REACTIVITY OF ANTHRACENE IN LIQUID SbCl$_3$-AlCl$_3$-N-(1-BUTYL)PYRIDINIUM
CHLORIDE MIXTURES

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Abstract

Mixtures of SbCl$_3$ and N-(1-butyl)pyridinium chloride (BPC1) containing 75-87 mol % SbCl$_3$ and SbCl$_3$-AlCl$_3$-BPC1 mixtures containing 60 mol % SbCl$_3$ and 17-24 mol % BPC1 were found to be liquid at 25°C. Dilute solutions of anthracene were stable in ternary mixtures containing 18 mol % AlCl$_3$, but in mixtures containing 22-24 mol % AlCl$_3$, anthracene reacted under the influence of the solvent, which behaved as both oxidant and H-transfer catalyst. The oxidized product was protonated anthracene, which was stable in this melt. The source of protons was provided by hydrogen-liberating Scholl condensations combined with the reduction of Sb(III). A part of the hydrogen from Scholl reactions reacted with anthracene to form 9,10-dihydroanthracene. By contrast, a liquid mixture without SbCl$_3$, AlCl$_3$-BPC1 (2:1 mole ratio), proved to be a much less active H-transfer catalyst than the SbCl$_3$-rich liquids even though it is a stronger Lewis acid, and it did not induce protonation beyond a trace attributable to protic impurities.

Introduction

Studies of polycyclic aromatic hydrocarbons and hydroaromatics in anhydrous SbCl$_3$-based melts have shown these melts to be extremely active catalysts for a variety of hydrogen redistribution reactions at surprisingly low temperatures, 80-130°C (1-5). This research has revealed that liquid SbCl$_3$ (m.p., 73°C) possesses a previously unrecognized redox functionality and reactions have been observed which involve SbCl$_3$ as an oxidant in both a catalytic (1-3) and stoichiometric (4,5) fashion. The melts investigated previously

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have either been pure SbCl₃ or SbCl₃ with 1-10 mol % of added chloride ion donor such as KCl or chloride ion acceptor such as AlCl₃. The added chloride ion donor reduces the oxidizing power of the melt while the added acceptor increases it.

The development by Osteryoung, et al. (6) of binary room-temperature melts consisting of N-(1-butyl)pyridinium chloride (BPCl) and AlCl₃ led us to investigate the possibility of preparing SbCl₃-rich mixtures that are molten at ambient temperatures. We felt these mixtures might retain the useful properties of the higher melting salts and, at the same time, have the advantage of being liquid under ambient conditions. We found that SbCl₃-BPCl mixtures containing 75-87 mol % SbCl₃ and SbCl₃-AlCl₃-BPCl mixtures containing 60 mole % SbCl₃ and 17-24 mol % BPCl are liquid at 25°C. The ternary mixtures were of particular interest to us because of the possibility of varying the melt acidity and oxidizing power over substantial ranges by making relatively small changes in the AlCl₃:BPCl ratio in the neighborhood of the 1:1 value. Consequently, we undertook investigations of the physical and electrochemical properties of these liquids and of the behavior of organics dissolved in them. The results of the first phases of our study are described in this and the following paper (7). In this paper we describe the reactions of anthracene in liquid SbCl₃-AlCl₃-BPCl mixtures at ambient temperatures. Anthracene was chosen for this investigation because of the extensive research (1,3-5) on its reactivity in SbCl₃-rich, high-melting mixtures.

**Experimental Section**

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**Materials.** — Antimony(III) chloride (Alfa, 99% minimum) was purified by the following procedure. It was first melted under argon and mixed with Sb metal in order to reduce any Sb(V) and with Sb₂O₃ to remove volatile chloride impurities. This was followed by two sublimations under dynamic vacuum and, then, by zone refining a minimum of thirty passes. The resultant colorless crystals melted to give a clear, colorless liquid.

