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.

Wurster'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 that 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,

$$+ \; H^+ \; + \; e \qquad (1)$$
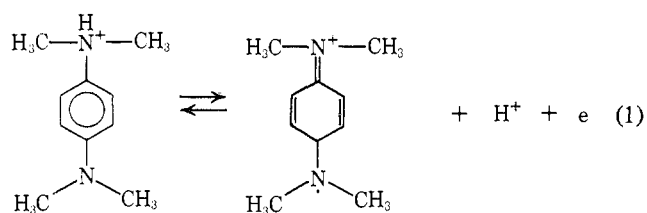
TMPD·C, could not dissociate to the two ion radicals TMPD·$^+$ and C·$^-$ in nonpolar media. This intermediate complex has been described.[6] It is a charge-transfer type.[7,8] To our knowledge, there is no published work describing the redox reaction of an oxidant like chloranil with the monoprotonated 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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(3) L. Michaelis and S. Granick, *ibid.*, 65, 1747 (1943).
(4) H. V. Willi, *Helv. Chim. Acta*, 40, 2019 (1957).

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(6) R. Foster, *Tetrahedron*, 10, 96 (1960).
(7) R. S. Mulliken, *J. Amer. Chem. Soc.*, 72, 600 (1950).
(8) R. S. Mulliken, *J. Phys. Chem.*, 56, 514 (1952).
(9) P. H. Gore and B. B. Wheals, *Anal. Chim. Acta*, 30, 34 (1964).

of the effect of acidity on an oxidation–reduction reaction in benzene.

Experimental Section

Reagents. Chloranil was an Eastman product, recrystallized from benzene and dried *in vacuo*. Tetrachlorohydroquinone (H$_2$C), an Eastman reagent, was recrystallized from benzene and sublimed *in vacuo*. *p*-Benzoquinone, Eastman, was treated similarly. Hydroquinone, a Fisher product, was recrystallized twice from ethanol and dried *in vacuo*. 2,5-Di-*tert*-amylhydroquinone was an Eastman inhibitor which was recrystallized twice from benzene and dried *in vacuo*. The corresponding quinone was prepared from the purified hydroquinone by oxidation with CrO$_3$ in glacial acetic acid and precipitation with water. The crystals were washed with water, recrystallized from benzene, and dried *in vacuo*.

All other reagents were described in the preceding article or were of the highest obtainable purity.

The following symbols are used for the various acids: TCA for trichloroacetic acid, DCA for dichloroacetic acid, MCA for monochloroacetic acid, 3,5-DNBA for 3,5-dinitrobenzoic acid, 2,5-DNBA for 2,5-dinitrobenzoic acid, *o*-NBA for *o*-nitrobenzoic acid, *p*-NBA for *p*-nitrobenzoic acid, and HPi for picric acid.

Apparatus and Procedures. Spectrophotometry. A Cary Model 14 spectrophotometer equipped with a thermostated cell holder was used. The special reaction–absorption cell described in the preceding article served for most measurements. One of the reactants was placed in the side arm. The other reagents were added to the cell itself. The spectrophotometer balance was set to read zero at 570 nm, the tube was inverted, and the components were mixed. The growth and decay of the absorbance at 570 nm was recorded as a function of time. Usually the maximum absorbance was reached within 2 min after mixing, followed by a decrease at the rate of 0.1–2%/min. The absorbance value used in the equilibrium calculations was obtained by extrapolating the measured values back to the time of mixing.

Stock solutions were prepared by the procedures described in the preceding article. Acids were analyzed by titration in ethanol with standardized NaOH. Concentrations of TMPD, C, and H$_2$C were checked by uv absorption.

Electron Spin Resonance Spectroscopy. A special cell was constructed for measurements in a Varian esr spectrometer. It consisted of a quartz esr tube (about 3.5 in. long) which was attached to a Pyrex pipet body (about 3 in. long, $^3/_4$ in. in diameter) by a graded seal. A Teflon stopcock with a 2-mm bore at the top of the pipet body permitted the introduction of reagents into the quartz tube. TMPD, acid, and benzene were added to the cell and dissolved oxygen was removed by bubbling purified nitrogen through a long hypodermic needle inserted through the stopcock bore. Immediately before placing the cell in the microwave cavity, chloranil in benzene was added with a syringe and the solution was mixed. Several spectra were recorded over a 30-min period.

Results and Discussion

A. Qualitative Observations. A test tube study was made of the oxidation of TMPD in benzene in the presence of various oxidants, acids, and other reagents. TCA and benzoquinone produced a blue color, MCA and benzoquinone produced a less intense blue, and acetic acid with benzoquinone produced practically no color change. TCA and chloranil produced a very intense blue color—much more intense than with benzoquinone. The addition of bases, proton acceptors, and salts capable of hydrogen bonding—*n*-propylamine, ethyl acetate, tetra-*n*-butylammonium bromide, and iodide, respectively—resulted in the disappearance of the blue color.

