An Investigation into the Electrochemical Oxidation of Some Aromatic Amines in the Room-Temperature Molten Salt System Aluminum Chloride–*n*-Butylpyridinium Chloride

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Abstract: The electrochemical oxidation of a number of aromatic amines [triphenylamine (TPA), *N,N*-dimethylaniline (DMA), *N,N*-dimethyl-*p*-toluidine (DMT), diphenylamine (DPA), and *N,N'*-tetramethylbenzidine (TMB)] in the low-temperature molten salt system aluminum chloride–*N*-butylpyridinium chloride has been investigated. In acidic melts TPA is oxidized reversibly to its radical cation which at more positive potentials undergoes a further, chemically irreversibly oxidation to the dication of the amine. In basic melts the stability of the radical cation is reduced and it couples to form tetraphenylbenzidine which is itself further oxidized. The oxidation of the other amines was more complex as a result of their being involved in complexation equilibria with acid species in the melt. In basic melts where they were uncomplexed, their behavior was similar to that of TPA, but, in acidic melts, the amine complexes underwent irreversible two-electron oxidations to their respective dications at potentials ~1 V positive of the first oxidation potential of the free amine. TMB, which, depending on the melt acidity, could be present as the free amine mono or di complex, was also oxidized to its dication. The actual mechanism of this oxidation was dependent upon the melt acidity. The oxidation of TMB was also shown to be dependent upon the temperature, the TMB cation radical being stable at low temperature but becoming unstable with respect to disproportionation as the temperature was increased.

Introduction

In recent years increasing interest has been shown in the use of tetrachloroaluminate melts ($AlCl_3$-alkali metal halide mixtures) as solvents for organic electrochemistry.[1-7] These systems are aprotic and totally anhydrous in nature thus affording stability to radical cations. The operating temperature of these systems (~175 °C), while low for molten salts, is, however, above the boiling point of many organic species and it has been shown that,[8] at these temperatures, homogeneous reactions can occur between these melts and certain organic species. Recent studies in this laboratory have therefore been directed toward the development of low melting point analogues of these chloroaluminates.

About 25 years ago Hurley and Wier[9] reported the use of the system 2:1 $AlCl_3$-ethylpyridinium bromide (EtPyBr), which was molten at room temperature, as a plating bath for aluminum. We have recently used this solvent and its mixtures with benzene, for both electrochemical[10-12] and photochemical[13] investigations. While the 2:1 $AlCl_3$-EtPyBr system was molten at room temperature, the melting point increased sharply as the composition was changed, thus precluding variation of the melt acidity at room temperature. A number of alkylpyridinium halide-$AlCl_3$ mixtures were therefore investigated with the purpose of finding a system molten at ambient temperatures over a wide composition range. As reported in an earlier publication,[14] mixtures of $AlCl_3$ and *n*-butylpyridinium chloride (BuPyCl) meet this criterion over the composition range 0.75:1 to 2:1 ($AlCl_3$-BuPyCl).

Raman studies of this solvent[15] indicate that, in the 1:1 mixture, aluminum is present almost entirely as $AlCl_4^-$ ions, whereas, in the 2:1 system, it is present as $Al_2Cl_7^-$. These observations are supported by potentiometric data[16] which shows that the Lewis acid-base properties of the melts are described by the equilibrium

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (1)$$

with an equilibrium constant at 30 °C of 3.8×10^{-13}. Thus, on changing the melt composition from 0.75:1 to 2:1, the pCl increases from 0 to 15, a variation more than twice that observed in the $AlCl_3$-NaCl system at 175 °C[17] and comparable with the pH variation in aqueous systems. Potentiometric data[18] shows that eq 1 also describes the acid-base equilibrium in 50 vol. % mixtures of $AlCl_3$-BuPyCl and benzene with an equilibrium constant of 2.4×10^{-13}. It is interesting to note that, in marked contrast to the NaCl-$AlCl_3$ system, no free $AlCl_3$, or Al_2Cl_6, is present in $AlCl_3$-BuPyCl melts and indeed even 2:1 melts can be heated to 175 °C without sublimation of $AlCl_3$.

It was stated earlier that one of the most interesting properties of the alkali metal tetrachloroaluminates was their ability to stabilize radical cations and it has recently been reported[14] that, at least in respect to the radical cations of some aromatic hydrocarbons, this is also true of the $AlCl_3$-BuPyCl system. In earlier studies[2,4,6] in the $AlCl_3$-NaCl system it was shown that radical cations of a number of tertiary aromatic amines exhibited greater stability in the melt than in common solvents, e.g., acetonitrile, and also that the electrochemical oxidation of these amines was very dependent on the melt acidity. It was therefore decided to investigate the electrochemical behavior of a number of amines in the $AlCl_3$-BuPyCl system, and the results of this study are presented here.

