the relationship between the two series is far from linear. It would appear for most of the acids (including picric) that the order of molecular parameters which determine proton transfer are not very different from those influencing simple ion-pair formation. On the other hand, the formation of homoconjugate ion pairs is not linked in any obvious way to the ability of the acid to transfer its proton to a base. Hydrogen bonding is the main factor here. The same lack of relationship to acid strength is evident in the dimerization constants of the chloroacetic acids in benzene.[5] Finally, the order of diprotonation of TMPD follows acid strength in the same general fashion as monoprotonation by the chlorinated acetic acids.

Formation of Wurster's Blue in Benzene at 25°

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Abstract: Wurster's Blue is the ion radical produced by the oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine in acid solution. In benzene, equivalent quantities of the diamine and trichloroacetic acid with added tetrachloroquinone yield very little of the ion radical, but an excess of acid markedly increases the yield. The Blue was identified by its electron spin resonance spectrum. The effects of different acids on the yield of the Blue in the presence of tetrachloroquinone were evaluated from the solution absorbance at 570 nm. The stoichiometry of the redox reaction showed that one more molecule of acid was required for the stabilization of the ion radical than was needed for the formation of any particular species of the salt of the monoprotonated diamine which was undergoing the oxidation. Thus, the simple ion pair of the diamine and trichloroacetic acid formed the homoconjugate ion pair of Wurster's Blue. The order of effectiveness of different acids in this stabilization at 25° was trichloroacetic acid > dichloroacetic acid > 2,5-dinitrobenzoic acid > 3,5-dinitrobenzoic acid > picric acid > monochloroacetic acid > o-nitrobenzoic acid > p-nitrobenzoic acid. With the exception of picric acid, this is the order of decreasing acid dissociation constants in water, and of the ion-pair formation constants of the reaction in benzene between 1 mol of diamine and 1 mol of acid. It was concluded that the acid excess necessary for the oxidation was involved in hydrogen bonding with the anion component of the Wurster's Blue salt.

$\mathbf{W}$urster's Blue is the ion radical which is produced by the oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD). Michaelis and his coworkers showed by potentiometric titration that it was formed in water, and magnetic susceptibility measurements demonstrated that it was the most stable radical of the entire group which can be derived from phenylenediamine.[2,3]

According to Michaelis, the maximum yield of the radical in water is found at pH 4.62.[2] The reduced form (TMPD) is a diacid base. The acidity constants of the acid forms are: $pK_1 = 2.20$ (for dissociation of $TMPDH_2^{2+}$) and $pK_2 = 6.35$ (for $TMPDH^+$).[4] It follows that the fraction present as $TMPDH^+$ is at its maximum value at pH 4.28. This means that the most suitable description of the oxidation of the base to Wurster's Blue is shown in eq 1.

In solvents other than water and the lower alcohols, the reaction takes on a different character. Isenberg and Baird concluded from esr measurements that the reaction of TMPD with tetrachloroquinone (C) to produce the ion radical would take place only in polar solvents.[5] They argued that the intermediate complex,

$$\text{(1)}$$
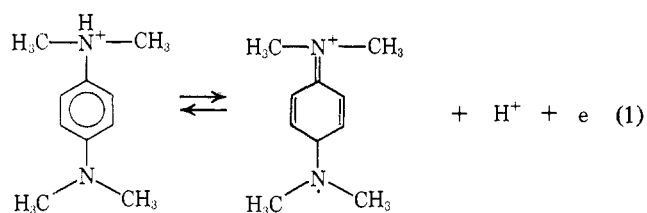
TMPD·C, could not dissociate to the two ion radicals TMPD·+ and C·⁻ in nonpolar media. This intermediate complex has been described.[6] It is a charge-transfer type.[7,8] To our knowledge, there is no published work describing the redox reaction of an oxidant like chloranil with the monoprotonated cation $TMPDH^+$ in nonpolar solvents. In one study in such a medium, it was reported that added acid caused dissociation of the charge-transfer complex, presumably by the formation of a salt of the aromatic amine.[9]

The present research is based on the observation that mixing equivalent quantities of trichloroacetic acid (TCA) and TMPD results in the formation of very little Wurster's Blue in benzene, but with the addition of excess acid the Blue is produced in good yield. The purpose of this paper is the elucidation of the equilibria of this reaction with different acids and the examination

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