Aluminum chloride (Fluka, puriss), to which 1 wt % purified NaCl was added, was refluxed over high-purity aluminum (Alfa, M6N) for 3 days in sealed quartz ampoules, and then distilled away from the NaAlCl₄ phase. This procedure was repeated twice and the resulting AlCl₃ crystals were then vacuum sublimed through a fine porosity Pyrex frit. The purified AlCl₃ crystals were colorless and melted to form a colorless liquid. The NaCl used in this procedure was prepared from reagent grade material, purified by vacuum drying in the solid state followed by melting and bubbling first HCl and then argon (both high-purity grades) through the melt.
BPC1 was prepared from pyridine (Fisher, certified ACS) and 1-butyl chloride (Matheson, Coleman and Bell, >98%). The starting materials were further purified by distillation from P₂O₅ under argon. The synthetic procedure given by Robinson and Österyoung (8) was followed. As an added precaution, each step was carried out under argon because BPC1 is exceedingly hygroscopic. The product was recrystallized five times under argon from acetonitrile (Fisher, certified ACS) which had been distilled under argon from P₂O₅. In the original procedure (8) ethyl acetate was used in recrystallizing the final product but we omitted this material because we were unable to remove it completely from crystalline BPC1 even after prolonged heating under vacuum at 110°C. The BPC1 was dried under vacuum in the presence of P₂O₅ in a drying pistol at 110°C and the drying pistol was transferred to the glovebox while still under vacuum. During preparation and all subsequent handling, BPC1 was shielded from exposure to light. The water content of the final product was determined by Karl Fischer analysis (Galbraith Laboratories) to be < 0.2%. The elemental analysis (Galbraith Laboratories) showed 62.75% C, 8.06% H, 8.34% N, 20.59% Cl and 0.14% O (calculated values: C 62.97; H 8.22; N 8.16; Cl 20.65). The BPC1 was further analyzed for organic impurities by dissolving a 1-g sample in a small amount of water and then extracting with three 30-ml aliquots of methylene chloride. After drying with CaSO₄ and reducing the volume to 5 ml the methylene chloride was analyzed using a Hewlett Packard model 5880 gas chromatograph equipped with a flame ionization detector and an OV-101, 12-m capillary column. No measurable levels of organic impurities were found in BPC1 that had been purified without the use of ethyl acetate. The melting point of the final product was 132.3-133.1°C (corr.).

Anthracene (Eastman, scintillation grade) was recrystallized from acetic acid and then toluene before sublimation. Analysis by HPLC and GC showed less than 0.1% impurities.

9H-anthracenium heptachlorodialuminate (C₁₄H₁₁Al₂Cl₇) 1 was prepared in Schlenk-ware according to the procedure of Koptyug (9). Thereafter it was stored and handled in a glovebox. The 200-MHz ¹H-NMR spectrum of a solution of this compound in molten SbCl₃-10 mol % AlCl₃ was that of the 9H-anthracenium 2 (the cation of 1, shown in Fig. 2) ion without extraneous peaks.

2-Ethylanthracene (Aldrich, 98%) was recrystallized twice from ethanol. No impurities were detected by GC or HPLC analysis.

Preparation of Solvents and Solutions. — All handling of salts (including weighing on an analytical balance) was carried out in an argon-atmosphere glovebox in which both water vapor and oxygen were monitored instrumentally and kept below 1 ppm by continuous circulation of the atmosphere through a purification train. In preparing the ternary SbCl₃-AlCl₃-BPC1 melts, SbCl₃ and BPC1 were mixed.
to form a binary liquid to which AlCl₃ was slowly added. This procedure allowed dissipation of the heat generated by the AlCl₃-BPCI reaction so that the rise in temperature was only slight. In the preparation of AlCl₃-BPCI melts a substantial temperature rise could not be avoided.

The formal compositions of ternary melts are specified here in terms of mole percentages of the three constituents in the order SbCl₃-AlCl₃-BPCI. Melts for which the mole ratio AlCl₃:BPCI exceeded unity are referred to as acidic while those for which this ratio was less than unity are termed basic.

For the preparation of solutions, anthracene and 2-ethylanthracene were weighed on a microbalance outside of the glovebox while 1 was weighed on an analytical balance in the glovebox. The quantity of solvent (SbCl₃-AlCl₃-BPCI) was determined by analytical weighing in the glovebox. Solvent volume was calculated from the density values reported below.

Density. — The densities of selected ternary compositions were measured by pycnometric weighing in the glovebox at 28°C (60:16:24, 1.998 ± 0.002 g/cm³; 60:19:21, 2.025 ± 0.002 g/cm³; 60:21:19, 2.042 ± 0.002 g/cm³). Values for other compositions were determined by linear extrapolation.

