CATALYTIC CHEMISTRY AND SPECTROSCOPIC STUDIES OF SbCl₃ MELTS CONTAINING POLYCYCLIC AROMATIC HYDROCARBONS (1)

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Abstract

SbCl₃ melts have been found to catalyze internal hydrogen transfer reactions for polycyclic aromatic hydrocarbons (arenes) under low temperature, aprotic conditions. The catalytic processes are driven by redox reactions in the melt with SbCl₃ acting as an oxidant. Spectroscopic studies indicate that arene radical cations and carbenium ions are important reactive intermediates in the chemistry observed in these melts. Changes in the reaction behavior of arenes in molten SbCl₃ resulting from the addition of a few mole % of a strong chloride donor [CsCl, KCl, (CH₃)₄NCI] or acceptor (AlCl₃) are shown to result from changes in the oxidizing power of the SbCl₃. The reduced form of antimony in melts containing SbCl₃ is a dissolved lower oxidation state species.

Introduction

Our current interest in molten salt catalysis stems from the fact that molten metal halides such as SbX₃ (X = Cl, Br, I), (2) BiX₃ (X = Cl, Br), (2) AsI₃, (2) ZnCl₂ (3) and ZnX₂–CuX (X = Cl, I) (4) have been found to be effective catalysts for the hydrocracking of coal. Furthermore, these catalysts have been shown to have a high selectivity for the production of distillate hydrocarbons, particularly those in the boiling point range for gasoline. These molten salt hydrocracking processes are typically carried out at 350–450°C with from 1800 to 3000 psi hydrogen gas. In addition, these metal halides are usually not free from proton sources, and the catalysis is generally described in terms of proton assisted Friedel–Crafts catalysis. For example, ZnCl₂ has been postulated to form a Brønsted acid, H⁺ (ZnCl₂OH)⁻, with the residual water in the ZnCl₂ (3).

Our research is oriented towards a basic study of molten salt catalysis in an effort to understand how the catalyst functions and what types of reactive intermediates, both organic and inorganic, might be important in the catalytic process. We are presently studying the
chemistry of polycyclic aromatic hydrocarbons (arenes), which are model compounds for some of the structural units of coal, in melts in which SbCl$_3$ is the primary constituent (5,6). SbCl$_3$ melts at 73°C to form a molecular liquid with a relatively high dielectric constant (36.3 at 75°C), and it is an excellent solvent for arenes (7). The low melting point of SbCl$_3$ makes it a convenient medium in which to study the chemistry of dissolved arenes by a variety of physical methods such as nuclear magnetic resonance spectroscopy (NMR) (5,6), electron spin resonance spectroscopy (ESR) (8), and spectroelectrochemistry (9) in an effort to identify possible key reactive intermediates.

We have thus far studied the chemistry of arenes in SbCl$_3$ melts at low temperatures (80-150°C) without added hydrogen gas. Moreover, we worked with highly purified salts under carefully controlled conditions so that the starting systems are essentially aprotic. In this paper, we will summarize results which show that under these reaction conditions, it is the redox properties of molten SbCl$_3$ that drive the catalytic chemistry.

**Catalytic Chemistry**

We studied the reactions of arenes in SbCl$_3$ melts as a function of melt acidity by the addition of chloride ion donors or acceptors. SbCl$_3$ is itself a very weak Lewis acid from which basic melts (chloride rich) can be prepared by dissolution of a strong chloride donor such as CsCl, KCl, or (CH$_3$)$_4$NCl. Acidic melts (chloride deficient) can be prepared by the addition of a strong chloride acceptor such as AlCl$_3$ for which SbCl$_3$ acts as a leveling solvent (10). In addition to altering the Lewis acidity of the medium, the addition of a strong chloride ion acceptor or donor also alters the redox properties of the SbCl$_3$ since the reduction of SbCl$_3$ liberates chloride.

$$\frac{1}{3} \text{SbCl}_3 + e^- \rightleftharpoons \frac{1}{3} \text{Sb} + \text{Cl}^-$$

The effect of added chloride donor or acceptor on the formal potential of the Sb$^{3+}$/Sb couple was measured by electrochemical methods by Bauer and coworkers, (11,12) and the results are shown in Figure 1. The melt composition is indicated along the abscissa with neat SbCl$_3$ in the center. The molar concentration units can be converted to the approximate mol % by multiplying by 10 (e.g. 0.5 M AlCl$_3 \approx 5$ mol % AlCl$_3$). The solid curve drawn through the experimental data points is the Nernst curve based on a model for the autoionization of neat SbCl$_3$. It is clear from the experimental points that the addition of a few mol % of a strong chloride donor (KCl) decreases the formal potential of the Sb$^{3+}$/Sb couple making it a weaker oxidant than in neat SbCl$_3$, while the addition of a few mol % of a strong chloride acceptor (AlCl$_3$) increases the Sb$^{3+}$/Sb formal potential making the couple a stronger oxidant than in neat SbCl$_3$. 