The oxidation reaction was found to be reversible, at least qualitatively. The addition of 2,5-di-*tert*-amylquinone to TMPD and TCA in benzene produced a faint blue color. The addition of *p*-benzoquinone to TMPD and TCA gave a stronger color, which was bleached by the addition of 2,5-di-*tert*-amylhydroquinone in excess, but was in turn restored by adding
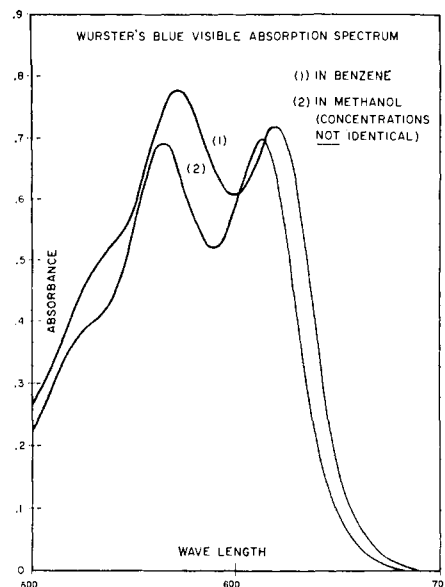

Figure 1. Spectra of Wurster's Blue in methanol and in benzene. Absorbance plotted against wavelength in nanometers.

more benzoquinone. The effect of successive additions of TCA and diethylamine to TMPD and chloranil was reversible.

B. Identification of Wurster's Blue by Electron Spin Resonance. An esr spectrum was obtained of a benzene solution containing TMPD, TCA, and chloranil. The characteristic pattern of Wurster's Blue which was described by Weissman[10] was observed. This spectrum has 13 triplets with 7.4 Oe between triplet centers, and 2.1 Oe between adjacent members of a triplet. Both the signal and color diminished markedly over a 30-min interval. This is a faster decrease than that observed in most of the spectrophotometric measurements, and may be due to different sample-handling techniques.

The results of the qualitative experiments suggest that it is possible to oxidize TMPD to Wurster's Blue in benzene, and that the yield is probably dependent upon the strength of the acid and the redox potential of the quinone. The order of redox potentials appears to be chloranil > *p*-benzoquinone > 2,5-di-*tert*-amylquinone, which is the same order obtained by Kvalnes.[11] Chloranil was used as the oxidant in the quantitative experiments which are described below.

C. Molar Absorptivity of Wurster's Blue in Benzene. Figure 1 shows the visible absorption spectrum of Wurster's Blue in methanol (containing perchloric acid) and in benzene (containing TCA and C). The concentrations of TMPD in the two solutions are not the same. The spectrum in methanol is almost identical with those obtained by Michaelis, Schubert, and Granick[2] and by Albrecht and Simpson[12] for the perchlorate in water. In the latter paper, the molar absorptivity at 565 nm is given as 12,470 l. mol^{-1} cm^{-1}. In benzene, this peak is shifted to 570 nm, and it becomes more prominent than the second peak. It is thus not possible to apply the absorptivity in methanol to benzene solutions of the Blue.

(10) S. I. Weissman, *J. Chem. Phys.*, **22**, 1135 (1954).
(11) W. H. Hunter and D. E. Kvalnes, *J. Amer. Chem. Soc.*, **54**, 2869 (1932); D. E. Kvalnes, *ibid.*, **56**, 667, 670, 2478, 2487 (1934).
(12) A. C. Albrecht and W. T. Simpson, *ibid.*, **77**, 4454 (1955).

There is a second difficulty. The radical ion is not completely stable in methanol because of the irreversible decomposition of the diimine with which it is in equilibrium.[2] Sufficient stability for measurements can be obtained by forming the Blue in the presence of a large excess of TMPD in relation to chloranil, diminishing the diimine concentration. The reaction between TMPD and C in methanol is known to be virtually complete in the presence of acid. Hence, if the quantity of added chloranil is accurately known, the yield of Blue can be accurately calculated, and the absorptivity can be determined. This technique was tried in a series of methanol–benzene mixtures, in the hope that extrapolation to pure benzene would give the molar absorptivity of the Blue in that solvent. The results are shown in Table I.

Table I. Molar Absorptivity of Wurster's Blue in Methanol–Benzene Mixtures

Mole fraction of benzene	λ_{max}, nm	a_M, (l. mol^{-1} cm^{-1}) $\times 10^{-3}$
0.0	565	13.1
0.312	568.5	12.8
0.515	569	12.7
0.646	570	12.4
0.803	570	10.0

The apparent absorptivity falls rapidly beyond 65 mol% benzene. As a consequence, extrapolation of the appropriate curve to pure benzene would be accompanied by considerable uncertainty. In addition, it is more than likely, in the light of experiments described later, that the low absorptivity in 80 mol% benzene is due at least in part to an incomplete redox reaction.

The absorptivity in benzene was determined by an indirect method. It was assumed that at any fixed acid concentration the following equilibrium existed

$$TMPDH^+ + {}^1\!/_2 C \rightleftarrows TMPD\cdot^+ + {}^1\!/_2 H_2 C \quad (2)$$

In this equation $TMPDH^+$ is the conjugate acid of TMPD, and $TMPD\cdot^+$ is the ion radical. No distinction is made at this point among the various ion-pair types which may coexist for either $TMPDH^+$ or $TMPD\cdot^+$. The equilibrium constant, Q, is given by

$$Q = \frac{[TMPD\cdot^+][H_2C]^{1/2}}{[TMPDH^+][C]^{1/2}} \quad (3)$$

If only TCA, TMPD, and C are initially present, the concentrations of the various species at equilibrium for a fixed acid concentration, f, are

$$[TMPDH^+] = f([TMPD]_0 - [TMPD\cdot^+A^-]) \quad (4)$$

$$[H_2C] = {}^1\!/_2[TMPD\cdot^+] \quad (5)$$

$$[C] = [C]_0 - {}^1\!/_2[TMPD\cdot^+] \quad (6)$$

In these equations the zero subscript refers to the initial concentration of the particular species.