Experimental Section

Triphenylamine (Aldrich), diphenylamine (Aldrich), *N,N'*-tetraphenylbenzidine (Eastman), and *N,N'*-tetramethylbenzidine (Eastman) were all recrystallized from ethanol while *N,N*-dimethylaniline (Mallinkrodt) and *N,N*-dimethyl-*p*-toluidine (K&K) were purified by distillation. The preparation of BuPyCl has been fully described previously[14] but consisted essentially of refluxing together *n*-butyl chloride (Aldrich) and pyridine (Aldrich) until crystals of BuPyCl separated. These were then purified by repeated recrystallization from acetonitrile–ethyl acetate mixtures. $AlCl_3$ (Fluka A.G. iron free) was purified by sublimation in a sealed tube as has been described previously.[14] The melts were then prepared by adding weighed amounts of $AlCl_3$ to BuPyCl being careful to prevent the temperature of the mixture rising above 100 °C (the mixing was highly exothermic). Trace oxidizing impurities were then removed from the melt by stirring it overnight in the presence of Al wire (m 5N Alfa

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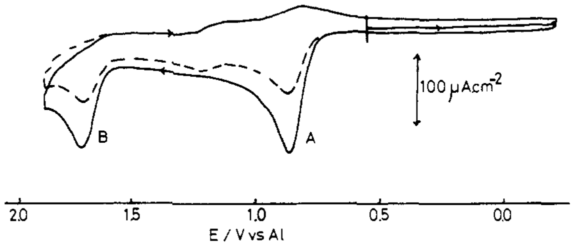


Figure 1. Cyclic voltammogram of 4.6×10^{-3} M TPA in a 2:1 melt (pCl 15) at 40 °C: sweep rate, 100 mV s^{-1}; solid line, first sweep; broken line, second sweep.

Inorganics). The essential details of the experimental techniques, electrochemical instrumentation, construction of the glass cells, construction and preparation of the glassy carbon electrodes, and operation of the dry box (Vacuum Atmospheres Co) have all been presented in earlier publications.[14,19] For all of experiments the reference electrode consisted of an Al wire immersed in a 2:1 melt which was separated from the working electrode compartment by a fine-porosity glass frit. The pCl of the melt was determined by measuring the potential difference between an Al wire in the working compartment and the above reference electrode.[16] This measurement could be made in the presence of the amines but not their oxidation products. Controlled potential coulometry was performed in a glassy carbon crucible (Atomergic Chemetals) which also served as the working electrode. UV-visible spectra were recorded on a scanning spectrophotometer (Cary Model 17). Except where otherwise stated all experiments were performed at 40 °C.

Results and Discussion

As will be seen later in this discussion the electrochemical oxidation of these aromatic amines is rather complex. The behavior of triphenylamine (TPA) is however the most straightforward, and can be used as a model with which to compare the behavior of the other compounds studied. The electrochemical oxidation of TPA will therefore be discussed first.

Oxidation of Triphenylamine. The oxidation of TPA in a 2:1 melt has been investigated by cyclic and pulse voltammetries and coulometry. Figure 1 shows a cyclic voltammogram; the solid line represents the first sweep and the broken one the second. When the sweep was reversed at a potential just positive of the first peak, labeled A, the behavior shown in Figure 2 was observed. The ratio of the anodic and cathodic peak currents in Figure 2, as determined by the method of Nicholson,[21] was unity, indicating that the electron transfer is reversible. The peak separation was 70 mV and this value increased slightly with increasing sweep rate. The theoretical peak separation for a reversible one-electron transfer is 62 mV at 40 °C. The experimental value is therefore a little high. However, the melt conductivity is low ($1.3 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$)[22] which can lead to significant iR drop. When cyclic voltammograms of TPA in a 50 vol. % mixture of benzene and 2:1 melt, a higher conductivity, lower viscosity medium, were recorded, similar behavior to that shown in Figures 1 and 2 was observed except that the peak heights were approximately doubled and the peak separation was reduced to 65 mV. It can be concluded that the first oxidation peak on the cyclic voltammograms of TPA in 2:1 melts and melt-benzene mixtures corresponds to the one-electron oxidation to the cation radical which is stable on the time scale of the cyclic voltammetry experiment.

This conclusion is supported by the pulse voltammetric experiment where it was found that, for the first oxidation wave of TPA, a plot of log $[(i_d - i)/i]$ vs. E (where i_d is the plateau current and i the current at potential E) was linear with a slope of 61 mV in agreement with the theoretical value for a one-electron reversible oxidation of 62 mV at 40 °C. The values of the diffusion coefficient of TPA in the 2:1 melt and in the 50 vol. % 2:1 melt-benzene mixture calculated from the cyclic and pulse voltammograms are given in Table I as are the values of $E_{1/2}$ and $E_{p/2}$.

