EFFECT OF MELT COMPOSITION ON THE REACTIONS OF THE ANTHRACENE RADICAL CATION IN SbCl₃-RICH MELTS: CHLORINATION VERSUS ARYL-ARYL COUPLING

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ABSTRACT

In SbCl₃-19-21 m/o melts (BPCl = N-(1-butyl)pyridinium chloride) reactions of anthracene (AN) oxidized either coulometrically or with Sb(V) were highly selective in a way that depended on melt composition. In basic 60-19-21 m/o melts the only significant products were 9-chloroanthracene (CA) and 9,10-dichloroanthracene (DCA) with CA constituting >99% of the yield for partial oxidations up to 80%, while in acidic 60-21-19 m/o melts the only products found in significant amounts were condensed AN's, principally 2,9'-bianthracene. In SbCl₃-10 m/o BPCI oxidative chlorination occurred without condensation, while in SbCl₃-6 m/o KCl both chlorination and condensation took place. These results are discussed in terms of the effect of the acid/base properties of SbCl₃-rich melts on the manifold of reaction pathways available to AN radical cations. It is proposed that the half-regeneration pathway (an ECE process) is the primary chlorination route with a Cl⁻/SbCl₃ complex we denote Cl⁻(cpx) serving as the nucleophile. In basic melts the concentration of Cl⁻(cpx) is substantial and chlorination reactions are dominant over condensation reactions while in acidic melts the concentration of Cl⁻(cpx) is enormously suppressed so that chlorination reactions become much slower and condensation predominates.

INTRODUCTION

Solutions of aromatic compounds in anhydrous SbCl₃-rich melts undergo a variety of reactions, some of which are quite unusual and most of which are strongly influenced by the presence of relatively small amounts of added chloride ion acceptors (Lewis acids, such as AlCl₃) or chloride ion donors (Lewis bases, such as KCl) (1-3). In the present study we examined the effect that such donors and acceptors have on the reactions of anthracene (AN) radical cations in

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molten SbCl₃ modified by the presence of ~2 M N-(1-butyl)pyridinium tetrachloroaluminate (BP[AICl₄]). We found the effect to be very large and in melts with excess BPCl to lead to an unusually selective chlorination reaction. (Structural formulae of AN and other relevant molecules are shown in Fig. 1).

The melts used in this study were prepared by mixing SbCl₃, AlCl₃, and BPCl in the following proportions: 60-19-21 m/o (mol %), respectively, and 60-21-19 m/o, respectively. These mixtures are liquid at 25°C and some of their physical and electrochemical properties have been reported (4). Since AlCl₃ and BPCl react virtually stoichiometrically, a 60-19-21 melt consists of SbCl₃, BP(AICl₄) and a small excess of BPCl (5). The Cl⁻ ions from the latter are complexed by SbCl₃ to give an entity we denote Cl⁻(cpx). Likewise, a 60-21-19 melt consists of SbCl₃, BP(AICl₄) and a small excess of AlCl₃. The latter reacts with SbCl₃ to form AlCl₄⁻ and a chloride-deficient species we denote SbCl₂⁺(cpx). (For a discussion of the structures of these complexes see Ref. (6).) The 60-19-21 and 60-21-19 melts are, respectively, basic and acidic in the Lewis sense. AN has been shown to be stable over extended periods in basic SbCl₃-AlCl₃-BPCl melts, and to undergo a very slow melt-catalyzed decomposition in acidic compositions of this system (5).

EXPERIMENTAL

Materials. — The synthesis and purification of BPCl, and the purification of SbCl₃ and AlCl₃ have been described (5). SbCl₅ (Alfa, Ultrapure), AN (Reilly Tar and Chemical Corp., Scintillation Grade), 9-chloroanthracene (CA) (Pfaltz and Bauer, Inc.) and 9,10-dichloroanthracene, (DCA) (Pfaltz and Bauer, Inc.) were used without purification. The preparation of solvents and solutions has been described (5) and all handling of materials, including weighings, was performed in an argon-atmosphere glove-box in which H₂O and O₂ were kept below 2 ppm.