$$[TMPD\cdot^+] = \frac{A_{570}}{a_M^{570}b} \quad (7)$$

Here b is the path length in centimeters, A_{570} is the measured absorbance at 570 nm, and a_M^{570} is the molar absorptivity of the Blue at that wavelength. Equation

3 is now expressed in the following form

$$Q/f =$$

$$\frac{(1/\sqrt{2})(A_{570}/(a_M^{570}b)^{1/2}}{([TMPD]_0 - A_{570}/a_M^{570}b)([C_0] - [1/2][A_{570}/a_M^{570}b])^{1/2}} \quad (8)$$

When H_2C is also added in large excess (compared to its yield in the reaction), eq 8 can be expressed in another way

$$Q/f =$$

$$\frac{[H_2C_0]^{1/2}(A_{570}/a_M^{570}b)}{([TMPD]_0 - (A_{570}/a_M^{570}b)([C]_0 - [1/2][A_{570}/a_M^{570}b])^{1/2}} \quad (9)$$

All quantities in eq 8 and 9 are known except for Q/f and a_M^{570}. It is therefore possible to eliminate Q/f between the two equations, and solve for a_M^{570} using data obtained from one solution to which no H_2C was added, and from another solution otherwise identical in initial composition with the first, to which H_2C was added. In practice, the solution was obtained by substituting different values for a_M^{570} into both equations until a value of the absorptivity was reached which produced no bias in Q/f.

In eq 9, the actual concentration of H_2C was used

$$[H_2C] = [H_2C]_0 + {}^1\!/_2[TMPD\cdot^+A^-] \quad (10)$$

In all cases, the amount of H_2C formed in the reaction was less than one-tenth that of the amount originally present.

Two examples of calculations of Q from assumed values of a_M^{570} are shown in Table II.

The value chosen for the molar absorptivity at 570 nm of Wurster's Blue in benzene at 25° was 10.8×10^3 l. mol^{-1} cm^{-1}. It was assumed that this applied to all solutions of the Blue regardless of the acid which was present. In one indirect test of this assumption, plots of log absorbance against wavelength of the Blue in TCA and in 3,5-DNBA solution were made. These showed no displacement of the maxima at 570 and at 620 nm in 3,5-DNBA solution and an almost constant difference between the two curves in the region 630–560 nm. This shows that the band shapes were not very different in the two acid solutions. It does not show that the molar absorptivities are the same. In view of the instability of the Blue in benzene solution, the chosen value for a_M^{570} must remain an assumed one.

D. Effects of Different Acids on the Redox Equilibrium in Benzene. 1. General. The reaction between TMPD and chloranil in water or methanol goes by way of the monoprotonated conjugate acid of the diamine. In benzene, the corresponding reaction undoubtedly involves ion pairs. When equivalent amounts of TCA and TMPD are mixed with chloranil in benzene, very little Wurster's Blue is formed, even though practically all the diamine is in the monoprotonated form. The addition of excess acid increases the yield of the Blue, and the stoichiometry suggests that the following reaction can be written.

$$TMPDH^+A^- + {}^1\!/_2 C + HA \rightleftarrows$$

$$TMPD\cdot^+(AHA)^- + {}^1\!/_2 H_2C \quad (11)$$
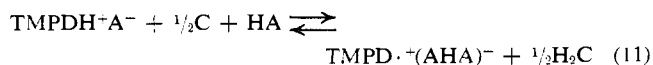
There was a linear variation of yield with free (mono-

Table II. Values of Q Corresponding to Assumed Values of $a_M{}^{570}$ for Wurster's Blue in Benzene

Run no.	Acid, mM	Q, eq 8, l. mmol^{-1}	Run no.	Q, eq 9, l. mmol^{-1}	$Q_9 - Q_8$, l. mmol^{-1}	% bias
		Assumed Value of $a_M = 12.5 \times 10^3$ l. mol^{-1} cm^{-1}				
1	TCA, 10	0.0341	6	0.0344	+0.0003	+0.9
2	TCA, 4	0.00611	7	0.00713	+0.00102	+15.5
3	TCA, 6	0.0290	8	0.0320	+0.003	+9.8
4	TCA, 6	0.0298	9	0.0328	+0.003	+9.6
5	DCA, 4	0.00819	10	0.00886	+0.00067	+7.9
					Total bias	+43.7
		Assumed Value of $a_M = 10.8 \times 10^3$ l. mol^{-1} cm^{-1}				
1	TCA, 10	0.0419	6	0.0410	−0.0009	−2.2
2	TCA, 4	0.00815	7	0.00832	+0.00017	+2.1
3	TCA, 6	0.0383	8	0.0377	−0.0006	−1.6
4	TCA, 6	0.0381	9	0.0384	+0.0003	+0.8
5	DCA, 4	0.0102	10	0.0103	+0.0001	+1.0
					Total bias	+0.1

meric) acid concentration, even when the acid concentration was so high that homoconjugate ion pairs were formed