Decomposition Reactions. — The decomposition of anthracene in acidic ternary melts was initiated by mixing a solution of anthracene in a basic 60:19:21 melt with an appropriate amount of an acidic melt. For anthracene solutions at the 150-mM concentration level the extent of reaction was measured by quench and separation at the end of a given reaction period. The same quench and separation procedures were followed as those used previously to study the decomposition of anthracene in SbCl₃-rich melts at elevated temperatures (1). These solutions contained 160-200 mg of solute. Product analysis included antimony metal as well as organics.

Studies of solutions at the 30-mM level included in situ optical spectroscopy (see below) in addition to quench and separation. Product analysis did not include antimony metal because of the small amounts of material involved. After a solution had been prepared, it was divided into two portions. One portion was weighed and left in the glovebox for quench and separation at the end of the reaction period. This portion contained 10 mg or more of solute. The other portion (~1 ml) was loaded into an optical cell (see below) which was then sealed, removed from the glovebox and placed in the spectrophotometer. In several runs, a second 1-ml spectroscopy sample was withdrawn from the quench-and-separation portion after 23 h. The spectrum of this second sample was the same as the 23-h spectrum of the sample that had been removed at the beginning of the run.
Optical Spectroscopy. — Optical absorption spectra were measured either with a Cary 14 or a Cary 219 spectrophotometer. The optical cell, shown in Fig. 1, consisted of a 1-cm pathlength quartz glass cuvette attached by means of a graded seal to a 100-cm long Pyrex glass neck with a #15 Ace threaded glass joint at the top. A quartz glass insert, to which an eyelet was attached, could be lowered into the cell by means of a glass rod with a hook on the end. A Teflon bushing and O-ring provided an air-tight seal. The quartz insert could be rotated so that two different optical pathlengths of about 60 and 110 µm were obtainable. The sample compartments of both spectrophotometers were modified to accommodate these cells. Pathlengths of cells with inserts in place were calibrated using the 373-nm band of K2CrO4 solutions in aqueous 0.05 N KOH [ε = 4842 M⁻¹ cm⁻² (10)]. Measurements were made with at least four independently prepared concentrations of dichromate for each calibration and the results were reproducible to within 0.5%.

ESR Spectroscopy. — The spectrometer, sample tubes and experimental procedures have been described previously (11). All material transfers were performed in a drybox. The loaded sample tubes were sealed under argon on a vacuum line. Concentration of anthracene in the melts was ~5 mM. ESR spectra were obtained at ambient temperatures (22-23°C).

Results and Discussion

Reactions Among Solvent Components. — The SbCl₃−AlCl₃−BPCL mixtures considered here have formal compositions with the following mole fractions: 0.60 SbCl₃, (0.20+a)AlCl₃ and (0.20−a)BPCL, where −0.04 < a < 0.03. Since these components vary enormously in chloride donor/acceptor strength, extensive chloride-exchange chemistry occurs on mixing. Aluminum trichloride is a strong chloride ion acceptor while SbCl₃ is a much weaker chloride ion acceptor and BPCL is a chloride ion donor. Therefore the dominant chloride exchange reaction is

\[
\text{BPCL} + \text{AlCl₃} + \text{BP}^+ + \text{AlCl₄}^-
\]

Since the AlCl₃:BPCL ratio is close to unity for all melts, the liquid may be regarded as consisting of the binary mixture SbCl₃−25 mol % BP(AlCl₄) with relatively small additions of AlCl₃ or BPCL. Pure, molten SbCl₃ is very slightly ionized as shown in Eq. [2] (12).

\[
\text{SbCl₃} \rightarrow \text{SbCl₂}^+(\text{solvated}) + \text{Cl}^-\text{(solvated)}
\]

It is plausible to suppose that the same equilibrium occurs in our low-melting mixtures and is displaced strongly to the left. Likewise, it has been shown that in liquid BPCL−AlCl₃ mixtures at ambient temperatures the AlCl₄⁻ ion is in equilibrium with Al₂Cl₇⁻.
and Cl\textsuperscript{−} ions (13). In our ternary mixtures a similar equilibrium must occur as shown in Eq. [3]

\[ 2\text{AlCl}_4\textsuperscript{−} \rightleftharpoons \text{Al}_2\text{Cl}_7\textsuperscript{−} + \text{Cl}^{−}\text(solvated) \]  