Procedures for experiments not involving product separation. — Cyclic voltammetry (CV) and spectroelectrochemistry (SE) were performed as described elsewhere (4). The reference electrode for all potentials reported here was SbCl₃-BPCl(liquid), SbCl₃(solid)/Sb. Optical spectra of a solution in the SE cell were measured before and after electrolysis with a Cary 14 spectrometer. The technique used to rapidly measure optical spectra during the chemical oxidation of AN was based on the use of an OMA-2 optical multichannel analyzer (EG&G model 1215), a linear diode array detector (EG&G model 1412), interfaced to a large-aperture flat-field spectrograph (Instruments SA model HR 320S). In particular, 31 spectra (visible region) were measured during a 180-s period immediately following the mixing of 0.54 mg of AN in 1.0 ml of a 60-19-21 melt with ~5 mg of SbCl₅ in 1.0
ml of a 60-19-21 melt at 40°C. The measurement of each spectrum required ~0.2 s.

Procedures for experiments involving product separation. — All macroscale reactions were performed in a glove box at 26 ± 2°C unless otherwise noted. Electrochemical oxidations of AN were done in a glassy carbon crucible that also served as the working electrode. The counter electrode was a large-area Pt foil contained in a compartment separated from the analyte by a medium porosity Pyrex frit. Oxidations of solutions of AN in 60-19-21 melts were carried out at a controlled potential of +0.625 V with currents in the range of 5-25 mA while stirring the melt. These solutions initially contained 50-80 mg of AN in 4 ml of 60-19-21.

The solution for the coulometric oxidation of anthracene in a 60-21-19 melt was prepared by mixing just prior to electrolysis 67 mg of AN dissolved in 4 ml of a basic 60-19-21 melt with 4 ml of an acidic 60-23-17 melt and then electrolysing at +0.90 V. The duration of the electrolysis (1 h) was short enough so that no significant decomposition of unoxidized AN took place (5).

Chemical oxidations of AN by Sb(V) were performed in the following three ways: (A) SbCl₅ (~10 μl) was added by syringe directly to a reaction mixture containing anthracene. (B) SbCl₅ (~100 μl) was added to 2 ml of a 60-19-21 melt. Aliquots of this solution were then added by pipette to AN solutions. (C) Sb(V) was generated coulometrically by oxidation of an appropriate composition of basic solvent (slightly rich in SbCl₃) at +0.9 V such that the composition after electrolysis was -60-19-21. Aliquots of this solution were then added to solutions of AN.

Separation and identification of products. — Reaction mixtures were removed from the glove box, hydrolyzed with 3 M HCl, and the organics were extracted into CH₂Cl₂. The CH₂Cl₂ layer was dried over MgSO₄, filtered and concentrated to 10 ml by rotary evaporation. Gas chromatography (GC), high-performance liquid chromatography (HPLC) and GC-mass spectrometry (GC-MS) were used to separate and identify reaction products. Authentic samples were used to calibrate GC retention times. HPLC fractions were quantitatively analyzed by UV-VIS spectroscopy. For chlorination reactions the mass balance between the total products collected after evaporation of CH₂Cl₂ (microbalance weighing) and the sum of the amounts of separated products (listed in Table I) agreed to within ±1%.

RESULTS AND DISCUSSION

Electrochemical and spectroscopic considerations. — The cyclic voltammetric (CV) and spectroelectrochemical (SE) behavior of molecular AN in 60-19-21 melts have been briefly reported (4). The onset of
Table I. Recovery of compounds after oxidation of anthracene in SbCl₃-AlCl₃-BPCl (60-19-21 m/o)