$$TMPDH^+(AHA)^- + {}^1\!/_2C + HA \rightleftarrows$$
$$TMPD \cdot {}^+(A \cdot 2HA)^- + {}^1\!/_2H_2C \quad (12)$$
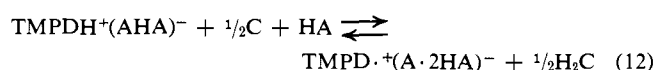
A general equation which describes this behavior is

$$TMPDH^+(A \cdot nHA)^- + {}^1\!/_2C + HA \rightleftarrows$$
$$TMPD^+(A \cdot (n + 1)HA)^- + {}^1\!/_2H_2C \quad (13)$$
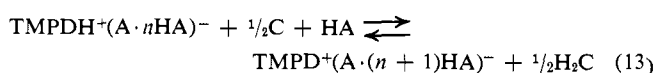
The equilibrium constant for this reaction is K_{ox}

$$K_{ox} = \frac{[TMPD \cdot {}^+(A \cdot (n + 1)HA)^-][H_2C]^{1/2}}{[TMPDH^+(A \cdot nHA)^-][C]^{1/2}[HA]} \quad (14)$$

This constant was evaluated for the acids described in the preceding article, at various levels of acid, diamine, and oxidant concentration. In general, after suitable corrections had been made for consumption of acid by dimerization, homoconjugate ion-pair formation and diprotonation of TMPD, the stoichiometry of eq 13 was observed.

The calculations required the use of the formal equilibrium constant Q', redefined as follows

$$Q' = \frac{[TMPD \cdot {}^+][H_2C]^{1/2}}{[TMPD]_T[C]^{1/2}} \quad (15)$$

The total base concentration, $[TMPD]_T$, is that of the initial base added, $[TMPD]_0$, minus the concentration oxidized to the Blue, $[TMPD \cdot {}^+]$. The other concentration quantities in eq 15 were obtained directly from the initial concentrations of H_2C and C, and the solution absorbance at zero time at 570 nm. The calculation of K_{ox}, in turn, requires a knowledge of [HA] and of $[TMPDH^+]$.

$$[TMPD]_T = [TMPD] + [TMPDH^+A^-] +$$
$$[TMPDH^+(AHA)^-] + [TMPDH_2{}^{2+}(AHA)_2{}^-] \quad (16)$$

The total acid consumed in forming these species is

$$[HA]_0 - [HA]_T = 0 + [TMPDH^+A^-] +$$
$$2[TMPDH^+(AHA)_2{}^-] + 4[TMPDH_2{}^{2+}(AHA)_2{}^-] \quad (17)$$

The first approximation for $[HA]_T$ is called ACIDI

$$ACIDI = [HA]_0 - [TMPD]_0 \quad (18)$$

This is then corrected for the acid consumed in homoconjugate ion formation, or for acid not consumed

because free TMPD remains in solution. The quantity of acid used in forming $TMPDH_2{}^{2+}$ was significant only in the case of TCA, and will be considered for this acid alone. For the other acids, $[HA]_T$ is then

$$[HA]_T = ACIDI + [TMPD] - [TMPDH^+(AHA)^-] \quad (19)$$

This is expressed in terms of the acid concentration as

$$[HA]_T = ACIDI - [TMPD]_T \times$$
$$\left[\frac{-1 + K_1K_2[HA]_M{}^2}{1 + K_1[HA]_M + K_1K_2[HA]_M{}^2}\right] \quad (20)$$

K_1 is the formation constant of the simple ion pair, $TMPDH^+A^-$. K_2 is the formation constant of the homoconjugate ion pair, $TMPDH^+(AHA)^-$. $[HA]_M$ is the concentration of the monomeric acid, that is, of the free acid corrected for dimerization. The initial estimate of the free acid concentration is ACIDI. The second is $[HA]_T$; when this is corrected for dimerization, it becomes $[HA]_M$, and successive approximations (usually three or less) yielded agreement between successive values of $[HA]_M$. The small correction for the additional molecule of acid necessary to form $TMPD \cdot {}^+$-$(A \cdot (n + 1)HA)^-$ is also made.

When $[HA]_M$ is known, $[TMPDH^+]$ can be calculated from $[TMPD]_T$ by

$$[TMPDH^+] = [TMPD]_T \times$$
$$\left[\frac{K_1[HA]_M + K_1K_2[HA]_M{}^2}{1 + K_1[HA]_M + K_1K_2[HA]_M{}^2}\right] \quad (21)$$

This equation does not take account of the monoprotonated amine which has been lost by conversion to $TMPDH_2{}^{2+}$. It is used for solutions in which the acidity is so low that the concentration of the diprotonated species is negligible. For the chlorinated acetic acids, for which correlating equations for the formation of $TMPDH_2{}^{2+}$ have been worked out, the correction takes the following form

$$[TMPDH^+] = q\frac{[TMPDH^+]}{[TMPDH^+] + [TMPDH_2{}^{2+}]} \quad (22)$$

in which q is the right-hand side of eq 21. A computer program was written in Fortran to assist in making these calculations.[13]

(13) Ph.D. thesis of W. Cronkright, 1968.