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On the right hand side of Figure 1, several arenes are shown along with their anodic $E^\ddagger$ values measured in SbCl$_3$ melts containing an excess chloride donor (13). The arenes shown are naphthalene (1), acenaphthene (2), pyrene (3), anthracene (4), 9,10-diphenylanthracene (5), 9,10-dimethylanthracene (6), perylene (7), and naphthacene (8). These arenes are listed in order of increasing oxidizability in the melt with naphthalene being the most difficult to oxidize and naphthacene the easiest to oxidize. For naphthalene, the oxidative $E^\ddagger$ lies beyond the anodic limit of the melt ($Sb^{3+} \rightarrow Sb^{5+}$), but from excellent correlations with arene $E^\ddagger$ values measured in other solvents (such as acetonitrile) we estimate the $E^\ddagger$ of naphthalene to be 0.90-0.95 V. Phenanthrene, the simple polycyclic isomer of anthracene, is also very difficult to oxidize and the $E^\ddagger$ for phenanthrene is predicted to fall within this same range. We have studied extensively the reactions of many of these arenes as a function of melt composition, and Figure 1 will provide a convenient reference point for the following discussion of this chemistry.

The reaction behavior of arenes in SbCl$_3$ melts was studied by in situ $^1$H NMR (80 MHz, $^1$H external lock) both with and without (CH$_3$)$_4$N$^+$ as an internal chemical shift reference. Products were identified from larger scale reactions performed in Schlenk-ware under argon following separation and identification procedures which have been previously described (5,6). All material transfers were performed in a controlled atmosphere glovebox.

In neat SbCl$_3$ we found arenes 1-3 to be unreactive in the melt over the temperature range studied, 80-175°C. Although weakly bound arene-SbCl$_3$ complexes are known in the solid state (14) (and have been suggested in the molten state), the $^1$H NMR of these solutions proved to be those of the molecular arenes only. An example is shown in Figure 2 for the case of naphthalene, 1, in SbCl$_3$ at 100°C. The well-resolved spectra for these unreactive arenes were closely similar to the corresponding spectra for solutions in CDCl$_3$ and gave no indication of any complexation with the SbCl$_3$ solvent.

More easily oxidized arenes such as 4, 5, and 8 were reactive in neat SbCl$_3$ and underwent a catalytic reaction (5) which is typified in Figure 3 for the case of anthracene, 4. As indicated, anthracene was found to undergo a disproportionation reaction in which some anthracene molecules were condensed to form primarily 2,9'-bianthracene (loss of two hydrogens), then anthra[2,1-a]aceanthrylene (loss of two more hydrogens). Other anthracene molecules were found to be hydrogenated to form 9,10-dihydroanthracene and then 1,2,3,4-tetrahydroanthracene. The condensation of arenes over Lewis acid catalysts (Scholl reaction) has been known for many years (15). However, it is interesting that this reaction takes place with a Lewis acid catalyst as weak as SbCl$_3$. Furthermore, in earlier Scholl chemistry, the fate of the hydrogen liberated upon condensation was not known. We were able to show that the hydrogen liberated upon the condensation of
anthracene is quantitatively transferred to unreacted anthracene molecules to form the hydroanthracene products described above. Other easily oxidized arenes such as $\Phi$ and $\Phi$ undergo an analogous catalytic hydrogen transfer reaction.

It is interesting that the addition of 3 mol % of a strong chloride donor reduces the oxidizing power of the SbCl$_3$ solvent relative to that of the neat melt. For the most easily oxidized arene, naphthacene $\Phi$, the rate of the catalytic reaction is not greatly affected by the presence of a strong chloride ion donor. These results raise the possibility that the suppression of catalytic activity upon adding a chloride donor may in some fashion be associated with a lowering of the oxidizing power of the melt.