| Method       | Temp. (°C) | Recovery, m/o of initial AN |  |
|--------------|------------|----------------------------|---|
|              |            | AN | CA | DCA | Total | n_{ox}/n_{Cl}^{a} |
| Anodic       | 26         | 63 | 26 | 0   | 89    | 2.2              |
| Sb(V), A     | 26         | 65 | 31 | 0   | 96    | 1.7              |
| Sb(V), B     | 26         | 22 | 75 | 0.2 | 97    | 2.5              |
| Sb(V), C     | 100        | 19 | 80 | 0.9 | 100   | 2.5              |
| Sb(V), C     | 26         | 75 | 21 | 0   | 96    | 2.2              |
|              | 26         | 33 | 66 | 0.3 | 99    | 1.8              |
|              | 26         | 23 | 77 | 0.6 | 101   | 1.8              |
|              | 26         | 20 | 79 | 0.6 | 100   | 2.0              |
|              | 26         | 2  | 93 | 3.5 | 99    | 2.2              |

^{a}n_{ox} = equivalents of Sb(V) or faradays of current, n_{Cl} = moles of Cl substituted.

^{b}Methods A, B and C for adding Sb(V) are described in the text.

^{c}Not measured.

irreversible oxidation of a solution of AN in a 60-19-21 melt occurred at +0.6 V vs the SbCl₃-BPCl (liquid), SbCl₃ (solid)/Sb electrode for a scan rate of 0.2Vs⁻¹, while the onset of solvent oxidation occurred at +0.8 V and corresponded to the conversion of Sb(III) to Sb(V). At a sweep rate of 0.2 Vs⁻¹, no well-defined reduction of oxidized substrate or reaction products was observed.

Previous SE studies (4) of the oxidation of AN in molten SbCl₃-10 m/o KCl at 75°C showed that, although the anthracene radical cation (AN⁺⁺) is very reactive in this melt, it is present at a sufficient concentration to be detected as a weak spectrum during the early stages of oxidation. In similar studies using 60-19-21 melts at 26°C (electrolysis at +0.825 V) the AN⁺⁺ spectrum was too weak to be observed against the background of AN and product spectra. From the present investigation (see below) we know that 9-CA is the stable reaction product when AN is oxidized in a 60-19-21 melt. We measured the spectrum of an authentic sample of this compound in a 60-19-21 melt (λ_{max} = 358, 378 and 396 nm) and found it to match the product spectrum in the previous SE study.

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We also used fast optical spectroscopy to search for reactive intermediates when AN was oxidized by Sb(V) in a 60-19-21 melt. However, just as in the case of the SE measurements, the only absorptions found were those of AN and 9-CA.

Macroscale reactions. — A series of reactions was run in which AN in basic 60-19-21 m/o melts was partially oxidized either coulometrically or by Sb(V). The degree of oxidation was controlled by controlling the quantity of current passed or the amount of Sb(V) added. The results, summarized in Table I, are grouped by oxidation method. Oxidation by Sb(V), method B, was carried out at 26 and 100°C, as indicated. All other oxidations were at 26°C. Oxidations by Sb(V), method C, are listed in the order of increasing degree of oxidation, as indicated by the amount of unreacted AN recovered. The recovery of organics in these reactions was >95% in all but one case and the only substances found by HPLC were CA, DCA and unreacted AN. CA was by far the dominant product. DCA was produced in amounts of less than 1% for conversions up to 80%, and only 3.5% was produced for a conversion near 100%. In these reactions the number of electrons transferred per chlorine atom in the products \( \text{n}_{\text{ox}}/\text{n}_{\text{Cl}} \) was 2. As shown in Table I, four different methods of oxidation involving different sources of error all gave consistent results. The oxidation of CA by Sb(V) in a 60-19-21 melt at 26°C was also investigated. The sole product found was DCA and the \( \text{n}_{\text{ox}}/\text{n}_{\text{Cl}} \) ratio was 2. These results for both AN and CA are consistent with the stoichiometry in equation [1]

\[
\text{ArH} + \text{Cl}^- \rightarrow \text{ArCl} + \text{H}^+ + 2\text{e}^- \quad [1]
\]

where ArH is an aromatic molecule. The source of \( \text{Cl}^- \) and the fate of \( \text{H}^+ \) will be discussed later.