Table III. Redox Equilibrium Data in the Formation of Wurster's Blue

[TMPD]$_0$, $M \times 10^{-3}$	[HA]$_0$, $M \times 10^{-3}$	[C]$_0$, $M \times 10^{-3}$	[H$_2$C]$_0$, $M \times 10^{-3}$	A_{570}	Q'	[HA]$_M$, $M \times 10^{-3}$	K_{ox}, l. mol^{-1}
			(a) TCA				
1.82	12.73	0.076	0.546	0.354	0.0562	7.46	10.7
2.61	12.17	0.073	0.522	0.445	0.0516	5.78	11.2
0.769	11.54	0.807	0.769	0.435	0.0554	8.56	10.0
1.54	11.11	0.779	0.741	0.803	0.0520	6.80	10.3
2.14	10.71	0.750	0.714	1.041	0.0492	5.52	10.9
0.769	10.57	0.807	0.039	1.079	0.0510	7.85	9.5
0.392	10.78	0.824	0.039	0.607	0.0487	8.75	8.7
0.182	10.00	0.765	0.036	0.330	0.0530	8.55	9.6
0.0952	10.47	0.800	0.038	0.187	0.0540	9.11	9.6
0.953	2.86	0.800	0.762	0.138	0.0134	1.25	10.8
1.48	1.85	0.778	0.037	0.096	0.0014	0.14	10.4
1.82	2.73	0.764	0.727	0.070	0.0035	0.32	10.9
0.77	2.82	0.808	0.770	0.132	0.0159	1.47	11.1
0.77	1.92	0.807	0.038	0.051	0.0078	0.73	10.8
1.82	3.64	0.0764	0.545	0.057	0.0079	0.81	9.9
1.13	3.78	0.0793	0.566	0.080	0.0181	1.75	10.6
0.769	3.85	0.0808	0.577	0.072	0.0239	2.36	10.6
2.46	3.50	0.0737	0.526	0.030	0.0031	0.30	10.3
0.953	2.86	0.800	0.762	0.133	0.0129	1.25	10.4
0.770	2.88	0.807	0.769	0.129	0.0155	1.52	10.4
0.952	23.81	0.0762	0.762	0.144	0.0472	16.3	8.8
1.82	22.72	0.0727	0.727	0.303	0.0557	14.3	9.8
2.61	21.74	0.0696	0.696	0.455	0.0631	12.0	10.9
2.06	10.0	0.0990	0	0.974	0.0419	5.14	9.8
2.06	10.0	0.0990	0.20	0.516	0.0410	5.13	9.6
0.206	8.0	0.492	0	0.386	0.0408	6.88	8.0
0.206	8.0	0.492	1.00	0.078	0.0521	6.87	10.3
0.206	2.5	0.492	0	0.247	0.0193	2.07	9.7
2.06	4.0	0.099	0	0.382	0.0081	0.79	10.4
2.06	4.0	0.099	0.20	0.124	0.0083	0.80	10.5
			(b) DCA				
1.00	4.12	1.046	0	0.618	0.0102	2.03	5.0
1.00	2.06	1.046	0	0.234	0.0023	0.507	4.7
0.200	4.12	1.046	0	0.284	0.0171	3.18	5.4
0.200	2.06	1.046	0	0.176	0.0079	1.56	5.1
1.00	4.12	1.046	0.403	0.174	0.0103	2.03	5.1
1.00	2.06	1.046	0.403	0.044	0.0025	0.512	5.2
0.200	2.06	1.046	0.403	0.149	0.0087	1.56	5.6
0.200	4.12	1.046	0.403	0.298	0.0177	3.17	5.6
0.986	20.52	0.0524	0.156	0.330	0.0687	11.5	6.3
0.986	20.52	0.094	0.156	0.452	0.0689	11.5	6.4
0.986	10.26	0.094	0.156	0.260	0.0358	6.23	5.9
0.986	10.26	0.211	0.156	0.389	0.0360	6.23	5.9
0.986	5.13	0.211	0.156	0.178	0.0153	2.82	5.4
0.986	5.13	0.188	0.312	0.123	0.0154	2.82	5.5
0.986	30.78	0.0536	0.155	0.410	0.0897	15.6	6.6
0.419	5.46	0.236	0.154	0.115	0.0217	3.83	5.7
0.419	10.91	0.236	0.154	0.211	0.0416	7.25	5.9
0.488	5.13	0.222	0.145	0.119	0.0192	3.51	5.5
0.488	10.26	0.222	0.145	0.213	0.0359	6.80	5.4
0.488	30.78	0.0536	0.155	0.235	0.0919	16.0	6.6
			(c) MCA				
0.890	22.2	1.33	0.133	0.295	0.0106	10.5	1.07
0.800	40.0	1.20	0.120	0.448	0.0189	15.7	1.26
0.667	66.7	1.00	0.100	0.554	0.0299	21.8	1.45
0.200	80.0	1.00	0	0.439	0.0367	24.5	1.59
0.200	120.0	1.00	0	0.548	0.0548	31.0	1.88
0.200	40.0	1.00	0	0.298	0.0189	16.0	1.24
0.200	80.0	1.00	0	0.448	0.0381	24.5	1.65
0.204	80.0	1.00	0	0.445	0.0367	24.5	1.59
0.204	16.0	1.00	0	0.192	0.0090	8.7	1.12
0.204	8.0	1.00	0	0.117	0.0041	5.2	0.91
0.204	24.0	1.00	0	0.239	0.0129	11.5	1.18
0.204	16.0	1.00	0	0.186	0.0086	8.7	1.06
0.204	8.0	1.00	0	0.116	0.0041	5.2	0.90
			(d) 2,5-DNBA				
0.385	3.08	0.385	0.0385	0.176	0.0156	2.68	6.0
0.625	2.50	1.56	0	0.458	0.0085	1.83	4.9
0.384	0.769	0.961	0	0.089	0.0014	0.38	4.6
0.909	1.46	0.364	0.0364	0.050	0.0017	0.54	3.5
0.909	1.46	0.909	0	0.166	0.0016	0.53	3.4
0.909	2.91	0.909	0	0.490	0.0084	1.96	4.5
0.909	2.91	0.364	0.0364	0.228	0.0087	1.98	4.5

