

Addition Compounds of Diphosphorus Trioxide Tetrachloride

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The formation of addition compounds with diphosphorus trioxide tetrachloride as donor molecule has been studied. The following new compounds have been prepared: $2\text{SbCl}_5 \cdot \text{P}_2\text{O}_3\text{Cl}_4$ and $\text{SnCl}_4 \cdot \text{P}_2\text{O}_3\text{Cl}_4$, and their infrared spectra have been recorded.

It has been established by a series of X-ray crystallographic structure determinations^{1,2} that in phosphoryl chloride POCl_3 , the oxygen atom functions as the donor in adduct formation. We have been interested in finding out how the related diphosphorus trioxide tetrachloride, $\text{P}_2\text{O}_3\text{Cl}_4$, reacts with typical acceptor molecules (Lewis acids) such as SbCl_5 and SnCl_4 . The molecular structure of $\text{P}_2\text{O}_3\text{Cl}_4$ is not known, but it can safely be predicted to contain an oxygen bridge between the two phosphorus atoms. The bridge oxygen cannot be expected to function as a donor atom as efficiently as the oxygen atoms of the two phosphoryl groups. A study of the compositions of the addition compounds formed was supposed to give some information about this problem.

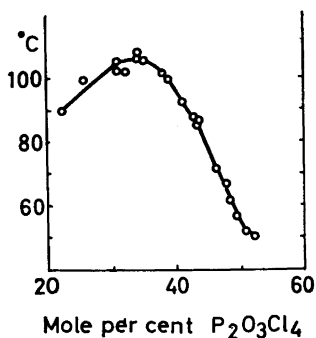


Fig. 1a. The system SbCl_5 - $\text{P}_2\text{O}_3\text{Cl}_4$.

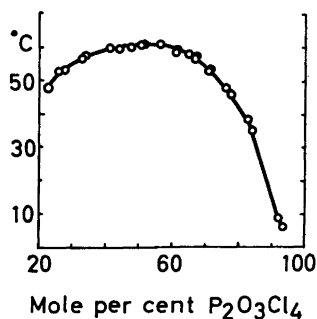


Fig. 1b. The system SnCl_4 - $\text{P}_2\text{O}_3\text{Cl}_4$.