Such highly selective oxidative chlorination reactions are quite unusual. More commonly, when aromatic hydrocarbons are oxidized in the presence of halide ions, a variety of halogenated products result together with products of aryl-aryl coupling reactions (7-14). Of the latter we found none in 60-19-21 melts.

The oxidation of AN in an acidic 60-21-19 melt at 26°C pursued an entirely different course from that in a 60-19-21 melt, described above. Following a partial (50%) coulometric oxidation of AN in a 60-21-19 melt at +0.90V, 60 w/o (wt %) of the starting AN was recovered as AN and 17 w/o was recovered as 2,9^-BA. A substantial amount of more highly condensed material was also found but no chlorinated and only a very little hydrogenated (<1%) material could be detected. Hydroaromatics are among the decomposition products of AN in 60-21-19 melts and their very low yield in the present experiment provides verification that the decomposition of AN was insignificant during the relatively brief period required for the oxidation reaction. This
result is not unexpected because the rate of decomposition is known to be very slow (5).

These experiments display the striking consequence of going from slightly on the basic side of the neutral (60-20-20) composition to slightly on the acidic side. Although the change in formal composition was small, the change in products was very large.

A few additional experiments were done in basic SbCl$_3$-rich melts with substantial Cl$^-$(cpx) concentrations but without an AlCl$_4^-$-containing electrolyte. For a SbCl$_3$-10 m/o BCPl melt at 100°C the products recovered following partial oxidation by Sb(V) were unreacted AN (26%), CA (50%) and DCA (11%), while a similar oxidation in SbCl$_3$-6 m/o KCl at 80°C yielded AN (53%), CA (13%), 2,9^-BA (10%), 1,1^-BA (10%), and small amounts of chlorinated bianthracenes.

Mechanistic considerations. — Mechanisms of the reactions of radical cations of aromatic substances have been intensively investigated in recent years with AN and substituted ANs frequently serving as model compounds, and nucleophilic substitution reactions receiving special emphasis. Key aspects of this chemistry are summarized in references (15-17). These studies have demonstrated that radical cations follow a multiplicity of reaction pathways. Two of these have been demonstrated for nucleophilic substitution, namely, half-regeneration and disproportionation. Both are plausible routes for chlorination in SbCl$_3$-rich melts although, for reasons given later, the disproportionation pathway may be inactive in the case of anthracene. There are also two proposed pathways for aryl-aryl coupling reactions, namely, radical-radical dimerization and radical-neutral dimerization, and both are plausible in SbCl$_3$-rich melts.

The half-regeneration pathway is summarized in Fig. 2. AN$^\ddagger\ddagger$, generated in reaction [2], undergoes nucleophilic attack by a Cl$^-$ donor to give the radical I$^\ddagger$ in reaction [3]. This radical is oxidized further to I$^\ddagger$ in reaction [4] with the regeneration of half of the total AN. Finally, I$^\ddagger$ is deprotonated in reaction [5]. In the disproportionation pathway (Fig. 3), AN$^\ddagger\ddagger$ disproportionates in reaction [6] to form the anthracene dication (AN$^\ddagger\ddagger$) which undergoes nucleophilic attack in reaction [7] to form I$^\ddagger$. The latter deprotonates in reaction [5].

It is doubtful that AN$^\ddagger$ in a 60-19-21 melt is stable with respect to oxidation of solvent Sb(III). For that reason the disproportionation pathway appears to be an improbable route for the oxidative chlorination of AN in this melt. The potential difference between the onset of oxidation of AN and the onset of oxidation of the 60-19-21 melt is only 0.2 V. This value is much smaller than the ~0.6-V difference between the peak potential for the irreversible oxidation of An$^\ddagger$ to An$^\ddagger\ddagger$ and that for the partially reversible oxidation of AN to AN$^\ddagger\ddagger$ reported (18) in a CV study of the oxidation of AN in a
molten AlCl₃-BPCI mixture with the mole ratio 1.2:1, respectively. Although this potential difference may be smaller in a 60-19-21 melt, it is unlikely to be smaller by a factor as great as three as would be required for AN⁺⁺ to be stable with respect to solvent oxidation. For example, the range of values for the difference between the formal potentials for the oxidation of diphenylanthracene (DPA) to DPA⁺⁺ and that for DPA⁺⁺ to DPA⁺⁺ in various aprotic solvents is 0.34 to 0.48 V (19).