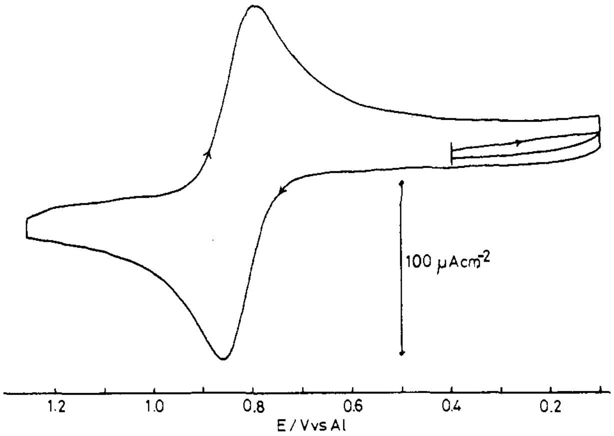


Figure 2. Cyclic voltammogram of 2.24×10^{-3} M TPA in a 2:1 melt at 40 °C: sweep rate, 100 mV s^{-1}.

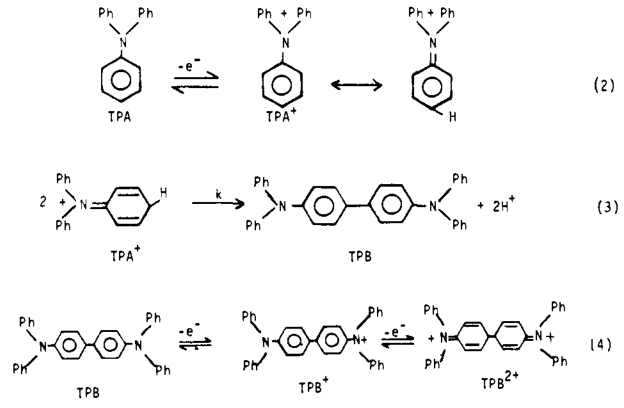
Table I. Diffusion Coefficients for TPA and the Oxidation Potential in 2:1 Melt and 50 vol. % 2:1 Melt-Benzene Mixture at 40 °C

medium	$D \times 10^7/cm^2\ s^{-1}$		$E_{p/2}$[c]	$E_{1/2}$
melt	3.4[a]	3.3[b]	0.800	0.814
melt-benzene	13.0	13.0	0.780	0.798

[a] From cyclic voltammetry. [b] From pulse voltammetry. [c] At a sweep rate of 100 mV s^{-1}.

It was shown in an earlier paper[14] that the potential of the Al/Al^{3+} (2:1 melt) electrode lies ~60 mV positive of SCE. The first oxidation potential of TPA in the melt ($E_{p/2}$ = 0.8 V vs. Al) and in acetonitrile[20] ($E_{p/2}$ = 0.92 V vs. SCE) can therefore be compared and are found to differ by only 60 mV.

This first oxidation was also investigated by controlled potential coulometry at a potential corresponding to the first cyclic voltammetry peak and the color of the melt was studied spectroscopically. Initially the solution turned deep blue (λ_{max} 685 nm) which agrees fairly well with the reported spectrum of TPA^+ in rigid media[23] (λ_{max} 655 nm). On standing, however, this blue solution slowly turned to a blue-green color. Continued electrolysis resulted in a total of two electrons per molecule of TPA being consumed and the solution turned orange (λ_{max} 480 nm). An overall two-electron oxidation of TPA in acetonitrile has been reported[24] and was attributed to the coupling of two TPA cation radicals to form *N,N'*-tetraphenylbenzidine (TPB) which was then oxidized further at the same potential to its dication according to the mechanism given in eq 2-4.



The cyclic voltammetric behavior of the solution left after exhaustive electrolysis of TPA in a 2:1 melt was identical with

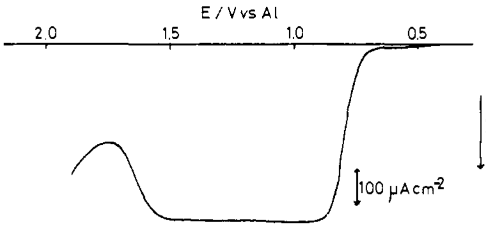


Figure 3. Normal pulse voltammogram of 4.6×10^{-3} M TPA in a 1.1:1 melt (pCl = 10.4): sweep rate, 2 mV/s^{-1}; pulse length, 48 mS; temperature 40 °C.

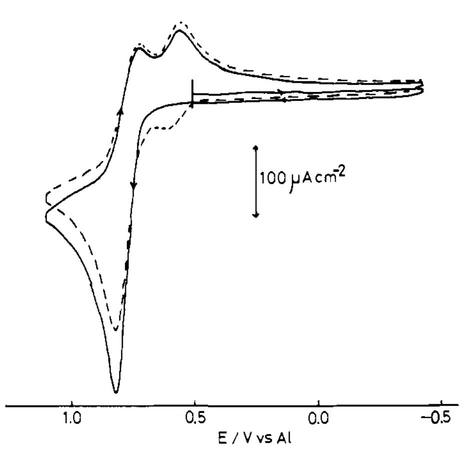


Figure 4. Cyclic voltammogram of 4.2×10^{-3} M TPA in a melt of pCl 6.8 at 40 °C: sweep rate, 100 mV s^{-1}; solid line, first sweep; broken line, second sweep.

that of TPB^{2+}, while the spectrum of this solution agreed with that reported for TPB^{2+} in acetonitrile (λ_{max} 480 nm).[20] It can thus be concluded that exhaustive oxidation of TPA at the potential of the first electron transfer results in an overall two-electron oxidation to form TPB^{2+}. In this respect the oxidation of TPA in these acidic melts is similar to that in acetonitrile; however, the initially formed TPA cation radical is significantly more stable in the melt as shown by the cyclic voltammetric behavior. In acetonitrile no reduction peak is seen for the cation radical except at very high sweep rates, whereas it is clearly seen even at 10 mV s^{-1} in the melt. As will be shown later, the stability of TPA^+ in this molten salt system varies markedly with the melt acidity.

