CHEMICAL REACTIONS AMONG THE COMPONENTS IN SbCl₃-AlCl₃-Sb MELTS

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Abstract

Although mixtures of SbCl₃, AlCl₃ and Sb metal are unreactive and mutually insoluble in the solid state, the electrical conductivity of molten SbCl₃-AlCl₃ mixtures and the substantial solubility of Sb metal in these molten mixtures show that reactions occur in the liquid state. We review research on these and related subjects in an effort to gain insight into what the underlying reactions might be.

Introduction

The SbCl₃-AlCl₃-Sb system is unusual. All available data indicate that the components are thermodynamically unreactive and mutually insoluble in the solid state. However, upon melting, SbCl₃ and AlCl₃ react readily and Sb metal dissolves in this liquid mixture, presumably through a reaction with SbCl₃ to form intermediate oxidation states. In this paper we review evidence pertaining to the kinds of entities that may be formed in these reactions. Our interest in this subject is derived from the use of SbCl₃-AlCl₃ melts as reaction media for organic substances. These melts serve as solvent/catalysts and as solvent/oxidants in which a variety of unusual organic reactions occur (1). When acting as oxidants, the reduced species in the melt are presumably the same as those formed upon dissolving antimony metal.

Properties of Antimony(III) Chloride

Antimony(III) chloride melts at 73.2°C and its normal boiling point is about 222°C (2). The melt is a molecular liquid not unlike water in its physical properties. It has a low viscosity (0.0184 poise at 99°C), a high dielectric constant (34.0 at 99°C), a low

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degree of auto-ionization (specific conductivity, $\kappa < 8.5 \times 10^{-7}$ S cm$^{-1}$ at 99°C), and is a good solvent for inorganic solutes.

X-ray and neutron diffraction data on the liquid at 80°C show it to consist of pyramidal SbCl$_3$ molecules with a significant degree of intermolecular association (3). Bond distances and angles are 235 pm and 96°, respectively, as compared with 233 pm and 100° for the gas phase species (4). (In this review bond distances are rounded to the nearest pm and bond angles to the nearest deg.) These molecules are associated in short chains with their dipole axes strongly correlated so that, on the average, the first coordination sphere of any given Sb atom contains, in addition to its three intramolecular Cl atoms at 235 pm, three other Cl atoms at 340 pm, which belong to another SbCl$_3$ molecule. The distance 340 pm is significantly shorter than 400 pm, the sum of the van der Waals radii (5), so that the intermolecular force between associated pairs of molecules must be much stronger than the van der Waals forces between unassociated molecules. The Raman spectrum of liquid SbCl$_3$ has been measured over wide temperature and frequency ranges, and the results lend strong support to the view that the melt is an associated liquid, not unlike hydrogen-bonded liquids (6).

The association between SbCl$_3$ molecules in the liquid phase is a manifestation of the general tendency for SbCl$_3$ to act as a chloride ion acceptor. In recent years a large number of crystal structures have been determined for binary compounds formed between SbCl$_3$ and chloride ion donors, such as alkali metal chlorides and alkylammonium chlorides (7). The first coordination sphere of antimony usually contains six, sometimes five, chlorine atoms at distances significantly less than the sum of the van der Waals radii. These bonded chlorine atoms are usually arranged with a distorted octahedral geometry. Two complex anions have been found, SbCl$_6^{3-}$ (exactly octahedral) and SbCl$_5^{2-}$, but in most crystals antimony completes its coordination shell by sharing chlorine atoms with other antimony atoms. The result is usually a polymeric chloroantimonate chain or network of infinite extent rather than finite molecular ions.

Bond distances in chloroantimonate(III) compounds span a wide range from about 230 pm to 370 pm without apparent preference for special values. There is, however, a correlation between the lengths of bonds that are trans to one another. Trans bonds of nearly the same length generally lie in the 260-270 pm range, while bonds significantly shorter than this are nearly always trans to bonds that are significantly longer.

Because there are some important analogies between the SbCl$_3$-AlCl$_3$ system and the SbBr$_3$-AlBr$_3$ system, we note that bonding in bromoantimonate(III) crystals is qualitatively like that in chloroantimonate(III) crystals (8).
Properties of Aluminum Chloride

The properties of liquid aluminum chloride and its mixtures with chloride ion donors are covered by other papers in this Symposium so that we limit our comments to a few facts. Crystalline AlCl₃ has a compact layer lattice with 6-fold coordination about aluminum but upon melting at 192.4°C a major atomic rearrangement occurs. The resulting liquid phase consists of Al₂Cl₆ molecules with 4-fold coordination about aluminum and with pairs of aluminum atoms linked by two chlorine atom bridges (9). Although liquid aluminum chloride is at most only slightly auto-ionized (κ < 1 × 10⁻⁷ at 200°C), it readily reacts with chloride ions from donor sources to form ionic melts containing small chloroaluminate anions, such as AlCl₄⁻, Al₂Cl₇⁻ and Al₃Cl₁₀⁻. Liquid aluminum bromide also consists of dimeric molecules, Al₂Br₆, and has a low electrical conductivity, but in this case the crystal also contains these Al₂Br₆ units rather than the close-packed geometry of AlCl₃.

