Addition Compounds of Antimony Chlorides with Sulfoxides and Sulfones

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The liquidus curves have been studied for the systems $SbCl_5$—$SO_2(CH_3)_2$, $SbCl_3$—$SO(CH_3)_2$ and $SbCl_3$—$SO_2(CH_3)_2$. The following new compounds have been prepared: $SbCl_5 \cdot SO(CH_3)_2$, $SbCl_5 \cdot SO(C_6H_5)_2$, $SbCl_5 \cdot SO_2(CH_3)_2$, $SbCl_5 \cdot SO_2(C_6H_5)_2$, $SbCl_3 \cdot 2SO(CH_3)_2$ and $SbCl_3 \cdot SO_2(CH_3)_2$. The melting point relations between these compounds have been discussed.

The suggestion by Groeneveld [1] that in the oxychlorides in many cases the oxygen atoms function as electron pair donors by the formation of solid addition compounds has recently been confirmed by X-ray work [2] on $SbCl_5.POCl_3$ and by infrared spectroscopy on different addition compounds [3]. These results have led to further studies of the occurrence of addition compounds which might be of the same type. It was proved by Groeneveld in his thesis that $SbCl_5$ forms 1:1 addition compounds with $SOCl_2$ and SO_2Cl_2. His results have been confirmed by us (congruent melting points of $+6°C$ and $—22°C$ were found). A stronger tendency to compound formation should be expected with sulfoxides and sulfones where chlorine is replaced by the less electronegative alkyl and aryl groups, resulting in a drift of electrons towards the oxygen atom and thus increasing its donor properties. We have therefore studied the system $SbCl_5$—$SO_2(CH_3)_2$ and have made additional experiments with $SO(CH_3)_2$, $SO(C_6H_5)_2$ and $SO_2(C_6H_5)_2$. As a complement the systems $SbCl_3$—$SO(CH_3)_2$ and $SbCl_3$—$SO_2(CH_3)_2$ have also been investigated, $SbCl_3$ in contrast to $SbCl_5$ being a dipole molecule.

EXPERIMENTAL

Chemicals used. $SbCl_5$ was purified by vacuum distillation and $SbCl_3$ by sublimation directly into a cool glass bulb placed 3 cm above the bulk of impure solid. $SO(CH_3)_2$ was repeatedly distilled until it had a final melting point of $+19°C$. The other sulfoxide and the sulfones were prepared and purified by Dr. B. Sjöberg whose help is gratefully acknowledged. They had the following melting points: $SO(C_6H_5)_2$ $+70°C$, $SO_2(CH_3)_2$ $+108—109°C$ and $SO_2(C_6H_5)_2$ $+125°C$.
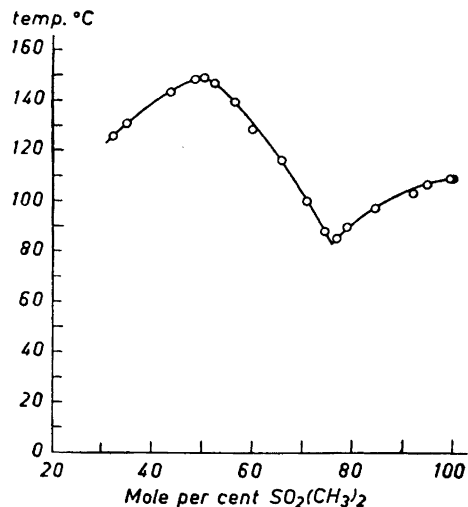
Fig. 1. The system SbCl$_5$—SO$_2$(CH$_3$)$_2$.

Phase diagrams. The liquidus curves were studied by the same methods as described earlier [4]. The reaction vessel was cooled down below 0°C before every addition of a reactant in order to prevent irreversible side reactions (elimination of organic halides, oxidation, etc.). If such precautions are not taken very vigorous reactions take place.
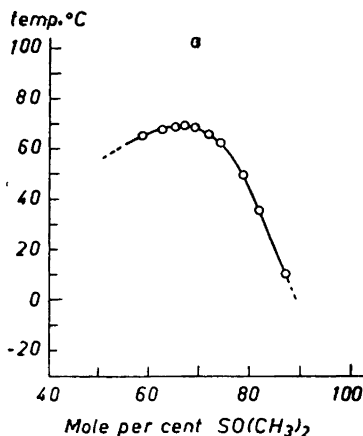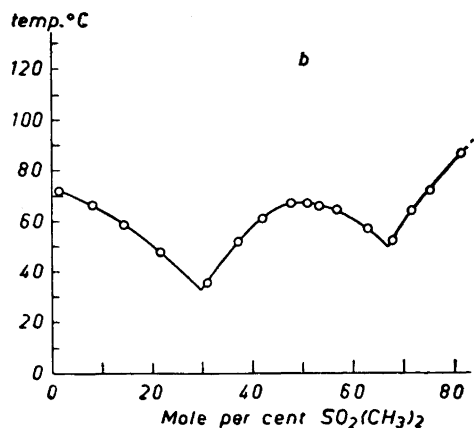
RESULTS