The catalytic chemistry of arenes in acidic melts also suggests that the redox properties of SbCl$_3$ play an important role. Most of the chemistry of arenes in acidic SbCl$_3$ melts that we examined was in melts containing 8-10 mol % (\~0.8 - 1.0 M) AlCl$_3$. As discussed above, this corresponds to a region where the oxidizing power of the SbCl$_3$ solvent has been enhanced. We found that arenes such as $\Phi$ now undergo a noncatalytic reaction which gives much insight into how the catalytic reaction proceeds. This chemistry will be described later during a consideration of the mechanism for the catalytic reactions. Recall that arenes of low oxidizability such as naphthalene, $\Phi$, and phenanthrene were completely unreactive in neat SbCl$_3$. In SbCl$_3$-10 mol % AlCl$_3$, however, they are quite reactive and undergo catalytic hydrogen transfer chemistry, but with a few new features not observed in neat SbCl$_3$. These features will now be described using naphthalene as an example.

From in situ $^1$H NMR and quench and separation studies, we found that naphthalene undergoes a very complicated sequence of reactions in SbCl$_3$-10 mol % AlCl$_3$ at 130°C (again, aprotic conditions and no added hydrogen). A typical gas chromatogram of the reaction products, shown in Figure 4, was obtained on a 30 m x 0.25 mm i.d. glass capillary column coated with an OV-101 liquid phase. Many of these more than 200 products have been identified by combined gas chromatography-mass spectrometry (GC-MS) and by coelution GC studies with standards. The salient features of this complex chemistry can be summarized as follows:

1) Naphthalene is condensed (Figure 5) to form binaphthalenes, benzo(j)-fluoranthene, benzo(k)fluoranthene, and perylene. (2) Some of the hydrogen liberated upon condensation hydrogenates unreacted naphthalene (Figure 5) molecules to form 1-methylindane, 1-methylindene, and tetralin. The presence of these rearranged products (methylindane and methylindene) indicates that the melt now has an isomerization functionality not observed in neat SbCl$_3$. (3) Most surprising of all was the finding that some of the initially formed condensed products (binaphthalenes and benzofluoranthenes) are internally hydrocracked.
in SbCl$_3$-AlCl$_3$, and this is what leads to the complex product mixture shown in Figure 4. This was evidenced by the presence of products such as phenyl and alkyl substituted naphthalenes. Thus, the addition of AlCl$_3$ to SbCl$_3$ melts not only increased the catalytic activity of the melt by increasing the oxidizing power of SbCl$_3$, but it also gave the melt isomerization and cracking functionalities.

Mechanistic Considerations

The catalysis described above produced many products (particularly in SbCl$_3$-AlCl$_3$ melts) and so consisted of many individual reactions occurring both sequentially and in parallel. Taken as a whole the types of products found were those that one gets under conventional Friedel-Crafts catalysis in which strong protic acids serve as catalytic agents. This is illustrated in Figure 6 in which benzene is used to represent the arene that is undergoing condensation. The hydrogen that is liberated by condensation can end up in various places depending on the reaction details.

Arenes are protic bases albeit very weak protic bases. Thus when a strong protic acid is present, there is a fast and reversible acid-base reaction that yields a small concentration of protonated arene, an example of a carbenium ion, as shown in the first step of Figure 6. This carbenium ion is very reactive and condenses with a molecule of starting material. In this step a proton is released for catalytic recycle. The condensed product of this reaction is also reactive and goes on to form a fully aromatized stable product by a series of reactions that are lumped together in the third step. The key feature of this standard mechanism is the catalytic role of the protic acid that activates the rather inert arene by forming a reactive carbenium ion.

In the catalytic reactions that we described above there were no obvious protic acids present. In fact, we took great care to work under aprotic conditions. Nevertheless, reactions that one normally associates with protic acid catalysis took place with unusual ease. How did SbCl$_3$ catalyze these reactions? We suggested earlier in this paper that the catalysis was driven by redox reactions in the melt. However, a stock answer that is often employed in this situation is that there was an adventitious proton source present.

We might have accepted this gratuitous explanation if it were not for the discovery of an unprecedented reaction which demonstrated that SbCl$_3$ can react with arenes to generate, internally, a powerful proton source (6). This is the unusual chemistry we alluded to earlier for arenes $\frac{1}{4}$ in SbCl$_3$-10 mol % AlCl$_3$. The experimental procedures that demonstrated this reaction are similar to those used to examine the catalytic chemistry previously described for $\frac{1}{4}$ and phenanthrene in SbCl$_3$-AlCl$_3$. The major difference is that the arenes
used in the experiments we will now describe were more oxidizable than the ones used in the catalytic studies.