Table III (*Continued*)

[TMPD]₀, M × 10⁻³	[HA]₀, M × 10⁻³	[C]², M × 10⁻³	[H₂C]₀, M × 10⁻³	A_{570}	Q'	[HA]_M, M × 10⁻³	K_{ox}, l. mol⁻¹
			(e) 3,5-DNBA				
0.476	3.05	0.381	0.0381	0.091	0.0060	2.56	2.6
0.909	2.91	0.364	0.0364	0.106	0.0037	1.99	2.1
0.476	3.05	0.762	0	0.247	0.0062	2.55	2.7
0.196	3.14	0.784	0	0.156	0.0077	2.93	2.8
1.07	2.86	0.714	0	0.279	0.0034	1.76	2.2
0.385	1.54	0.769	0	0.104	0.0020	1.14	2.2
0.385	1.54	0.385	0.0385	0.033	0.0026	1.15	2.7
			(f) o-NBA				
0.769	7.69	0.645	0	0.249	0.0042	6.90	0.67
0.588	7.05	0.989	0	0.270	0.0050	6.44	0.87
2.00	6.00	0.840	0	0.270	0.0016	3.98	0.46
0.909	7.27	0.764	0	0.274	0.0037	6.33	0.66
0.909	7.27	0.363	0.0363	0.109	0.0038	6.35	0.67
1.37	3.45	0.725	0	0.139	0.0009	2.07	0.58
0.91	7.57	0.303	0.0303	0.120	0.0043	6.64	0.71
0.77	3.08	0.645	0	0.107	0.0011	2.30	0.65
			(g) p-NBA				
0.91	1.45	0.91	0	0.010	0.0001	0.54	0.3
0.222	1.78	0.445	0	0.006	0.0001	1.56	0.1
0.705	1.57	0.785	0	0.011	0.0001	0.86	0.2
			(h) HPi				
1.18	3.64	0.364	0	0.206	0.0027	2.45	1.1
1.00	5.00	0.200	0.020	0.107	0.0036	3.99	0.9

2. TCA. In order to carry out the calculations described in the preceding sections, it was necessary to have the value of K_2, the formation constant of the homoconjugate ion pair, TMPDH⁺(AHA)⁻. This could not be determined directly from acid–base reaction data, because the formation of simple ion pairs was virtually complete (see preceding article).

K_2 was evaluated from the decrease in Q' produced by increasing the initial TMPD concentration. The effect is evident in Figure 2, which shows values of Q' plotted against ACIDI—*i.e.*, [HA]₀ − [TMPD]₀—for two solutions which differed in the initial concentration of TMPD. The decrease in Q' in the solution with a higher TMPD concentration is due to the consumption of acid in the formation of homoconjugate ion pairs. A series of 13 solutions was prepared with [TMPD]₀ ranging from 4 × 10⁻⁵ to 2.5 × 10⁻³ M, and [HA]₀ less than 4 × 10⁻³ M. At this level of acid concentration, dimerization and diprotonation of TMPD can both be ignored. The biggest single effect in calculating K_{ox} from Q' is due to the correction for acid consumption in homoconjugate ion-pair formation. Different values of K_2 were assumed, and K_{ox} was calculated for each solution. The standard deviation in K_{ox} was obtained as a function of the assumed value of K_2. This standard deviation had its minimum value at $K_2 = 1.5 \times 10^3$ l. mol⁻¹. This was taken as the best value of K_2.

In calculating K_{ox} for solutions with relatively high TCA concentrations, a function was used to correct [TMPDH⁺] for the formation of TMPDH₂²⁺. The preceding article showed that where diprotonation by TCA took place, it was safe to conclude that the two principal forms of the protonated base were TMPDH⁺·(AHA)⁻ and TMPDH₂²⁺(AHA)₂⁻. The correcting function then is

$$\frac{[\text{TMPDH}^+]}{[\text{TMPDH}^+] + [\text{TMPDH}_2{}^{2+}]} = \frac{1}{1 + K_4[\text{HA}]_M{}^2} \quad (23)$$

in which K_4 is the equilibrium constant for the formation of TMPDH₂²⁺(AHA)₂⁻ from TMPDH⁺(AHA)⁻, and has the value 7.5 l.² mol⁻² at 25°. An equation was also used to correct for the acid consumed in the formation of TMPDH₂²⁺(AHA)₂⁻ and of TMPDH⁺(AHA)⁻. It is

$$[\text{HA}]_T = \text{ACIDI} - [\text{TMPD}]_T \times$$
$$\left[\frac{-1 + K_1 K_2 [\text{HA}]_M{}^2 (1 + 3K_4[\text{HA}]_M{}^2)}{1 + K_1[\text{HA}]_M + K_1 K_2 [\text{HA}]_M{}^2 (1 + K_4[\text{HA}]_M{}^2)} \right] \quad (24)$$

The value of K_1 (from the preceding article) is 4×10^5 l. mol⁻¹.
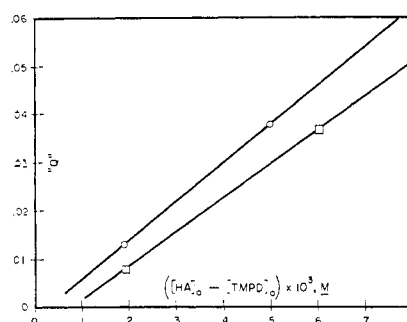

Figure 2. Q plotted against the difference in initial concentrations between TCA and TMPD, for varying TCA concentrations at two fixed initial TMPD concentrations: O, 10⁻³ M [TMPD]₀; ◇, 2 × 10³ M [TMPD]₀.