1. The liquidus curve of the system SbCl$_5$-SO$_2$(CH$_3$)$_2$ is given in Fig. 1. The addition compound SbCl$_5$·SO$_2$(CH$_3$)$_2$ has a congruent melting point of +149°C. This compound can also be prepared from solutions in carbon tetrachloride. The crystals are very hygroscopic.

2. Analogous compounds were also prepared with SO(CH$_3$)$_2$, SO(C$_6$H$_5$)$_2$ and SO$_2$(C$_6$H$_5$)$_2$ by melting the reactants together or by precipitation from carbon tetrachloride solutions. The melting points of the colorless addition compounds, SbCl$_5$·SO(CH$_3$)$_2$ SbCl$_5$·SO(C$_6$H$_5$)$_2$ and SbCl$_5$·SO$_2$(C$_6$H$_5$)$_2$ are +135 C°, +150—155°C and +141°C. The compound SbCl$_5$·SO(CH$_3$)$_2$ is partially decomposed by melting and its melting point is continuously decreasing by remelting.

3. These addition compounds can all be dissolved in ethylene chloride and in benzene. It was observed that they give colourless solutions with benzene while the corresponding addition compounds with POCl$_3$ and SeOCl$_2$ give the same kind of dark colour as SbCl$_5$ itself.

4. The liquidus curve of the system SbCl$_3$-SO(CH$_3$)$_2$ is shown in Fig. 2a. At mole fractions of SO(CH$_3$)$_2$ smaller than 0.60 strong supercooling prevents a reliable study of the phase diagram. The addition compound SbCl$_3$·2SO(CH$_3$)$_2$ has a congruent melting point of +70°C. Attempts to prepare the compound by precipitation from chloroform solution (SbCl$_3$ does not dissolve in carbon tetrachloride) only led to the formation of a liquid phase dispersed as oil drops in the solution.

Fig. 2a. The system SbCl₃—SO(CH₃)₂.

Fig. 2b. The system SbCl₃—SO₂(CH₃)₂.

5. The liquidus curve of the system SbCl₃—SO₂(CH₃)₂ is given in Fig. 2b. The addition compound SbCl₃·SO₂(CH₃)₂ has a congruent melting point of +67°C. The direct precipitation from chloroform solution offered the same difficulties as with the sulfoxide.

DISCUSSION

The melting points of compounds with appreciable dipole moments are mainly deteimined by two factors, the dipole moment and the mole volume. (The shape of the molecule is also of importance as it might permit or prevent particularly favourable packings of the dipole molecules. In the cases discussed here that effect will, however, probably parallel the effect of increasing volume if it is of any importance at all.) With low dipole moments the variations in the London-van der Waals attraction forces also play an important role. The effect of the two factors is clearly demonstrated in the sequence SO_2Cl_2, $SO_2(CH_3)_2$, $SO_2(C_2H_5)_2$ and $SO_2(C_6H_5)_2$ where the dipole moments are 1.80, 4.41, 4.41 and 5.04 while the melting points are —54°C, +109°C, +74°C and +125°C. The big difference in dipole moment between SO_2Cl_2 and the sulfones is reflected in a big difference in melting points. Within the sulfones with rather similar dipole moments the mole volumes are of larger importance and $SO_2(C_2H_5)_2$ has a appreciably lower melting point than $SO_2(CH_3)_2$. Of the sulfoxides only the dipole moment of $SO(C_6H_5)_2$ is known (~4), which is much larger than the value 1.44 foi $SOCl_2$. The melting points are also very different: +70°C and —105°C.