Referring back to Figure 1 it can be seen that TPA in the 2:1 melt also undergoes a further electron transfer, labeled B, subsequent to the formation of the TPA cation radical and from the absence of any well-defined peaks on the reverse sweep (there is a small peak at ~1.1 V, which has a corresponding oxidation peak on the second sweep, and also a small peak at 0.76 V *due* to the reduction of TPA^+) this oxidation appears to be chemically irreversible. A similar second oxidation peak has been observed[25] for the oxidation of TPA in acetonitrile and was attributed to the formation of the dication. This species was then shown to couple to form the dication of TPB. This, however, is not the product in the melt as TPB^{2+} shows well-defined reduction peaks at potentials negative of TPA^+ reduction. The normal pulse voltammetry of TPA in a 2:1 melt, as shown in Figure 3, also shows interesting behavior in the potential region of this second oxidation. There is a well-defined wave for the oxidation of TPA to its radical cation and, then, at a potential corresponding to the second oxidation step; the current begins to decrease rather than increase as would be expected. Such behavior can only be explained if complex chemical steps are involved in the overall oxidation mechanism. The most probable product of the second electron transfer, as in acetonitrile,[25] is the dication of TPA which is a very reactive species. To explain the observed reduction in the pulse voltammetry current, this dication must react with unoxidized TPA thus reducing the concentration of this species at the electrode and hence reducing the current. When controlled potential electrolysis was performed at a potential corresponding to the second oxidation, i.e., ~1.75 V, approximately one electron per molecule was consumed and cyclic voltammetry of the resulting emerald green solution showed two poorly defined couples with reduction peak potentials of ~1.05 and 0.85 V. The form of this voltammogram was similar to that observed for the reduction of benzidine dications; however, the peak potentials did not correspond to the reduction of TPB^{2+} and also the observed currents were significantly lower than would be anticipated if this were the sole product. The most probable explanation is that dication of TPA being very reactive reacts with TPA to yield several products one of which is of the benzidine dication type (possibly a benzidine coupled through a position other than 4,4′). However, a number of other products are also probably formed which are electrochemically undetectable. It was stated earlier that the stability of TPA^+ depends on the acidity of the solvent; this can readily be seen from the cyclic voltammetric behavior. Figure 4 shows such a voltammogram of TPA in an approximately neutral melt (pCl 6.8). The behavior is very different from that shown in Figure 1 for the oxidation of TPA in an acidic melt. If it is assumed that the diffusion coefficient determined for TPA in acidic melts (Table I) can be used in neutral ones, then the oxidation peak observed at 0.80 V in Figure 4 now corresponds to a two-electron oxidation and there are two distinct reduction peaks, at 0.72 V and 0.55 V, on the reverse sweep. On the second sweep (shown by the dotted line) a new peak, negative of the original TPA oxidation, at 0.6 V is seen. This is identical with the behavior observed for the oxidation of TPA in acetonitrile.[20] That is the TPA^+ first formed rapidly dimerizes to form TPB which is oxidized further at the same potential to the dication. This is the mechanism already outlined in eq 2-4. The two reduction peaks correspond to the reduction of the dication, first to the monocation radical and then to TPB. The peak seen at 0.6 V on the second sweep thus corresponds to the oxidation of TPB to its monocation radical. When the melt acidity was reduced still further to a pCl of ~2.5, the reduction peaks disappeared altogether but the oxidation peak at 0.80 V remained a two-electron one. Thus the melt acidity also affects the stability of the TPB dication rendering it unstable at low pCl's. The process by which the solvent pCl affects the stability of TPA^+ is readily explained by considering the mechanism given in eq 2-4 for the formation of TPB^{2+} from TPA. The important step is that give by eq 3 which involves a deprotonation. This will obviously be favored by basic media and hindered by acidic ones thus explaining the greater stability of TPA^+ with respect to dimerization, in acidic melts. The instability of TPB^+ in the most basic melts can probably be explained in the same way as the decomposition of this species will probably also involve a deprotonation.

The peak potential for the first oxidation remains approximately constant ($E_p = 0.82 \pm 0.2$ V) irrespective of the melt composition. This suggests that the amine is not as involved in acid-base equilibria with the acid species in the melt. This is to be expected as TPA is a poor base, the nitrogen lone pair electrons being located nearly all of the time on the phenyl rings. Such complete delocalization is not possible with the other amines studied and they are therefore stronger bases. The electrochemical oxidation of these other amines will now be discussed.