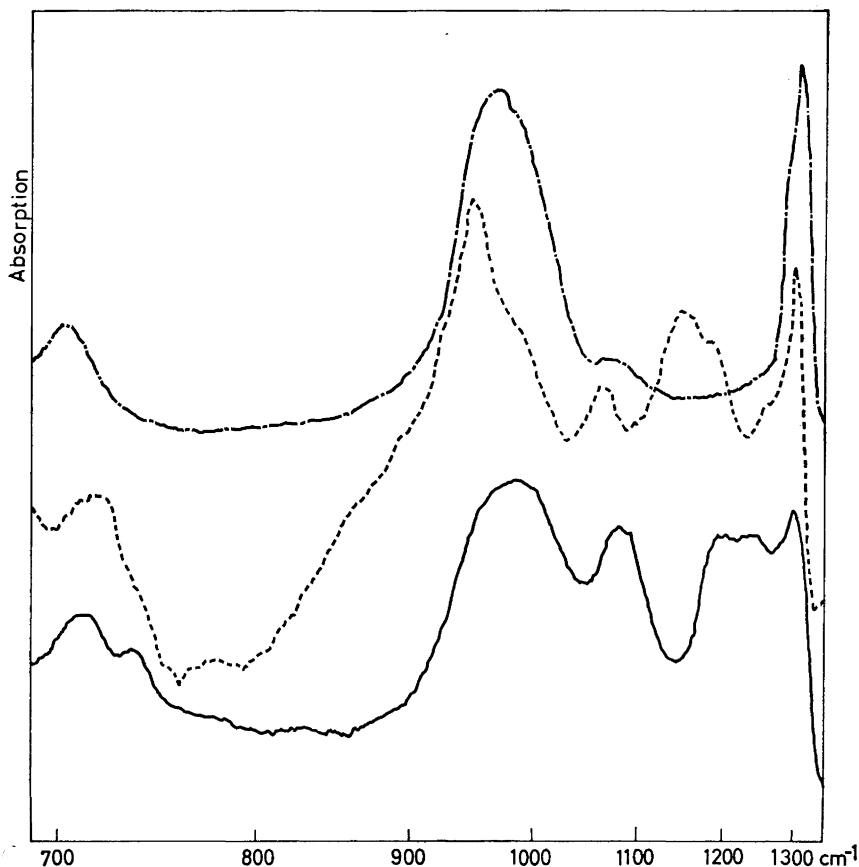


Fig. 2. The IR spectra of $P_2O_3Cl_4$ (broken line), $2SbCl_5 \cdot P_2O_3Cl_4$ (dashed line) and $SnCl_4 \cdot P_2O_3Cl_4$ (full line). In order to obtain a clearer picture the spectra have been arbitrarily displaced along the absorption axis.

EXPERIMENTAL

$P_2O_3Cl_4$ was prepared according to Grunze³. $SbCl_5$ and $SnCl_4$ were purified by vacuum distillation. Liquidus curves were studied by a method described earlier⁴. Infrared spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer equipped with a NaCl prism (in the Institute of Biochemistry). The spectrum of $P_2O_3Cl_4$ was run with the liquid in a thin layer between two NaCl plates. The spectra of the addition compounds were run in Nujol between NaCl plates.

RESULTS

1. The liquidus curve of the system $SbCl_5$ - $P_2O_3Cl_4$ (Fig. 1a) shows a maximum at the composition $2SbCl_5 \cdot P_2O_3Cl_4$ where the entire liquid phase solidifies. The melting point is $+107-109^\circ C$. At higher mole ratios of $P_2O_3Cl_4$ the study is prevented by strong super-cooling.

2. The liquidus curve of the system $\text{SnCl}_4\text{-P}_2\text{O}_3\text{Cl}_4$ (Fig. 1b) has one rather flat maximum at the composition $\text{SnCl}_4 \cdot \text{P}_2\text{O}_3\text{Cl}_4$. The melting point is $+72^\circ\text{C}$.

3. The infrared spectra (in the region $7.5\text{--}14.5 \mu$) are shown in Fig. 2.

DISCUSSION

1. The existence of the compounds $2\text{SbCl}_5 \cdot \text{P}_2\text{O}_3\text{Cl}_4$ (*cf.* $\text{SbCl}_5 \cdot \text{POCl}_3$) and $\text{SnCl}_4 \cdot \text{P}_2\text{O}_3\text{Cl}_4$ (*cf.* $\text{SnCl}_4 \cdot 2\text{POCl}_3$) clearly indicates that in $\text{P}_2\text{O}_3\text{Cl}_4$ the oxygen atoms of both phosphoryl groups but not the bridge oxygen can function as donor atoms. In $2\text{SbCl}_5 \cdot \text{P}_2\text{O}_3\text{Cl}_4$ two molecules of SbCl_5 would thus be attached to the same molecule of $\text{P}_2\text{O}_3\text{Cl}_4$. In $\text{SnCl}_4 \cdot \text{P}_2\text{O}_3\text{Cl}_4$ two alternatives are possible. One possibility is that the two oxygen donor atoms in $\text{P}_2\text{O}_3\text{Cl}_4$ are bonded to the same molecule of SnCl_4 in *cis*-position (*cf.* the *cis*-structure of $\text{SnCl}_4 \cdot 2\text{POCl}_3^2$). Another possibility is that two different SnCl_4 molecules interact with the same molecule of $\text{P}_2\text{O}_3\text{Cl}_4$. The structure would then not contain discrete molecular units of the addition compound.

2. The analysis of the spectrum of $\text{P}_2\text{O}_3\text{Cl}_4$ is very complicated, but we had hoped to be able to identify at least the phosphoryl bond stretching frequency by comparison with the spectra of the addition compounds. We do not feel competent, however, to attempt a correlation. Splitting and decrease of the phosphoryl frequency have probably both taken place as earlier found with POCl_3^5 , but in this case the complex nature of the pure $\text{P}_2\text{O}_3\text{Cl}_4$ spectrum makes the interpretation more difficult.

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