The SbCl₃-AlCl₃ Reaction

The SbCl₃-AlCl₃ phase diagram has a simple eutectic without solid compound formation (10) while the SbBr₃-AlBr₃ phase diagram shows a low-melting 1:1 compound (10a). This formation of a crystalline compound in the bromide system but not in the chloride system has been attributed to the much higher lattice energy of crystalline AlCl₃ as compared with AlBr₃ (11). On the other hand, the liquid phases of both systems show ionic conduction so that in both cases a halide-exchange reaction occurs on melting. Conductivity data are given in References 11 and 12 for the SbCl₃-AlCl₃ system and in References 13-15 for the SbBr₃-AlBr₃ system. Some examples of the conductivity of these melts are shown in Fig. 1. Data for the chloride system are limited to the compositional range shown in this figure while data for the bromide system extend all the way to AlBr₃.

Even before much was known about the structures of haloantimony(III) entities, it was recognized that aluminum(III) is such a strong halide ion acceptor that any ionizing reaction between SbX₃ and AlX₃ (X = Cl or Br) must involve a halide transfer from antimony to aluminum. On this basis it was postulated that the charge transporting entities are SbX₂⁺ and AlX₄⁻. Furthermore, from conductivity data for dilute solutions of AlX₃ in SbX₃ and cryoscopic i values in the bromide case, it was concluded that ionization is incomplete (12, 15). Additional evidence for ion pairing or neutral molecule formation comes from the temperature dependence of the conductivity. As shown in Fig. 2, the conductivity of SbCl₃-AlCl₃ mixtures containing 2.5-10 mole % passes through a maximum with changing temperature (11). The temperature at which the maximum occurs increases with increasing AlCl₃ content so that there
may be a maximum beyond the temperature range investigated for 
AlCl₃ concentrations above 10%.

Temperature dependence data for the bromide system are much 
more limited but a conductivity maximum was found for an AlBr₃-rich 
melt containing 88.26 mol % AlBr₃ (13). Such temperature maxima for 
conductivity also occur for various other liquid systems, and it is 
generally believed that these result from ion pairing or neutral 
molecule formation that is aided by expansion of the liquid with 
increasing temperature. Substantial support for this view is pro-
vided by studies of the effect of pressure on conductivity at ele-
vated temperatures (16).

NQR spectra of the crystalline adduct SbBr₃·AlBr₃ showed the 
presence of a V-shaped SbBr₂⁺ moiety and a distorted tetrahedral 
AlBr₄⁻ moiety with antimony also weakly bonded to bromine atoms of 
AlBr₄⁻ (17). Although crystalline SbCl₃·AlCl₃ is unknown, the 
crystal structure of the adduct SbCl₃·GaCl₃ serves as a reasonable 
model since GaCl₃ and its mixtures with chloride ion donors form 
entities in the liquid phase that have structures quite similar to 
those formed by AlCl₃. The structure of SbCl₃·GaCl₃ (18) is similar 
to that of SbBr₃·AlBr₃ and the SbCl₂⁺ and GaCl₄⁻ moieties are 
strongly bonded through chlorine bridges formed by the chlorine 
atoms of GaCl₄⁻. A diagram of the coordination sphere of antimony 
is shown in Fig. 3. It contains 4 chlorine atoms. Two of these 
with medium bond lengths of 271 and 277 pm are trans related and 
also belong to the coordination sphere of gallium. The other two, 
with very short bonds of 230 pm, belong only to antimony and form a 
bond angle of 97°. The latter have no trans partners. The geometry 
of the GaCl₄⁻ moiety is that of a very distorted tetrahedron. Each 
SbCl₂⁺ moiety is bonded to two GaCl₄⁻ moieties so as to form zig-zag 
chains of indefinite length.

These considerations suggest the following representation for 
the entities in antimony trihalide-rich melts

\[ \text{SbX}_2\text{AlX}_4 + n\text{SbX}_3 \neq \text{SbX}_2^+ \cdot n\text{SbX}_3 + \text{AlX}_4^- \]

where \(X = \text{Cl or Br}\). Solvation is explicitly indicated for SbX₂⁺ 
because it is probably more than a weak association, but the other 
entities are also probably solvated via long halogen bridge bonds.