Oxidation of *N,N*-Dimethylaniline. A cyclic voltammogram of *N,N*-dimethylaniline (DMA) in a basic (pCl 3.0) benzene-melt mixture is shown in Figure 5. As before the presence of 50 vol. % benzene, at a fixed pCl, did not affect the nature of the observed electrochemistry other than to double the observed currents for the same concentration of amine. If DMA

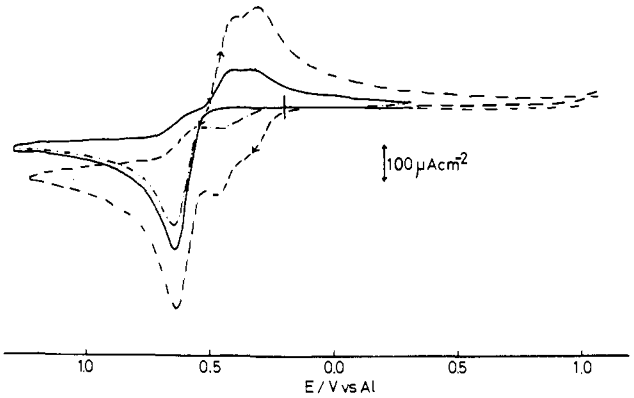
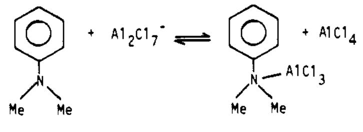


Figure 5. Cyclic voltammograms in a 50 vol. % melt-benzene mixture (pCl 3.0) at 40 °C: sweep rate, 100 mV s^{-1}; solid line shows the behavior observed for 4.1 × 10^{-3} M DMA on the first sweep while the line represented by (-·-) shows the behavior on the second sweep; the broken line shows the effect of adding TMB to this solution.

is assumed to have approximately the same diffusion coefficient as was calculated for TPA (Table I), then the peak of 0.750 V corresponds to a two-electron process. This is identical with what has been observed in both basic NaCl-AlCl$_4$ melts[14] and also in acetonitrile[26] and is attributed to the formation of the dication of tetramethylbenzidine (TMB) by an ECE mechanism similar to that represented in eq 2-4. Thus the peak on Figure 5 at 0.750 V corresponds to the formation of TMB^{2+}, while the two peaks on the reverse sweep at 0.51 and 0.42 V correspond to the reduction of TMB^{2+}, first to its monocation radical and secondly to TMB. The broad peak seen on the second sweep at ~0.55 V corresponds to the oxidation of TMB to its dication. That this assignment is correct is readily shown by the addition of TMB to the solution and again running the cyclic voltammogram as shown by the dashed line of Figure 5. The reduction peaks at 0.51 and 0.42 V have been greatly increased in size as has the oxidation peak at 0.55 V (this peak is also now resolved into two). In the most basic melts (pCl <1.5) the dication of TMB becomes unstable and now reverse peaks are observed.

Increasing the acidity causes changes in the observed cyclic voltammetric behavior. Figure 6a shows a cyclic voltammogram obtained at a pCl of 8.4; similar behavior was observed in all melts more acidic than this. When the diffusion coefficient of TPA is used as an approximate value for DMA, then the peak at 2.23 V corresponds to a two-electron oxidation. There is also an ill-defined reduction peak on the reverse sweep at −0.15 V. At slightly lower pCl values (Figure 6b), new oxidation peaks appear at 0.75 and 1.97 V and a reduction peak also appears at 0.55 V. The peak at 2.23 V is decreased in amplitude. On reducing the acidity still further the peak at 0.75 and 0.55 V, and to a lesser extent that at 1.97 V, increased still further in size at the expense of the peak at 2.23 V until finally it disappeared altogether and voltammograms similar to that shown in Figure 5 were observed. Figure 6c shows a cyclic voltammogram recorded at the same acidity as that in Figure 6b, but the sweep was reversed prior to the peak at 2.23 V.

These rather complex results can be explained by the presence of an acid-base equilibrium between the melt and the amine as shown in eq 5.



(5)

In the most acidic melts this equilibrium lies totally to the right; all of the amine is present as the complex thus stabilizing it with respect to oxidation. When it is oxidized, however, it goes immediately to the dication as the oxidation potential of the cation radical lies negative to that of the complex. This is the process occurring at 2.23 V. The dication, being very reactive, undergoes following chemical reactions; thus no reduction peaks are seen on the reverse sweep, except that at −0.15 V. This corresponds to the reduction of a product of the decomposition of the dication, probably protons which have been observed to reduce at this potential.[14]