If we now consider the addition compounds, the same effects should determine the melting points. (If the molecule is dissociated into one acceptor and one donor molecule by melting this is not true. In that case, with very weak acceptor-donor interaction, lower melting points might be obtained than would be expected from the total dipole moment and mole volume of the
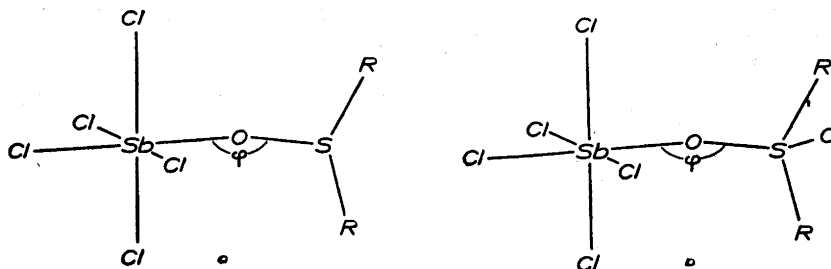
Fig. 3. a The probable structure of the addition compounds of SbCl₅ with SOCl₂ and the sulfoxides, *b* The probable structure of the addition compounds of SbCl₅ with SO₂Cl₂ and the sulfones.

addition compound molecule.) In the common case when the interaction between the complex molecules is the determining factor for the cohesion in the solid and liquid state we will first discuss the resultant dipole moment. Addition compounds with different donor molecules and the same acceptor molecule are easiest to compare. As a rule the donor molecules are not very much changed in structure by the complex formation while the acceptor molecules always are changed in shape because the acceptor atom has increased its coordination by new bonds to the donor atoms in the donor molecules. This is demonstrated in Fig. 3 for addition compounds with $SbCl_5$. The angle φ is generally not 180°. (For $SbCl_5 \cdot POCl_3$ the angle 146°5 is reported [2].) As a first approximation the dipole moment of the complex molecule is the vector sum of the dipole moments of the acceptor molecule (in the configuration which it has in the complex molecule) and of the donor molecule. The resultant dipole moment thus depends on the angle between the two vectors and it is obvious that the coupling probably will be less favourable for the sulfones than for the sulfoxides. The acceptor-donor bonds Sb-O will modify the results obtained by simple vector addition in such a way that the dipole moment is further increased by a strong acceptor-donor bond. Knowledge of the structures *and* the dipole moments might thus give information about the acceptor-donor bond. The resultant dipole moment is, however, mainly determined by the vector addition.

In the systems discussed here this would imply that the melting points of the addition compounds of $SbCl_5$ with $SOCl_2$ and sulfoxides would show a larger increase compared with the simple donor molecules than SO_2Cl_2 and the sulfones would do. The values are: $+111°C$ for $SOCl_2$, $+115°C$ for $SO(CH_3)_2$ and $+80$—$85°C$ for $SO(C_6H_5)_2$, $+32°C$ for SO_2Cl_2, $+40°C$ for $SO_2(CH_3)_2$, $+22°C$ for $SO_2(C_2H_5)_2$ and $+16°C$ for $SO_2(C_6H_5)_2$. (The addition compound $SbCl_5 \cdot SO_2(C_2H_5)_2$ with a melting point of $+96°C$ has been prepared by Klages [5].) The result is thus what could be expected from the simple considerations although a strong Sb—O bond might also have enhanced the effect.

With $SbCl_3$ one must also take into account the dipole moment of the free acceptor molecule (∼4) and the possibility that the two dipole moments will be coupled in a very unfavourable way in the addition compound. The mole

volume increase might then be the dominating factor. The compounds $SbCl_3\cdot2SO(CH_3)_2$ and $SbCl_3\cdot SO_2(CH_3)_2$ have thus both melting points below that of $SbCl_3$.

One should not try to elaborate too much on qualitative discussions of this type until the structures are known. The contribution of the London-van der Waals forces to the cohesion energy has also been considered to be equal for similar addition compounds. It is clear, however, that the strength of the acceptor-donor bond is not reflected in an obvious way in the melting point relations discussed here.

One indication about the strength of the bonds might be offered by the absence of colour in benzene solution. A dark colour is obtained with free $SbCl_5$ in benzene which readily leads to the conclusion that the acceptor-donor bond Sb-O in the addition compounds with sulfoxides and sulfones are stronger than with $POCl_3$ and $SeCCl_2$ which give a darker colour. Further studies are required, however.

An interesting feature is that $SbCl_3$ forms a 1:2 addition compound with $SO(CH_3)_2$. The same tendency for $SbCl_3$ to form 1:2 compounds has been observed in other connections. The compound $SbCl_3\cdot2POCl_3$ has thus been prepared [6] in contrast to only $AsCl_3 \cdot POCl_3$ described earlier [4].

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