Let us consider the role of the melt in the chlorination reaction. The Cl⁻(cpx) complex is the strongest Cl⁻ donor in a SbCl₃-rich melt while SbCl₂⁺(cpx) is the strongest acceptor. The concentrations of these species are related through equation [8]

\[ SbCl₃ \rightleftharpoons SbCl₂⁺(cpx) + Cl⁻(cpx) \]  

The ion product constant \( K_i \) for this reaction is not accurately known but is unquestionably very small. Conductivity data for molten SbCl₃ indicate that \( K_i < 3 \times 10^{-11} \) M² at 99°C (20). Assuming that \( K_i \) is this small or smaller for SbCl₃-AlCl₃-BPCI melts at 26°C, it can be shown that

\[ \frac{\text{Conc. of Cl⁻(cpx) in 60-19-21}}{\text{Conc. of Cl⁻(cpx) in 60-21-19}} > 10^9 \]  

Therefore, in a basic 60-19-21 melt the probable Cl⁻ donor is Cl⁻(cpx) and equation [3] becomes equation [10].

\[ AN⁺⁺ + Cl⁻(cpx) \rightleftharpoons I⁺ \]  

Given the facts that SbCl₃ is the solvent with a virtually constant activity, that AN⁺⁺ and Cl⁻ are dilute, and that the ionic strength is fixed by the concentrated spectator electrolyte, BPAICl₄; it can be shown from equation [10] that the I⁺/AN⁺⁺ ratio is approximately proportional to the Cl⁻(cpx) concentration. In an acidic melt the Cl⁻(cpx) concentration is so small compared with that of SbCl₃, that if chlorination occurred, SbCl₃ would be the more probable donor and equation [3] would take the form of equation [11]

\[ AN⁺⁺ + SbCl₃ \rightleftharpoons I⁺ + SbCl₂⁺(cpx) \]  

However, [10] and [11] are thermodynamically related through [8] in such a way that the I⁺/AN⁺⁺ concentration ratio is proportional to the Cl⁻(cpx) concentration irrespective of what the actual donor may be. (Physically, this is a consequence of the presence in acidic melts of SbCl₂⁺(cpx) with which any other Cl⁻ acceptor must compete.) Thus, equation [9] implies equation [12]
I*/AN* in 60-19-21
\[ \frac{I*/AN*}{I*/AN*} \text{ in 60-21-19} > 10^9 \]  

It follows that chlorination reactions which proceed readily in basic melts will be very much slower in acidic melts.

A consideration of the deprotonation reaction [5] does not alter the above conclusion. In a basic melt Cl-(cpx) is the most plausible proton acceptor, yielding HCl as the end product. In acidic melts, as discussed below, experiments show that unreacted AN is the proton acceptor with the 9H-anthracenium ion being the final product. Combining these considerations with equation [1] we obtain equations [13] and [14] (Fig. 4) as the net oxidative chlorination reactions for AN and CA, respectively, in basic melts.

The experiments show that when AN is oxidized by Sb(V) in a 60-19-21 melt the almost exclusive product is CA until most of the AN is consumed even though Sb(V) readily oxidizes CA to DCA in the absence of AN. Almost certainly CA oxidizes at a higher potential than AN so that reaction [15] may provide an effective means of reducing CA** in the presence of AN and thereby blocking DCA formation. Another possibility is that CA oxidizes more slowly than AN.

\[ \text{CA}^{**} + \text{AN} \rightarrow \text{CA} + \text{AN}^{**} \]  