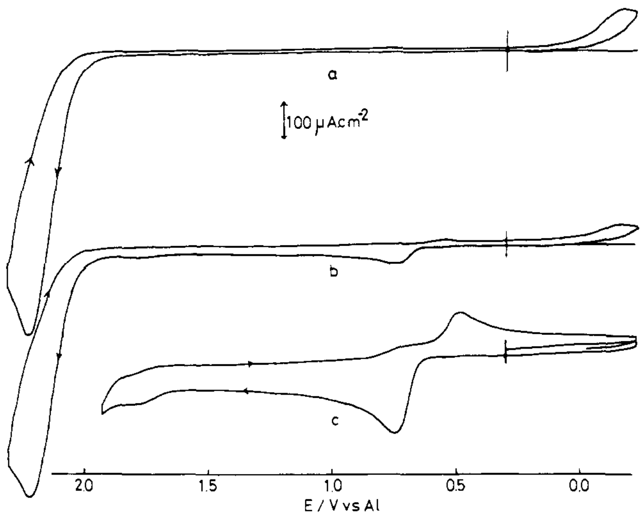


Figure 6. Cyclic voltammograms of 1.16 × 10^{-2} M DMA at a sweep rate of 100 mV s^{-1} and a temperature of 40 °C: (a) melt pCl 8.4; (b) melt pCl 5.8; (c) as (b), but current sensitivity × 5.

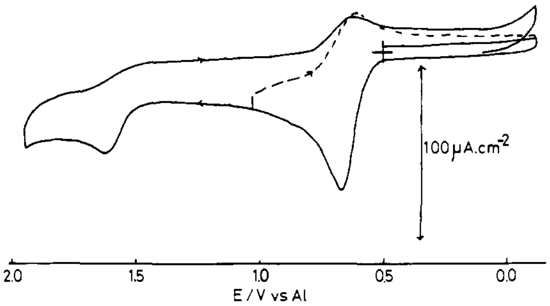


Figure 7. Cyclic voltammograms of 1.6 × 10^{-3} M DMT in a melt of pCl 5.5 at 40 °C: sweep rate, 100 mV s^{-1}.

When the acidity of the melt is reduced the equilibrium in eq 5 lies less to the right and some DMA becomes uncomplexed. The oxidation peak at 0.75 V in Figures 6b and 6c corresponds to the oxidation of this free amine to its radical cation, while the small peak at 1.75 V corresponds to the oxidation of this cation radical to the dication. This second oxidation peak is significantly smaller than the first since DMA$^+$ is unstable and rapidly dimerizes. The rate of this dimerization, as was shown earlier for TPA$^+$, increases with decreasing pCl and in melts more basic than that used for Figures 6b and 6c the peak at 1.97 V disappeared altogether. At a fixed pCl the relative heights of the peaks corresponding to the oxidation of the free and complexed DMA were constant as the sweep rate was varied from 0.01 to 10 V s^{-1}; the equilibrium in eq 5 appears therefore to be slow. Finally in the most basic melts the equilibrium lies totally to the left, only free amine is present, and the behavior already seen in Figure 5 is observed.

Two other aromatic amines [*N*,*N*-diphenylamine (DPA) and *N*,*N*-dimethyl-*p*-toludine (DMT)] were investigated and were shown to exhibit behavior similar to that of DMA, differing only in the stability of the amine cation radical and of course the values of the oxidation potentials and of the formation constant of the melt-amine complex. Figure 7 for example shows a cyclic voltammogram of DMT in a melt of the

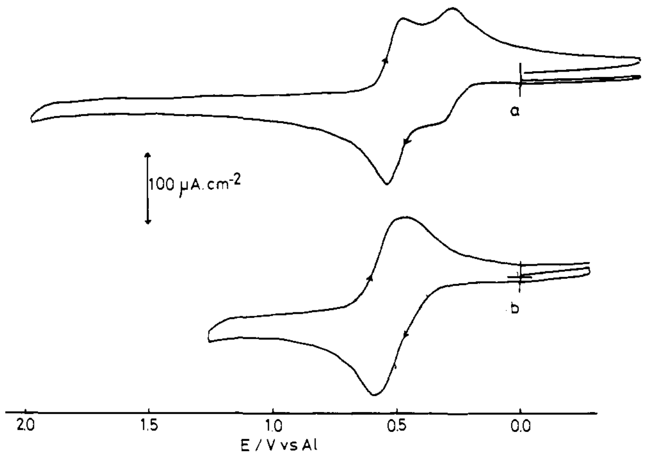


Figure 8. Cyclic voltammograms of 2.5×10^{-3} TMB in a melt of pCl 8.3 at a sweep rate of 100 mV s^{-1}: (a) at 40 °C; (b) at 150 °C.