where Cl\textsuperscript{−} is solvated by SbCl\textsubscript{3} molecules. Since Al\textsubscript{2}Cl\textsubscript{7}\textsuperscript{−} is a much stronger chloride ion acceptor than SbCl\textsubscript{3}, the equilibrium in Eq. [3] is strongly displaced to the left. The Al\textsubscript{2}Cl\textsubscript{7}\textsuperscript{−} anion should also be a stronger chloride ion acceptor than SbCl\textsubscript{2}\textsuperscript{+}(solvated) so that the equilibrium in Eq. [4]

\[ \text{Al}_2\text{Cl}_7\textsuperscript{−} + \text{SbCl}_3 \rightleftharpoons \text{SbCl}_2\textsuperscript{+}(solvated) + 2\text{AlCl}_4\textsuperscript{−} \]  

should be displaced to the right. This also appears to be the case in SbCl\textsubscript{3}-AlCl\textsubscript{3} mixtures at elevated temperatures (12). Thus, when AlCl\textsubscript{3} is added to liquid SbCl\textsubscript{3}-BP(AlCl\textsubscript{4}), the dominant acidic species should be SbCl\textsubscript{2}\textsuperscript{+}(solvated) rather than Al\textsubscript{2}Cl\textsubscript{7}\textsuperscript{−}. On the other hand, BP(Cl is expected to dissolve in SbCl\textsubscript{3}-BP(Cl to form BP\textsuperscript{+} cations and Cl\textsuperscript{−}(solvated) anions with the concomitant suppression of the formation of SbCl\textsubscript{2}\textsuperscript{+}(solvated), according to Eq. [2].

In summary, for all of the SbCl\textsubscript{3}-AlCl\textsubscript{3}-BP(Cl compositions considered here, the primary constituents are SbCl\textsubscript{3} molecules, BP\textsuperscript{+} cations and AlCl\textsubscript{4} anions. Secondary constituents are SbCl\textsubscript{2}\textsuperscript{+}(solvated) and Cl\textsuperscript{−}(solvated). When the formal mole ratio AlCl\textsubscript{3}:BP(Cl exceeds unity to a significant degree, the concentration of SbCl\textsubscript{2}\textsuperscript{+}(solvated) is correspondingly increased while that of Cl\textsuperscript{−}(solvated) is greatly suppressed. This situation is reversed when the AlCl\textsubscript{3}:BP(Cl ratio is significantly less than unity. The Al\textsubscript{2}Cl\textsubscript{7} anion is probably no more than a minor constituent in all of the ternary melts considered here.

Optical Spectra. — During the decomposition of anthracene the principal species observed by optical spectroscopy are unreacted anthracene and the anthracenium ion. Therefore, for purposes of both identification and quantification the spectra of these species were measured in SbCl\textsubscript{3}-AlCl\textsubscript{3}-BP(Cl melts under non-reactive conditions.

Fig. 2 shows the spectrum of a 31.1-mM solution of anthracene in a basic 60:18:22 melt and that of a 9.75-mM solution of 9H-anthracenium heptachlorodialuminate \textsuperscript{1} in an acidic 60:22:18 melt. The positions and molar absorptivities of the three maxima in the anthracene spectrum are 347 nm, 4130 M\textsuperscript{−1} cm\textsuperscript{−1}; 366 nm, 4660 M\textsuperscript{−1} cm\textsuperscript{−1}; 384 nm, 3830 M\textsuperscript{−1} cm\textsuperscript{−1}. We attribute these bands to vibronic components of the \textsuperscript{1}L\textsubscript{a} + \textsuperscript{1}A electronic transition (14). By comparison we found that the corresponding bands for anthracene in methanol have as coordinates 339 nm, 5447 M\textsuperscript{−1} cm\textsuperscript{−1}; 356 nm, 8130 M\textsuperscript{−1} cm\textsuperscript{−1}; 375 nm, 7967 M\textsuperscript{−1} cm\textsuperscript{−1}. Other bands in this group that we
shall make use of later have maxima at 309 and 323 nm. The vibra-
tional spacing for all 5 bands is close to 0.14 μm\(^{-1}\). The bands of
anthracene in the molten salt are much broader than those of anthra-
cene in methanol so that the band areas and oscillator strengths are
more nearly comparable than are the molar absorptivities.

The spectrum of the solution of 1 in Fig. 2 consists of an
intense band with maximum at 424 nm and molar absorptivity of 34,500
M\(^{-1}\) cm\(^{-1}\). This is plausibly attributed to the 9H-anthracenium
cation 2, the structure of which is shown in the figure. The
spectrum of this ion in anhydrous HF at 25°C (15) has a similar band
at 408 nm (37,400 M\(^{-1}\) cm\(^{-1}\)) while in concentrated H\(_2\)SO\(_4\) at 25°C (16)
the band maximum is at 424 nm (ca. 30,000 M\(^{-1}\) cm\(^{-1}\)).