The average value of K_{ox} is 10.1 l. mol⁻¹ with a standard deviation of ±7.7%, based on 30 determinations at 25.0°. Runs which were not made at controlled temperature, runs which had very low absorbance readings at 570 nm, and runs in which the absorbance decreased at a rate greater than 15%/min were excluded from this calculation. The relevant data are shown in summary form in Table IIIa.

Table IV. Values of K_{ox} and Various Acidity Constants for Different Acids in Benzene and in Water at 25°

Acid	K_{ox}, l. mol⁻	K_1, l. mol⁻¹	K_2, l. mol⁻¹	K_D, l. mol⁻¹	$K_a^{H_2O}$ [a]
TCA	10.1 ± 0.8	4.15×10^5	1.5×10^3	6.7	2.2×10^{-1}
DCA	5.6 ± 0.2	1.6×10^4	3×10^3	27	5×10^{-2}
2,5-DNBA	4.5 ± 0.8	1.3×10^4			2.39×10^{-2}
3,5-DNBA	2.5 ± 0.1	4.3×10^3			1.50×10^{-3}
HPi	1.0	1.33×10^5			1.96×10^{-1}
MCA	$0.7 +$ $0.039[HA]_M$	4.9×10^2	4×10^2	48	1.4×10^{-3}
o-NBA	0.66 ± 0.012	1.7×10^3			6.1×10^{-3}
p-NBA	0.2	2.8×10^2			3.6×10^{-4}

[a] Taken from ref 15.

3. DCA. The function which was used to correct the concentration of TMPDH⁺ for the formation of TMPDH₂²⁺ is

$$\frac{[TMPDH^+]}{[TMPDH^+] + [TMPDH_2{}^{2+}]} = \frac{1}{1+R} \quad (25)$$

and R is obtained from

$$\log R = -3.96 + 2.64 \log [HA]_M \quad (26)$$

In fact, this correction had a negligible effect on the concentration of monomeric free acid under the conditions of the redox experiments.
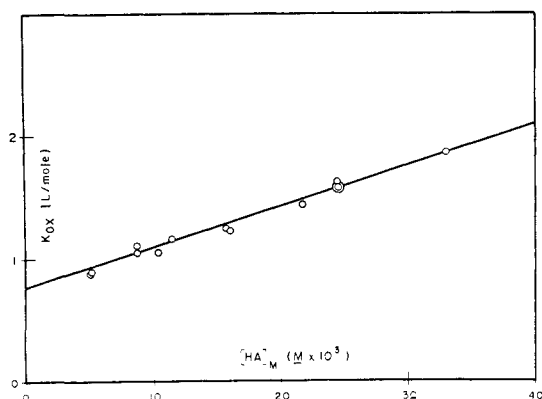

Figure 3. Variation of K_{ox} with concentration of monomeric MCA. K_{ox} (l. mol⁻¹) plotted against MCA concentration (M).

A small upward trend was noted in the value of K_{ox} as the acid concentration increased. The average value of the constant is 5 l. mol⁻¹ when the monomeric acid concentration was less than $2 \times 10^{-3} M$; it rises to 6.7 l. mol⁻¹ in 0.016 M acid. This is a 30% increase in K_{ox} for an increase in acid concentration of 800%. All values, however, were averaged together.

The data are shown in summary form in Table IIIb.

4. MCA. The function used to correct the concentration of TMPDH⁺ for the formation of TMPDH₂²⁺ is

$$\frac{[TMPDH^+]}{[TMPDH^+] + [TMPDH_2{}^{2+}]} = \frac{1}{1 + 2[HA]_M} \quad (27)$$

K_{ox} increases steadily with increasing acid concentration. Figure 3 shows this effect. Extrapolation to zero free acid gives 0.7 l. mol.⁻¹ as the limiting value for K_{ox}. The empirical equation describing this relationship is

$$K_{ox} = 0.7 + 0.039[HA]_M \quad (28)$$

Evidently the Wurster's Blue salt, like the TMPD salts themselves, requires more than one additional acid molecule beyond the number already associated with the reduced species.

5. Other Acids. Dimerization constants and homoconjugate ion-pair formation constants were not available for 2,5-DNBA, 3,5-DNBA, HPi, o-NBA, and p-NBA. The values of the apparent ion-pair formation constants presented in the preceding article were used to find the concentration of TMPDH⁺ by

$$[TMPDH^+] = [TMPD]_T \frac{K_1[HA]_M}{1 + K_1[HA]_M} \quad (29)$$

The value used for [HA]ₘ was simply the difference between the concentrations of acid and base. The data and the results are shown in Table IIId–h. The limited solubility of p-NBA was responsible for low and somewhat inaccurate absorbance readings for the Blue. The value of K_{ox} in the table is an approximate one. Picric acid behaved differently from the carboxylic acids. For the latter, the maximum absorbance at 570 nm was usually found in less than 2 min. With the phenol, it took about 1 hr.