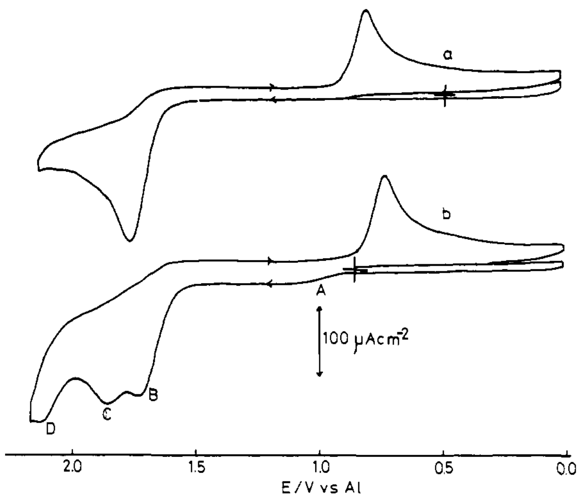


Figure 9. Cyclic voltammograms of 3.8×10^{-3} M TMB at 40 °C and a sweep rate of 100 mV s^{-1}: (a) pCl 15; (b) pCl 10.5.

same acidity as was used for Figure 6b. The differences compared to the DMA behavior are first that all of the DMT is present as free amine at this pCl and second the stability of the cation radical of DMT is significantly greater. This is shown by the broken line of Figure 7 corresponding to the cyclic voltammogram obtained when the sweep was reversed after the first oxidation peak which clearly shows a reduction peak for DMT$^+$. The ratio of the heights of the cathodic and anodic peaks approaches unity as the sweep rate is increased. This observation is to be anticipated as it has been shown that the decomposition of DMA$^+$ involves para substitution of one cation radical by another to form a benzidine derivative. When this para site is blocked, as in DMT, the attack has to be at the sterically less favored ortho position and therefore occurs less readily. An alternative decomposition step for DMT$^+$ has been reported by Melicharek and Nelson[27] involving deprotonation of the ring methyl group of DMT$^+$ to yield a benzyl-type free radical which then complexes to form the corresponding bitoluidine. Controlled potential oxidation of DMT, in a melt of the same acidity as used for Figure 7, at the first oxidation potential resulted in two electrons/molecule being consumed. In acetonitrile[27] the oxidation potential of the bitoluidine cation radical lies well positive of the oxidation potential of DMT; therefore, if this were also true in the melt, controlled potential coulometry at the first oxidation peak should, if the cation radical couples by the benzyl route, yield an *n* value of 1.5. This is therefore evidence that DMT oxidation in the melt yields a benzidine and not a bitoluidine derivative.

It has been seen in the above studies that the amine cation radicals couple to form benzidines and it was therefore decided to study the oxidation of benzidines in these media, in particular tetramethylbenzidine (TMB).

Tetramethylbenzidine. Figures 8a, 9b, and 9a show cyclic voltammograms of TMB at 40 °C in melts of increasing pCl. It can immediately be seen that TMB, like the other amines studied, must be involved in complexation equilibria. However, there are two nitrogen atoms in TMB and it can form both mono- and dicomplexes as shown:

$$\mathrm{TMB} + \mathrm{Al_2Cl_7^-} \rightleftarrows \mathrm{TMB\text{-}AlCl_3} + \mathrm{AlCl_4^-} \quad (6)$$

$$\mathrm{TMB\text{-}AlCl_3} + \mathrm{Al_2Cl_7^-} \rightleftarrows \mathrm{TMB\text{-}2AlCl_3} + \mathrm{AlCl_4^-} \quad (7)$$

Since the behavior shown in Figure 8a is seen in all melts more basic than a pCl of 8.5, except at very low acidities (pCl <1.5) where no reverse peaks are seen, it can be concluded that this represents the behavior of the free amine.

The two oxidation peaks correspond to the oxidation of TMB first to the cation radical and then to the dication; the reduction peaks correspond to the reverse of these processes. This behavior is very similar to that observed in neutral acetonitrile[29] and indeed the oxidation potentials in the two media are very similar. Confirmation that the final oxidation product was TMB^{2+} was obtained from controlled potential electrolysis. A total of two electrons/molecule were consumed and the resulting solution was bright orange (λ_{max} 483 nm) which agrees well with the reported λ_{max} value for TMB^{2+} in acetonitrile. Controlled potential electrolysis was also carried out at a potential corresponding to the first oxidation peak (0.35 V) with identical results. This is either due to overlap of the two processes or to the cation radical disproportion into the dication and free amine. Support for this latter mechanism is obtained from cyclic voltammetry at higher temperatures. Figure 8b, for example, shows the cyclic voltammogram observed at 150 °C (in all other respects the conditions were identical with those for Figure 8a). The oxidation and reduction processes are now no longer resolved into two peaks. This behavior is identical with that observed in NaCl-$AlCl_3$ melts at 175 °C.[6] Thus it appears that TMB$^+$ becomes unstable at higher temperatures.

Saget and Plichon[29] have shown that TMB becomes protonated in acidic acetonitrile and that the diprotonated species has a λ_{max} value of ~250 nm while the monoprotonated and free forms have λ_{max} values between 300 and 310 nm. Earlier studies[14] in $AlCl_3$-BuPyCl melts have shown that $AlCl_3$ complexes of hydrocarbons have almost identical UV-visible spectra with those of their proton analogues. If this is also true of amine complexes, then the spectrum of TMB in the melt should indicate the degree of complexation. Unfortunately, the melt has a low wavelength cutoff of 280 nm, so the results are not conclusive. However, no absorption was observed between 280 and 600 nm for a solution of TMB in 2:1 melt. Thus it can be assumed that TMB is present as the dicomplex. A similar conclusion was reached in acidic $AlCl_3$-NACl melts.[6] The cyclic voltammetric behavior shown in Figure 9a is therefore that of the dicomplex. Since the nitrogen lone pairs are no longer available, the complex is much harder to oxidize than the free amine. The peak at 1.78 V corresponds to the two-electron oxidation of the complex to the TMB dication (this can be shown by coulometry and spectroscopy as before). The reduction of the dication occurs at 0.83 V, ~0.5 V positive of the reduction potential in a basic melt. This shift is due to the complexation of the TMB. In these acidic melts it appears that the cation radical of TMB is unstable in accord with the findings of Saget and Plichon[29] in acidic acetonitrile.