Spectral data and the results of analysis by hydrolysis and
separation show that both the solution of anthracene in the basic
melt and that of 1 in the acidic melt are stable. Their spectra
remained unchanged after 24 hr. Following hydrolysis of the anthra-
cene solution, the starting material was recovered and no decom-
position products were found. Hydrolysis of the solution of 1
resulted principally in the deprotonation of 1 and led to recovery
of anthracene equivalent to 85% of the starting material. A simi-
lar recovery factor was found when solutions of 1 in SbCl\(_3\)-10 mol %
AlCl\(_3\) were hydrolyzed by the procedure used here.

**Anthracene Decomposition Reaction.** — We found that the reac-
tions by which anthracene decomposes in acidic SbCl\(_3\)-AlCl\(_3\)-BP\(_3\)Cl
mixtures at 28-40°C are closely related to those that occur in
SbCl\(_3\)-rich melts at 80-175°C. These elevated-temperature reactions
are of two types. First, in SbCl\(_3\)-10 mol % AlCl\(_3\), anthracene reacts
rapidly and completely with the solvent in a redox process that is
schematically illustrated in Eq. [5]\(^*\) (4). The oxidized product is
the 9H-anthracenium ion 2, produced in 55-65% yields. The source of
protons for this product is a combination of Scholl-type
condensation-dehydrogenation reactions and the reduction of Sb(III).
The dominant condensed product is anthra[2,1-a]acenaphthylene 3, pro-
duced in yields of ~20 wt % of the starting anthracene. The
remaining organic material (~15-25 wt %) consists of a variety of
condensed compounds. The accompanying reduction reaction converts
Sb(III) into a lower oxidation state, which, when hydrolyzed,
disproportionates into Sb metal and Sb(III) (17). Stoichiometry
requires that the mole ratio 2:Sb(metal) be 3:1.

The second type of reaction occurs when anthracene is dissolved
in SbCl\(_3\) without AlCl\(_3\). This reaction is a relatively slow catalytic
hydrogen-transfer with the melt serving as solvent/catalyst (1).

\(^*\)This equation is at the end, with the figures.
Part of the anthracene is hydrogenated to form mostly 9,10-dihydroanthracene and the source of hydrogen is Scholl-type condensation-dehydrogenation reactions. A wide variety of condensed products is formed, including 3, but no single product predominates.

In the present study we find that both of the above types of reactions occur simultaneously for anthracene in acidic SbCl$_3$-AlCl$_3$-BPCI mixtures at 28-40°C. Evidence regarding the formation of 2 comes from the optical spectroscopic measurements. As noted earlier, this cation is destroyed by hydrolysis so that its presence in the melt cannot be established by quench and separation. The spectra in Fig. 3 are typical of those obtained when ~30 mM anthracene reacts in the acidic melt during a 23-h run at 28-30°C. These spectra are referenced to air and can be converted to absorbance by subtracting the curve labelled solvent. The solvent melt was quite transparent except at the shortest wavelengths so that over most of the wavelength-range in Fig. 3 the apparent absorption of the solvent consists of light losses due to reflections at cell windows.

After 20 min reaction time, the concentration of anthracene fell to ~95% of its starting value of 34.4 mM. A shoulder at ~420 nm is attributed to 2 at a concentration estimated to be 1-2 mM. Bands at 510 and 530 nm are due to unidentified reaction products. With increasing time absorption due to anthracene slowly decreased while that due to 2 slowly increased along with bands due to other reaction products at longer wavelengths. At the end of 1380 min (23 h) some anthracene remained but the concentration could not be evaluated accurately because of interference from the band of 2. The concentration of 2 reached ~7.5 mM, which is 22% of the initial anthracene concentration.

Identified substances obtained from quench and separation were the following: anthracene (partly unreacted starting material and partly from the hydrolysis of 2); 3; 4; 4 isomers of bianthracene, grouped together here as 5 (2,9'-isomer produced in highest yield); a dihydroanthraaceanthrylene 6, (not identified as to isomer); and antimony metal (recovered only for runs at the 150 mM-concentration level). In addition small quantities of unidentified products (usually ~5 wt % of the initial anthracene) were obtained and when the HPLC column was washed with CH$_2$Cl$_2$, some highly condensed material came off.