In a typical experiment a few mol % of an arene was dissolved in a mixture of SbCl$_3$ and 10 mol % AlCl$_3$ at 100°C. As soon as mixing was complete, $^1$H NMR spectra were obtained such as those shown in Figure 7. The top spectrum, A, is that obtained for a solution in which anthracene was the starting material. This spectrum can be unambiguously assigned to anthracene protonated in the 9 position as shown. The lower spectrum, B, is that of a solution formed from naphthacene that can be unambiguously assigned to the carbenium ion formed by protonating this molecule in the 5 position as shown. As indicated earlier, similar results were obtained for arenes $^4$, $^5$, and $^6$. By integrating appropriate bands in these spectra with reference to (CH$_4$)$_4$N$^+$ as an internal standard, we found that in all cases 55-65% of the starting material had been protonated. Thus, protons were generated in quantities much too large to be accounted for by impurity proton sources. The protonated arenes of $^4$, $^5$, and $^6$ were unusually stable, and their $^1$H NMR spectra remained unchanged for hours even at 130°C.

All of these arenes are very weak proton bases and can only be protonated on the massive scale that we observed by the presence of some strong protic acid (16,17). This raises the question of what the proton source for this reaction is. The complete reaction stoichiometry was elucidated from the work up of quenched melts and quantitative determination of the products not seen by NMR. A typical case is shown in Figure 8 in which anthracene was the starting material. Several condensed products were found with the one shown, anthra[2,1-a]aceanthrylene, being the major one. The number of moles of protons consumed in forming the protonated anthracene was consistent with the number of moles of hydrogen atoms that were lost upon condensation. More significantly, we recovered finely divided Sb metal, and the number of moles of metal recovered equaled 1/3 of the number of moles of protonated anthracene formed. The recovery of stoichiometric quantities of Sb metal is a clear illustration of the involvement of SbCl$_3$ as an oxidant in arene chemistry in the melt. Similar stoichiometry was observed for the other arenes that underwent this self-protonation reaction.

We also found an exception to this reaction. Perylene, $^7$, is oxidized but, within the times and at the temperatures used in the present study, it did not undergo the condensation/protonation reaction described above to any significant extent. This point will be examined later and a possible explanation for this behavior offered.

We shall now return to the question of how SbCl$_3$, acting as an oxidant, was able to generate a proton source strong enough to protonate a stoichiometric portion of the arene. There is an
alternative mechanism for aromatic condensation, shown in Figure 9, which suggests some possibilities (18). The initial step is the reversible oxidation of the arene (for which benzene is used as a model) to its radical cation. This is followed by an irreversible reaction of the radical cation with another radical cation (second step) or a neutral arene (third step) to form an intermediate charged condensed molecule. In each case, the ipso hydrogen on the charged ring, that is, the hydrogen next to the C-C bond that joins the rings, should be very acidic and protonate unreacted arene molecules. This reaction yields the final condensed product and the protonated starting material.

The key to the mechanism shown in Figure 9 is the ability of the arene to be oxidized to a radical cation by SbCl₃. We used ESR spectroscopy in an effort to find out if the predicted radical cations are in fact formed from oxidizable arenes (8). In order to do this, very dilute solutions were employed in the hope of slowing the downstream reactions of the radical cations. Figure 10 shows typical ESR spectra for three radical cations which are spontaneously formed in SbCl₃-rich melts at 80°C. Only one-half of the acenaphthene, 2, ESR spectrum is shown with the computer simulation of the spectrum given below. The hyperfine structure in these spectra is exceedingly well resolved so that identification of the radical cations is totally unambiguous. From the g-values and hyperfine coupling constants for these radical cations, there is no indication of any unusual medium effects, such as complexation with the solvent. Such high resolution proved to be the rule rather than the exception for the radical cations we observed in these melts.