The various values of K_{ox} are shown in Table IV, together with the ion-pair formation constants (K_1), the homoconjugate ion formation constants (K_2), dimerization constants (K_D), [14] and the dissociation constants in water ($K_a^{H_2O}$). [15]

The order of effectiveness of the various acids in promoting the oxidation of TMPDH⁺ follows the general order of their dissociation constants in water, and that of the ion-pair formation constants in benzene (i.e., $K_a^{H_2O}$ and K_1, respectively). There is one significant exception to this generalization: picric acid. It is very much less efficient in stabilizing the ion radical in benzene than its acidity constants would suggest. Ortho-substituted nitrophenols have a strong internal hydrogen bond [16] which markedly reduces the formation of homoconjugate ion pairs. [17] This suggests that the low value of K_{ox} for picric acid is due in large part to its inability to hydrogen bond to its anion, and that homoconjugate ion-pair formation plays an important part in the oxidation of TMPD in excess acid. One cannot, however, look to the order of the values of K_2 for the chlorinated acetic acids as a guide to the order of the values of K_{ox}.

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In the former case there is extensive ion-pair formation between the TMPDH⁺ cation and the AHA⁻ anion, with two types of hydrogen bond involved: N–H–O and O–H–O. While conductivity studies of carboxylate homoconjugate ion-pair formation in benzene show a tenfold increase in the specific conductance over that of ion pairs,[17] and hence a markedly increased dissociation of the homoconjugate, nevertheless the very low value of the specific conductance ($\sim 10^{-11}$ ohm^{-1} cm^{-1} for a 0.0027 M solution of TCA in 0.0065 M triethylammonium trichloroacetate) means that a very small fraction of the homoconjugate ion pair is undergoing dissociation. This is also evident from molecular-weight studies in benzene. Thus, Bruckenstein and Saito referred to the homoconjugate salt formed by TCA and a tertiary amine as a homoconjugate ion pair —an uncharged ion aggregate.[18] The cation radical of Wurster's Blue may behave quite differently from TMPDH⁺ as a counterion to the various hydrogen-bonded anionic species which are present in the various solutions. It may be much less capable of forming a hydrogen bond than TMPDH⁺, since it carries no proton, there is a positive charge on the particle, and there is only one electron rather than a lone pair on a nitrogen

atom. The stabilizing effect of the hydrogen bond formed between TMPDH⁺ and the various anionic species is thus removed. The general pattern of the TMPD–C· redox reaction in benzene is the following: regardless of the number of acid molecules associated with TMPDH⁺ prior to oxidation, one additional molecule of acid is needed to form the Wurster's Blue. This additional molecule may be needed to stabilize the counteranion to the cation radical because of the disappearance of the hydrogen bond between TMPDH⁺ and the carboxylate species which existed prior to the oxidation.

It appears, from Table IV, that the chlorinated acetic acids show at least three different orders of acidity in benzene. For dimerization, the order is MCA > DCA > TCA. For simple ion-pair formation with TMPD, the order is TCA > DCA > MCA. The latter sequence is also found for the formation of Wurster's Blue, but the range of values of the equilibrium constants is diminished from three orders of magnitude to one. The values of K_{ox} for the three acids may represent their differing capacities for homoconjugate particle stabilization in the presence of a nonhydrogen-bonding cation.

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A Diffusion Study at 25° with a Shearing Diffusiometer. A Comparison with the Gouy and Conductance Methods

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Abstract: A new procedure is described for evaluating diffusion coefficients from experimental data obtained with a shearing diffusiometer of Ingelstam design, and diffusion coefficients are reported for aqueous solutions of each of the solutes, sucrose, *n*-butyl alcohol, magnesium sulfate, tetra-*n*-propylammonium bromide, tetra-*n*-butylammonium bromide, thiourea, glycine anhydride, ε-caprolactam, and mannitol. Using a Gouy diffusiometer, diffusion data have also been obtained for the systems MgSO₄–H₂O, *n*-Pr₄NBr–H₂O, and thiourea–H₂O. Data for the system MgSO₄–H₂O are used to compare the shearing diffusiometer with the Gouy and conductance methods.

In 1955 Ingelstam[1] described an optical system which first used a Savart plate[2-5] to shear a plane-polarized wave front of monochromatic light after passage through a cell in which free diffusion was taking place, and then employed an analyzer to permit the sheared light beam to produce a symmetrical system of straight interference fringes. He also indicated a method for obtaining an *approximate* binary diffusion coefficient from the variation with time of the fringe separations. Later Bryngdahl[6,7] developed the method much further

and reported diffusion coefficients for dilute solutions of the system sucrose–H₂O. Additional theoretical developments were discussed in a further publication.[8] It should be noted that in 1951 Tsvetkov[9] and in 1957 Tsvetkov and Klenin[10] also described diffusion measurements with a somewhat similar shearing diffusiometer.

The purpose of this paper is to report diffusion data which were obtained for nine aqueous binary systems with a shearing diffusiometer of Ingelstam and Bryngdahl design,[1,6,7] and to compare these results with similar data obtained with a Gouy diffusiometer which has been previously described,[11] and with the data in the

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