Quench and separation was performed for 8 runs, each terminated after 23 h. Five of these runs were made with 60:22:18 melts at

*Structure displayed at the end, with the figures.
28-30°C and used initial anthracene concentrations of 31, 34, 34, 141 and 157 mM. One run was made with a 60:22:18 melt at 40°C and an initial concentration of 31 mM, while 2 runs were made with slightly more acidic 60:23:17 melts at 28-30°C and initial concentrations of 28 and 139 mM. The only substantial differences in the relative amounts of substances recovered from these runs was between those with initial concentrations of 28-34 mM and those with initial concentrations of 139-157 mM. Table 1 summarizes the 5 runs made with 60:22:18 melts at 28-30°C. In this table the amounts of substances are given as wt % of the initial weight of anthracene.

Results for the three runs with initial concentrations of 31, 34 and 34 mM are averaged under the column headed ~30 mM and those with initial concentrations of 141 and 157 mM are averaged under ~150 mM. Typical of deviations about the average values were those for anthracene, namely: 57-67% and 27-30%, respectively. The amounts of anthracenium ion for runs with initial concentrations of ~30 mM were obtained from optical spectra and those for the other runs were calculated from the amounts of Sb metal recovered from quench and separation (moles of anthracenium = 3 × moles of Sb).

Table 1. Substances recovered from anthracene decomposition in liquid SbCl$_3$-AlCl$_3$-BPcI(60:22:18) after 23 h at 28-30°C.

| Substance                              | Amount (wt %) |
|----------------------------------------|---------------|
|                                        | ~30 mM        | ~150 mM       |
| Anthracene                             | 63            | 29             |
| Dihydroanthracene 4                    | 4             | 10             |
| Dianthracenes 5                        | 11            | 11             |
| Anthracene[2,1-a]aceanthrylene 3       | 3             | 4              |
| Dihydroanthraceneaceanthrylene 6       | 2             | 13             |
| Anthracenium ion 2                     | 20            | 14             |
| Highly condensed material              | trace         | large          |

The anthracene recovered from quench and separation consisted of unreacted starting material plus that regenerated from hydrolysis of the anthracenium ion. We estimate a recovery factor of 85% for hydrolysis, hence the amounts of unreacted anthracene were on the order of 43-47% and 15-18% for initial concentrations of ~30 mM and ~150 mM, respectively. Identified products typically accounted for ~80% of the starting material for the former and ~70% for the latter concentration. In both cases an additional amount of material (~5%) consisted of small amounts of various unidentified products observed.
during chromatography. The highly condensed material accounted for an appreciable part of the remainder in runs with initial concentrations of ~150 mM, but very little of this material was found for runs with initial concentrations of ~30 mM.

These results show that a part of the hydrogen lost in forming condensed products was consumed in forming hydroarenes while the rest was consumed in protonating anthracene. The same reactions occurred in melts with initial anthracene concentrations of 31-157 mM. At the higher concentrations the conversion of anthracene was greater and relatively less protonated product formed than at the lower initial concentration. Thus, the decomposition of anthracene in acidic SbCl$_3$-AlCl$_3$-BP Cl melts proceeded by a combination of the same types of reactions found at elevated temperatures in SbCl$_3$-10 mol % AlCl$_3$ and in SbCl$_3$ alone. It is as though the low-melting mixtures were intermediate in oxidizing power to SbCl$_3$ with and without 10 mol % AlCl$_3$. Further evidence that this is, in fact, the case is provided by the ESR studies described below and the EMF studies in the following paper (7). The reactions in the low-melting mixtures at 28-40° were very much slower than those at higher temperatures in SbCl$_3$ and SbCl$_3$-10% AlCl$_3$.