As shown by Figure 9b the behavior at intermediate pCl values is complex owing to the amine being present in several forms. As the pCl is reduced from a value of 1.5 the peaks at

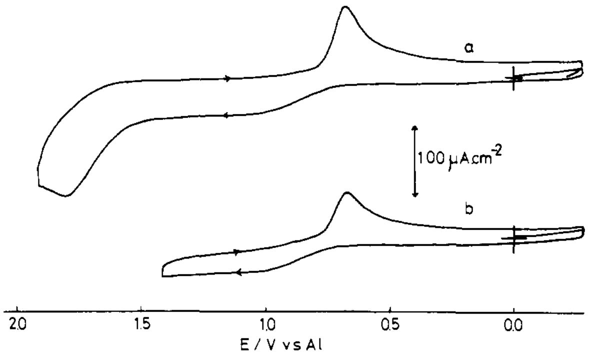


Figure 10. Cyclic voltammogram of 2.3×10^{-3} M TMB at 100 °C, a pCl of 10.5, and a sweep rate of 100 mV s^{-1}.

1.74 and 2.13 V (labeled B and D on Figure 9b) first appear at a pCl of ~12 and slowly increase at the expense of the peak at 1.82 V (labeled C); this latter peak is the same one observed at 1.78 V in Figure 9a, the peak potential shifting slightly with pCl. As the acidity is reduced further, the broad wave labeled A becomes apparent and then develops a peak shape. This peak grows at the expense of the others until they disappear at a pCl of ~9. Finally peak C resolves into two peaks and the behavior already seen in Figure 8a is observed. Referring back to Figure 9b only one peak is seen on the reverse sweep if the sweep is reversed after any of the peaks A, B, C, or D, but the height of the peak does increase with increasing positive sweep limit. Thus the product of all these oxidation processes appears to be the same. From the above discussion it can be concluded that peak C is due to the two-electron oxidation of the dicomplex of TMB while the broad wave, A, is due to the two-electron oxidation of the free TMB. Peaks B and D appear under similar conditions and are of approximately equal height at all sweep rates; it can therefore be concluded that they are closely related.

At a pCl of 11.2, the cyclic voltammetry is the same as in Figure 9b except that wave A is absent. If a controlled potential coulometry experiment was carried out at this acidity at a potential of 1.65 V, i.e., a potential corresponding to peak B, a total of one electron/molecule was consumed. Cyclic voltammetry was carried out on the resulting solution; if the first sweep was made in the negative direction, a peak was seen at 0.74 V, while, if the first sweep was positive going, a small peak was seen at the potential of peak C and a large peak was seen at the potential of peak D. Further electrolysis, at the potential of C or D, resulted in the consumption of a further electron/molecule and the product was TMB^{2+}. From this it can be concluded that the product of the oxidation at peak B is the cation radical of TMB, not the free form but the monocomplexed one. This complexed cation radical, owing to its positive charge, is harder to oxidize than the dicomplexed amine; thus peak D is the oxidation of this cation radical to the dication. The cation radical complex is also involved in a disproportionation mechanism with the dication and amine (complexed or free). This explains the small peak, at potential C, seen after electrolysis at peak B and also that the reduction of the cation radical complex occurs at the same potential as the reduction of the dication.

It was observed earlier that the cation radical of TMB in basic melts becomes increasingly unstable with respect to disproportionation as the melt was heated. This is also true in melts of intermediate pCl as shown by the cyclic voltammograms in Figure 10. These were obtained in a melt of the same pCl as for Figure 9b (10.5) but at 100 °C. This behavior at higher temperatures, which is identical with that observed in $AlCl_3$-NaCl melts at 175 °C,[6] is easily explained. The broad wave beginning at ~1 V corresponds to the kinetically controlled two-electron oxidation of the free amine and the peak at ~1.8 V corresponds to the two-electron oxidation of the complexed amine.

The electrochemical behavior of TMB in these melts can therefore be summarized as follows. The TMB is involved in complexation equilibria as shown by eq 6 and 7. In the most basic melts all TMB is uncomplexed and undergoes two reversible one-electron oxidations to the radical cation and then the dication, while in the most acidic melts it is present as a dicomplex which is oxidized, at higher potentials, in a two-electron step to the dication. At intermediate acidities a monocomplexed species is present as well as the dicomplex and free amine. This undergoes two one-electron oxidation steps to the monocomplexed cation radical and the dication.

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