Charge Transport Mechanism in SbCl₃·AlCl₃ Melts

The addition of NaCl to SbCl₃-rich melts in amounts equivalent 
to or less than the AlCl₃ content results in a substantial decrease 
in the specific conductivity despite the small size of the Na⁺ ion 
(11). Possibly the presence of these small ions causes some sort of 
structural lock-up that greatly reduces ionic mobility, but a
simpler explanation is that charge transport in SbCl$_3$-rich SbCl$_3$-AlCl$_3$ melts takes place by a non-Stokesian chloride exchange process in which the SbCl$_2^+$ moieties play a key role. The addition of NaCl removes these moieties by the reaction

$$\text{SbCl}_2^+ + \text{Cl}^- \rightarrow \text{SbCl}_3$$

and leaves only the less effective diffusive motions of Na$^+$ as a means of charge transport. The following sequence represents an elementary step in the envisaged exchange process

| Initial state: | Cl$_2$Sb$^+$ ——— ClSbCl$_2$ |
| Transition state: | Cl$_2$Sb$^+$ — Cl$^-$ — SbCl$_2^+$ |
| Final state: | Cl$_2$SbCl ——— SbCl$_2^+$ |

The known variability of the Sb-Cl bond length suggests that the transition state does not represent a particularly high activation energy barrier. The fact that SbCl$_3$ molecules tend to form short chains with their dipoles oriented in the same direction offers the possibility of rapid chloride exchange along such a chain. A more complete set of arguments is given in the original paper (11).

Auto-Ionization of SbCl$_3$

Closely related to the above subjects is the auto-ionization of SbCl$_3$. The simplest representation of such a process is

$$\text{SbCl}_3 \rightarrow \text{SbCl}_2^+(\text{solvated}) + \text{Cl}^-(\text{solvated})$$

in which the solvation forces are very strong and could be viewed as intramolecular forces rather than intermolecular forces. However, there is no objective evidence as to specific formulae for the molecular ions formed. Certainly an earlier formulation in which Cl$^-(\text{solvated})$ was represented as the anion SbCl$_4^-$ (2) must be regarded with skepticism since antimony never has such low a coordination number in anionic chloroantimonate(III) complexes in crystals.

The potential of the Sb$^{3+}$/Sb couple was measured at 99°C in molten SbCl$_3$ containing various amounts of KCl to increase the Cl$^-(\text{solvated})$ activity and various amounts of AlCl$_3$ to increase the SbCl$_2^+(\text{solvated})$ activity (19). Antimony immersed in SbCl$_3$ saturated with KCl served as the reference electrode. In order to fit these data to a Nernst equation in which the concentration of Cl$^-$ served as the only composition variable, the concentration of SbCl$_2^+$ was eliminated by choosing a suitable value for the ion product constant.
\[ K_f = [\text{SbCl}_2^+]\text{[Cl}^-\text{]} \]

The value \( \log K_f = -7.8 \pm 0.5 \) at 99°C gave a satisfactory fit. However, this value is inconsistent with that obtained from conductivity data, namely, \( \log K_f < -10.5 \) at 99°C (2). The reason for such a large discrepancy is unknown but one possibility is the presence of the junction potential.

The solvated \( \text{Cl}^- \) anion has an abnormally high mobility in \( \text{SbCl}_3 \) and is believed to carry most of the current in mixtures where it is present (2). For solutions of KCl and NH\(_4\)Cl in \( \text{SbCl}_3 \) transport numbers have been directly determined and that for the chloride ion is about 0.9 at 99°C. A non-Stokesian chloride-exchange transport mechanism is clearly a plausible explanation for this high mobility.

### Solubility of Antimony Metal in \( \text{SbCl}_3-\text{AlCl}_3 \) Melts

Antimony metal has a very low solubility in molten \( \text{SbCl}_3 \) [mole fraction of \( 1.8 \times 10^{-4} \) at 273°C (20) and \( 2.5 \times 10^{-4} \) at 405°C (21)] but when \( \text{AlCl}_3 \) is added to the melt, the solubility of Sb becomes substantial. Measurements have been reported (21) over the temperature range of 235-430°C and representative isotherms are shown in Fig. 4 where \( X_{\text{Sb}} = \frac{n_{\text{Sb}}}{(n_{\text{Sb}} + n_{\text{SbCl}_3})}, \)
\[ X_{\text{AlCl}_3} = \frac{n_{\text{AlCl}_3}}{(n_{\text{AlCl}_3} + n_{\text{SbCl}_3})} \]
and \( n \) is the number of moles. The temperature dependence of this solubility is small and passes through a maximum except at low \( \text{AlCl}_3 \) concentrations. There is no direct evidence regarding the species formed by Sb in solution, but it is plausible to suppose that a reaction occurs between the metal and \( \text{SbCl}_3 \) to form entities in oxidation states intermediate to 3+ and zero. The important role of \( \text{AlCl}_3 \) strongly suggests that the \( \text{Sb} / \text{SbCl}_3 \) reaction is accompanied by a substantial release of chloride ions.