Figure 1 provides a convenient vehicle for summarizing the ESR results and for identifying a correlation between the occurrence of arene radical cations and the oxidizing power of SbCl₃ as a function of melt composition. We measured the ESR spectra at 80°C of dilute solutions of the arenes shown at the right of the Figure in melts containing 8 mol % (CH₃)₄NCl, in pure SbCl₃, and in melts containing 8 mol % AlCl₃. In melts containing 8% (CH₃)₄NCl, the only arene that was oxidized sufficiently to give a strong, stable signal was the most easily oxidized arene, naphthacene, 8. Arenes 6 and 7 showed fleeting traces of radical cations. No other arene gave a detectable signal. In pure SbCl₃, stable radical cations were found for arenes 5-8, while only a trace of unstable radical cation was observed for anthracene, 4. Arenes 1-3 again gave no observable ESR signal. In SbCl₃ melts containing 8% AlCl₃, stable radical cations were found for arenes 3-8 while acenaphthene, 2, was weakly oxidized. Naphthalene, 4, may have been weakly oxidized in this melt but no spectrum for the parent radical cation was observed. Instead, the ESR spectrum for perylene, 7, (a downstream reaction product) was observed.

These results strongly support the view that SbCl₃ in these melts can oxidize arenes to their radical cations. These results also show
that the oxidizing power of SbCl$_3$ can be tuned, in qualitative agreement with the electrochemical results, by the addition of a strong chloride donor or acceptor. Furthermore, if a dilute solution of an arene in a particular melt results in the oxidation of the arene to its radical cation (stable or unstable), then more concentrated solutions of the arene in this melt will show either catalytic hydrogen transfer chemistry or condensation/protonation chemistry. The type of chemistry that is actually observed will probably depend on the degree of oxidation of the arene in the particular melt being studied. Note that the condensation/protonation reaction (in which the massive reduction of SbCl$_3$ is observed) only occurs for the most oxidizing melt (with added AlCl$_3$) and only for the most oxidizable arenes.

From what has been discussed thus far, one might assume that the arene oxidation reaction would take place at the interface between the melt and Sb metal. However, we found that antimony has lower oxidation states in between 3$^+$ and the metal, and these lower oxidation states form stable solutions in these melts (19). These states occur in the form of different species depending on whether the melt contains an excess of chloride donor (CsCl) or acceptor (AlCl$_3$). When the concentration of the lower oxidation state species becomes sufficiently high, or when these melts are hydrolyzed, the species becomes unstable with respect to disproportionation into metal and 3$. Thus, the oxidation of arenes by SbCl$_3$ in these melts appears to take place homogeneously.

The fact that SbCl$_3$ is reduced to a soluble species rather than the metal requires some modification in the use of Figure 1 for predicting the conditions under which radical cations will form in significant quantities. The potential of the Sb$^{3+}$/lower-state couple will equal that of the Sb$^{3+}$/Sb couple when the lower state species is at the concentration for thermodynamic disproportionation. This concentration is highly dependent on the concentration of chloride donors or acceptors, respectively (19). When the concentration of the lower state species is smaller than that for the disproportionation equilibrium, the potential of the Sb$^{3+}$/lower-state couple will be higher than that of the Sb$^{3+}$/Sb couple. Thus, an arene at a low concentration will be oxidized to a greater extent than would have been predicted from Figure 1. Furthermore, we found that in melts containing AlCl$_3$ there is a substantial kinetic barrier to the nucleation of Sb metal by disproportionation of the lower state. As a consequence one can obtain metastable solutions in which the lower state is present at a concentration much higher than that for the disproportionation reaction. For such metastable solutions the Sb$^{3+}$/lower-state couple will, of course, have a lower potential than that of the Sb$^{3+}$/Sb couple. Thus, when an arene is present at a rather high concentration, the fraction oxidized may be substantially less than would be predicted from an uncritical use of Figure 1 for two reasons: First, the concentration of reduced antimony may substantially exceed that for thermodynamic disproportionation and, second, the reduction of SbCl$_3$ releases chloride ions.
that reduce the concentration of chloride acceptors or increase the concentration of chloride donors, depending on which is initially present in excess.

We are currently studying the chemical and electrochemical oxidation reactions of arenes with the aid of a fast optical multichannel analyzer. Although research is too preliminary to justify an overview at this time, we have observations that address the question of why perylene, \( \mathcal{J} \), is an exceptional case. As was mentioned earlier in this paper, perylene does not undergo oxidative protonation under conditions in which other arenes of similar oxidizability undergo this reaction rapidly. We found that, by a wide margin, perylene yields the most unreactive arene radical cation that we have encountered. When perylene was dissolved in \( \text{SbCl}_3-10 \text{ mol } \% \text{AlCl}_3 \), oxidation took place rapidly and quantitatively (9). However, the downstream reactions of this radical cation occurred at a very slow rate in these melts in comparison with the downstream reactions of the other arene radical cations we studied. The reason for this kinetic barrier is yet to be determined.