ESR Spectra. — The fact that Sb(III) in acidic SbCl$_3$-AlCl$_3$-BP Cl melts acts as a mild oxidizing agent toward anthracene was established by the recovery of Sb metal. It is interesting, therefore, that we were also able to identify the presence of the anthracene radical cation in these solutions by means of ESR spectroscopy. Dilute solutions (~5 mM) of anthracene in two acidic melts, 60:22:18 and 60:21:19, were examined by ESR at ambient temperatures (22-23°C). In both cases the ESR spectrum of the anthracene radical cation was observed, and the measured proton hyperfine coupling constants ($a_1 = 3.05$, $a_2 = 1.37$, and $a_9 = 6.47$ G) were similar to those measured in SbCl$_3$-8 mol % AlCl$_3$ at elevated temperatures (11). However, these spectra were much less intense than the corresponding anthracene radical cation spectrum observed in SbCl$_3$-8 mol % AlCl$_3$, suggesting that the SbCl$_3$-AlCl$_3$-BP Cl melts are weaker oxidants. EMF studies presented in the following paper support this conclusion (7). Thus, the acidic SbCl$_3$-AlCl$_3$-BP Cl melts can act as oxidants toward anthracene producing radical cations that may be key reactive intermediates in the protonation-condensation reaction as previously proposed for arenes in SbCl$_3$-10 mol % AlCl$_3$ (4).

Anthracene in AlCl$_3$-BP Cl (2:1). — The important role that SbCl$_3$ played in the anthracene decomposition reactions in acidic SbCl$_3$-AlCl$_3$-BP Cl melts is emphasized by comparison with the behavior of this solute in a solvent containing only AlCl$_3$ and BP Cl. For this comparison we chose the formal composition AlCl$_3$-BP Cl (2:1), which is, in fact, the liquid compound N-(1-butyl)pyridinium heptachlorodialumininate BP Al$_2$Cl$_7$ (13). This is a very strong Lewis acid
and if Lewis acidity in combination with such protonic impurities as our melts may contain is sufficient to catalyze the decomposition of anthracene, then the 2:1 melt should be a very active catalyst.

Studies using optical spectroscopy and quench and separation were carried out on a 35-mM solution of anthracene in the 2:1 melt and followed the same general procedures used with acidic SbCl₃-AlCl₃-BPCl melts in so far as possible. The calculation of concentrations was based on the value 1.33 g cm⁻³ for the density of the melt (19). The reaction temperature was 30°C, the time to quench was 24 h, and optical spectra were measured at intervals from 0.5 h to 29 h after mixing and included a spectrum taken at the time of quench.

After quench and separation the only substances found in more than trace amounts were anthracene (78 wt %), 4 (2 wt %) and 5 (6 wt %). No more than a trace of highly condensed material was found when the HPLC column was washed with CH₂Cl₂. Spectra measured after 0.5 h and 24 h are shown in Fig. 4. These are referenced to air and can be converted to solute absorbance by subtracting the curve labelled solvent. In between 0.5 and 24 h the spectra changed slowly and progressively, never exceeding the extremes shown in the figure. The spectrum measured at 29 h was almost indistinguishable from that measured at 24 h.

The AlCl₃-BPCl solvent melt transmitted further into the ultraviolet than did SbCl₃-AlCl₃-BPCl mixtures so that for the anthracene solution 5 vibronic bands of the 1₁₄ + 1A electronic transition were exposed at 312 (sh), 328, 344, 362 and 381 nm with a 0.14 μm⁻¹ vibrational spacing. These are slightly red shifted with respect to the corresponding bands of anthracene in methanol (see above), and the 344, 362 and 381-nm bands are very close to the corresponding bands for anthracene in SbCl₃-AlCl₃-BPCl. Assuming the concentration of anthracene after 0.5 h to be 35 mM or slightly less, the molar absorptivity of the 362-nm band is calculated to be about 6 x 10³ M⁻¹ cm⁻¹. This value is intermediate to those for anthracene in methanol and in SbCl₃-AlCl₃-BPCl, respectively, which is in keeping with the fact that the band widths for anthracene in the 2:1 melt are likewise intermediate.

The only absorption in the 0.5-h spectrum not attributable to anthracene was a band at ~420 nm that we attribute to 2. Assuming that the molar absorptivity of 2 has a value similar to that for 2 in SbCl₃-AlCl₃-BPCl, we estimate that its concentration in AlCl₃-BPCl was ~1 mM. This small amount of 2 probably came from impurity proton sources. With increasing time the concentration of 2 diminished although a small amount persisted after 24 h.
The only product absorption (other than 2) found after 24 h was a very broad band centered near 640 nm. This does not correspond to either of the major products found on quench and separation; the bands of 4 should lie well out of range in the UV and those of 5 should lie in the same general region as the anthracene bands. The most reasonable source of the 640-nm absorption is a trace of a highly condensed arene in a protonated or oxidized form. Such cations usually have intense absorptions in the visible range and the parent arenes are usually more easily protonated and oxidized than anthracene, 4 or 5.