Antimony metal has a much higher solubility in \( \text{SbI}_3 \) than in \( \text{SbCl}_3 \) and the addition of \( \text{AlI}_3 \) to \( \text{SbI}_3 \) has little effect on this solubility (22). Studies of \( \text{SbI}_3-\text{Sb} \) melts provide strong evidence that the reaction
\[ 2\text{Sb} + 4\text{SbI}_3 + 3\text{I}_2\text{Sb-SbI}_2 \]
takes place, where the \( \text{I}_2\text{Sb-SbI}_2 \) molecule is presumed to be structurally similar to \( \text{I}_2\text{As-AsI}_2 \) and \( \text{I}_2\text{P-PI}_2 \). It is reasonable to suppose that the chlorine analog, \( \text{Cl}_2\text{Sb-SbCl}_2 \), is the dominant species when Sb dissolves in \( \text{SbCl}_3 \) alone or with a low concentration of \( \text{AlCl}_3 \) but the occurrence of this neutral species does not account for the large effect that \( \text{AlCl}_3 \) has on Sb solubility.
Bismuth, the Group V element immediately below Sb, forms several homopolynatomic cluster ions with formal oxidation states in between 3+ and zero, and the structures of most of these are known from X-ray crystallography (23). They include Bi₅³⁺, Bi₂²⁺, and Bi₉⁵⁺. These ions, which are not bonded to chlorine atoms, provide examples of the types of species that should be favored by the addition of AlCl₃ to SbCl₃.

When the solubility data (21) are plotted on a log-log scale, as shown in Fig. 5, a set of parallel straight lines is obtained for 0.05 < xAlCl₃ < 0.40. The mean value of the slope is 2.080 ± 0.036. This result is consistent with the assumption that the solute species is Sbn²⁺, a cluster ion with the charge 2+, formed by the reaction

\[ 2 \text{SbCl}_2^+ + (n - \frac{2}{3}) \text{Sb(metal)} \rightleftharpoons \text{Sb}_n^{2+} + \frac{4}{3} \text{SbCl}_3 \]

provided that activity coefficients change little with changes in AlCl₃ content. For melts with a mole fraction of AlCl₃ less than 0.05, antimony proves to be much more soluble than is predicted by the above model. This behavior is consistent with the supposition that Cl₂Sb-SbCl₂ is formed (in addition to Sbn²⁺) at a low concentration.

The dissolution of Sb in SbCl₃-AlCl₃ is reversible only in the presence of Sb metal (21). Without the metallic phase present, the disproportionation of the dissolved species is kinetically hindered and highly supersaturated solutions can be prepared by evaporating some of the solvent. When an SbCl₃-AlCl₃-Sb melt is solidified in the absence of metallic Sb, a finely divided brown powder is found, dispersed among the clear crystals of SbCl₃ and AlCl₃. This brown substance, presumably an unstable compound, slowly turns black on exposure to light. Although this behavior remains unexplained, it is of considerable importance not only in experimental studies of the SbCl₃-AlCl₃-Sb system but also in the application of this system as a reaction medium for organic substances.

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Figure 1. Conductivity isotherms for SbCl$_3$-AlCl$_3$ melts at 100-200°C and for SbBr$_3$-AlBr$_3$ melts at 100°C.

Figure 2. Temperature dependence of the conductivity of SbCl$_3$-AlCl$_3$ melts containing 2.5-25.0 mol % AlCl$_3$. Curves are labelled according to composition in the order mol % SbCl$_3$-mol % AlCl$_3$. 
Figure 3. Schematic diagram of the coordination sphere of antimony in the adduct SbCl$_3$-GaCl$_3$.

Figure 4. Solubility of Sb in SbCl$_3$-AlCl$_3$ mixtures at two temperatures.
Figure 5. Log-log plot of the solubility of Sb in SbCl₃-AlCl₃ mixtures at 5 temperatures for $X_{AlCl₃}^0$-values of 0.05-0.40.