The fact that perylene gave such a stable radical cation in the \( \text{SbCl}_3-\text{AlCl}_3 \) melt led us to try another experiment which also gave an unexpected result (9). As indicated above, the dissolution of perylene in \( \text{SbCl}_3-10\% \text{AlCl}_3 \) gave the spontaneous and quantitative oxidation of perylene to its radical cation. The optical spectrum obtained for the perylene radical cation in \( \text{SbCl}_3-\text{AlCl}_3 \) at 135°C is shown in Figure 11, curve a. The radical cation was then electrochemically oxidized to give the optical spectrum shown in curve b of Figure 11, and the optical spectrum can be identified as that of the perylene dication (9). Much to our surprise, this dication is quite stable in dilute solutions in this melt. Other arene dications were also prepared in a similar fashion and, although less stable than the perylene dication, they were stable enough to allow their characterization. These findings are of fundamental importance because arene dications are among the least studied intermediates in organic chemistry. We shall investigate further the chemical properties of these arene dications in halide melts.

**Conclusion**

In this paper we have described the low temperature catalytic hydrogen transfer chemistry that is observed for arenes in melts in which \( \text{SbCl}_3 \) is the primary constituent. Under these aprotic reaction conditions, we were able to show that the driving force for the catalytic chemistry is associated with redox reactions in the melt in which \( \text{SbCl}_3 \) is an oxidant, and arene radical cations are important reactive intermediates. The decrease or increase in the activity of these melts as a function of added chloride donor or acceptor, respectively, is related to the decrease or increase in the oxidizing
power of the SbCl$_3$. Furthermore, combined electrochemistry and optical spectroscopy of dilute solutions of arenes in these melts appears promising for a more detailed investigation of the production and reactions of important arene cationic intermediates.

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Figure 1.
Formal potential of $\text{Sb}^{3+}/\text{Sb}$ couple as a function of melt composition, and anodic $E_\text{a}$ values for selected arenes obtained in SbCl$_3$ melts with excess chloride.

Figure 2.
$^1H$ NMR of naphthalene in SbCl$_3$ at 100°C.

Figure 3.
Principal disproportionation route for anthracene in SbCl$_3$. 
Figure 4. GC profile of the organic products, dissolved in CH$_2$Cl$_2$, from a reaction of naphthalene in SbCl$_3$-10% AlCl$_3$ (130° for 25 min).

Figure 5. Principal route for condensation (upper) and hydrogenation (lower) of naphthalene in SbCl$_3$-10% AlCl$_3$.

Figure 6. Proposed mechanism for proton catalyzed condensation of arenes.
Figure 7. $^1$H NMR of some arenium ions formed in SbCl$_3$-10% AlCl$_3$ at 100°C: (A) anthracenum; (B) naphthacenium.

\[
\begin{align*}
6 \text{C}_10\text{H}_8 + 4/3 \text{SbCl}_3 & \xrightarrow{\text{SbCl}_3-\text{AlCl}_3} 4 \text{C}_8\text{H}_9 + 4\text{Cl}^- \\
+ \text{C}_{10}\text{H}_8 & + 4/3 \text{Sb} + 4\text{Cl}^-
\end{align*}
\]

Figure 8. Condensation-self protonation reaction for anthracene in SbCl$_3$-10% AlCl$_3$ at 100°C.

\[
\begin{align*}
\text{C}_8\text{H}_8 + & \xrightarrow{\text{H}^+} \text{C}_8\text{H}_9^- \\
2 \text{C}_8\text{H}_8 & \xrightarrow{\text{H}^+} \text{C}_8\text{H}_7^- + \text{C}_8\text{H}_7^+ \\
\text{C}_8\text{H}_7^- + & \xrightarrow{\text{H}^+} \text{C}_8\text{H}_6^- \\
\text{C}_8\text{H}_6^- + & \xrightarrow{2\text{H}^+} \text{C}_8\text{H}_5^-
\end{align*}
\]

Figure 9. Proposed mechanism for redox driven condensation of arenes.
Figure 10. ESR spectra of arene radical cations in molten SbCl₃-8% AlCl₃ at 80°C.

Figure 11. Optical spectrum of a solution of perylene in SbCl₃-AlCl₃ at 135°C: (a) before electrolysis showing the perylene radical cation; (b) after electrolysis showing the perylene dication.