The long-wavelength absorption bands of bianthracenes in methanol were found to be very similar to those of anthracene in the same solvent. Among other small differences, they were somewhat red shifted. Assuming that a similar state of affairs holds in the 2:1 melt, the absorption in the 300-400 nm region of the spectrum after 24 h was what one would expect for a mixture of anthracene and 5 in the ratio found on quench and separation with an anthracene concentration reduced to roughly 80% of its initial value.

Thus we find that the 2:1 melt, unlike the acidic SbCl₃-AlCl₃-BPCI melt, did not promote the oxidative protonation of anthracene to an appreciable extent. It did catalyze the Scholl condensation-dehydrogenation reaction (to form 5) accompanied by a partial hydrogenation of the substrate (to form 4), but even for these reactions the 2:1 melt was not nearly as active a catalyst as the less acidic melts containing SbCl₃.

Effects of Impurities. — Because of the low concentration of anthracene used in the spectrometric studies, we found it necessary to pay close attention to the effects of impurities. Thus, it was not until water and ethyl acetate were identified and eliminated as impurities in BPCI that we obtained consistently reproducible results. Since BPCI is a widely used constituent in low-melting salt mixtures and since studies of the spectroscopy and electrochemistry of solutes in these melts is commonly done at low concentrations, we describe what we learned about impurity effects.

We found that when BPCI was dried by a less rigorous procedure than that described above and then used to prepare acidic SbCl₃-AlCl₃-BPCI melts, solute anthracene was protonated at a much faster rate and the concentration of 2 reached a much higher level than it did in the reactions described above. When BPCI was dried under vacuum over P₂O₅ at 110°C for progressively longer times, the amounts of 2 diminished. The concentration level for promptly formed 2 achieved after prolonged drying was about 1-2 mM and this we attribute to impurities (not necessarily water).

In the literature procedure (8) for the preparation of BPCI, ethylacetate is used as a cosolvent along with acetonitrile in the

259
recrystallization of the product. In our initial experiments, which followed this procedure, an unknown product was observed in 16% yield from the reaction in an acidic room temperature melt containing 11 mM anthracene. This product was identified by GC-MS as three isomeric ethylanthracenes. The ethyl group could not have come from the fragmentation of anthracene since no other fragments of the parent arene were found. It is well known (18) that esters will alkylate arenes in organic solvents with a Lewis acid present as catalyst. Analysis of the BPC1 showed that the small ethylacetate content of the sample could account for all of the ethylanthracene found in the reaction of anthracene in the acidic SbCl₃-AlCl₃-BPC1 mixture. Vacuum drying of the BPC1 crystals resulted in a decrease in the ethylacetate content and thus in the yield of ethylanthracene. However, traces of ethylacetate remained even after a week of drying. To determine whether the presence of ethylacetate and thus ethylanthracene would significantly effect our results, the reaction of 2-ethylanthracene was followed spectroscopically in the acidic, room temperature melts under the same conditions utilized for the reaction of anthracene. Protonated ethylanthracene was formed and found to absorb at 424 nm (the same wavelength observed for the anthracenium ion). In addition ethylanthracene reacted more rapidly than anthracene, probably because ethylanthracene is more easily oxidized and protonated than anthracene. Since the presence of ethylanthracene would obviously interfere with the investigation of the anthracene reaction, all subsequent purifications of BPC1 excluded the use of ethylacetate.

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6 + 4/3 SbCl₃ → 4

2

+ + 4/3 Sb + 4 Cl⁻
Fig. 1. Optical cell. A, Pyrex glass rod with hook; B, threaded Teflon bushing; C, threaded Pyrex glass joint; D, FETFE O-ring; E, quartz glass insert; F, quartz glass optical cell.

Fig. 2. Spectra of anthracene and the 9H-anthracenium ion in SbCl₃-AlCl₃-BPCl melts with compositions of 60:18:22 and 60:22:18, respectively.
Fig. 3. Spectra measured during the decomposition of anthracene in an SbCl₃-AlCl₃-BPCl (60:22:18) melt at 30°C together with the spectrum of the solvent. All spectra referenced against air.

Fig. 4. Spectra measured during the decomposition of anthracene in an AlCl₃-BPCl (2:1) melt at 30°C together with the spectrum of the solvent. All spectra referenced against air.