The pathways leading to condensed products are illustrated in Fig. 5 (radical-radical dimerization) and Fig. 6 (cation-neutral dimerization). Both pathways involve the formation of very strong protic acids, II in reaction [16], V in [19], and VII in [20]. The manner in which such acids deprotonate during the oxidative condensation of AN in acidic SbCl$_3$-rich melts was demonstrated in a study in which SbCl$_3$-10 m/o AlCl$_3$ served as the medium (21). It was shown by means of in situ $^1$H-NMR that unreacted AN quantitatively captures these protons to form the 9H-anthracenium ion (IV) as shown in equation [18]. Although AN is a very weak protic base, it is apparently the strongest available and in SbCl$_3$-10 m/o AlCl$_3$ it proved to be quite stable at elevated temperatures. It has also been shown (5) that IV is stable in a 60-22-18 melt. When such melts are quenched with aqueous HCl, hydrolysis of IV regenerates AN (21). We anticipate a similar behavior in a 60-21-19 melt so that prior to quenching, IV was a stable product and the AN recovered after quenching included the hydrolysis product in addition to unreacted AN.

The above considerations suggest that in acidic SbCl$_3$-rich melts the rate of anthracene chlorination is greatly suppressed by the virtual absence of an effective Cl$^-$ donor and that aryl-aryl coupling reactions take over. A prior study of the ESR spectra of AN** in SbCl$_3$-8 m/o AlCl$_3$ melts indicated that these coupling reactions are quite sluggish (22). The oxidation of 1-10 mM solutions of AN in this...
melt gave strong, well-resolved spectra of \( AN^+ \) that were very persistent at temperatures as high as 125°C. In basic melts with their substantial \( \text{Cl}^- \) concentrations chlorination becomes very much faster. In \( \text{SbCl}_3-10 \text{ m/o BP(Cl)} \) at 100°C, and 60-19-21 at both 26 and 100°C this effect was so strong that only chlorinated products were found. On the other hand in \( \text{SbCl}_3-6 \text{ m/o KCl} \) at 75°C chlorination and condensation proceeded at similar rates and it is interesting to note that previous SE studies (4), described above, indicate that \( AN^+ \) reacts more slowly in \( \text{SbCl}_3-10 \text{ m/o KCl} \) at 75°C than in a 60-19-21 melt at 26°C. There is also a known case in which a condensation reaction is the dominant mode in \( \text{SbCl}_3-10 \text{ m/o KCl} \) (3). In this case the substrate was 1,2-di-9-anthrylethane and the coupling was intramolecular.

Concluding remarks. — This study demonstrates a close coupling between the acid/base properties of \( \text{SbCl}_3 \)-rich melts and the reaction pathways followed by solute \( \text{AN}^+ \) radical cations. This coupling is rationalized in terms of the wide swing in \( \text{Cl}^- \) donor strength that occurs about the neutral point of these melts and the effect that this has on the rates of chlorination reactions in competition with condensation reactions. This study also demonstrates that in basic melts other compositional factors including the presence or absence of \( \text{BP(AlCl}_4 \) and \( \text{K}^+ \) exert a strong control over the selectivity of chlorination reactions to such a degree that a single isomer can be produced in substantial yields, virtually free of other products. In most other media radical cation halogenations are rarely this selective. Such selectivity suggests potential uses for \( \text{SbCl}_3 \)-rich melts in organic synthesis.

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Figure 1. Structures and notations for anthracene (AN) and the principle reaction products, 9-chloroanthracene (CA), 9,10-dichloroanthracene (DCA), 1,1′-bianthracene (1,1′-BA) and 2,9′-bianthracene (2,9′-BA).

Figure 2. The half-regeneration pathway for oxidative chlorination.

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Figure 3. These reactions, preceded by [2] and followed by [5] (Fig. 2) form the disproportionation pathway for oxidative chlorination.

Figure 4. Reaction stoichiometries for the two observed oxidative chlorination reactions in basic melts.
Figure 5. The radical-radical dimerization pathway to bianthracene.

Figure 6. The cation-neutral dimerization pathway to bianthracene.