Preparation and Vibrational Spectra of Me₂Sn(O₂PMe₂)₂, Cl₂Sn(O₂PMe₂)₂ and Al(O₂PMe₂)₃

Abdel-Fattah Shihada* and Hekmat R. Yousif

Department of Chemistry, College of Science University of United Arab Emirates, Al-Ain P.O. Box 17551, United Arab Emirates


Reactions, Preparations, Vibrational Spectra

Me₂Sn(O₂PMe₂)₂ has been prepared from the reaction of Me₂PO₂H and Me₂SnS in benzene, and Al(O₂PMe₂)₃ and Cl₂Sn(O₂PMe₂)₂ have obtained from the reaction of Me₂PO₂H with AlCl₃ and SnCl₄, respectively in CH₂Cl₂. The vibrational spectra of the compounds were found to be consistent with polymeric structures with hexacoordinated metal atoms.

Introduction

It has been found that dimethylphosphinic acid reacts with covalent metal chlorides to produce dimethylphosphinates and HCl. Accordingly, e.g. Cl₂Ti(O₂PMe₂)₂ and (Cl₂SbO₂PMe₂)₂ were prepared from TiCl₄ and SbCl₅, respectively [1]. Dimethylphosphinic acid also reacts with compounds of the type MM₄(M = Al, Ga, In) or with SbMe₅ with evolution of methane to give products Me₃MO₂PMe₂ [2] and Me₃SbO₂PMe₂ [3], respectively. The synthesis of Al(O₂PMe₂)₃ [4] and Me₂SnO₂PMe₂ [5] from Me₂PO₂H and AlH₃ or Me₃SnH were found to occur with formation of H₂. Furthermore the reaction between dimethylphosphinic acid and Me₃SnNEt₂ leads to Me₃SnO₂PMe₂ and Et₂NH₂·Me₂PO₂⁻ [6]. Most of these reactions give gaseous by-products which facilitates the separation of the prepared compounds.

We describe here the reaction of dimethylphosphinic acid with AlCl₃ and with Me₂SnS and discuss the vibrational spectra of the products Al(O₂PMe₂)₃, Me₂Sn(O₂PMe₂)₂ and Cl₂Sn(O₂PMe₂)₂.

Results and Discussion

Dimethylphosphinic acid reacts with AlCl₃ in CH₂Cl₂ with the formation of HCl to give a white precipitate of Al(O₂PMe₂)₃. Flagg and Schmidt have prepared Al(O₂PMe₂)₃ from the reactions of AlH₃·0.3O(C₂H₅)₂ or (C₂H₅)₃Al with Me₂PO₂H [4].

Dimethylphosphinic acid reacts readily with Me₂SnS in benzene at ambient temperature to afford Me₂Sn(O₂PMe₂)₂ and H₂S.

(Me₂SnS)₃ + 6 HO₂PMe₂ →
3 Me₂Sn(O₂PMe₂)₂ + 3 H₂S

Pudovik et al. have studied the reaction between dialkylphosphinic acids and SnCl₄. They isolated the adduct (Me₂PO₂H)₂·SnCl₄ from a CH₂Cl₂ solution of Me₂PO₂H and SnCl₄ and obtained Cl₂Sn(O₂PMe₂)₂ by heating the adduct in a vacuum to 120–140 °C [7]. We prepared Cl₂Sn(O₂PMe₂)₂ in a one step reaction by heating Me₂PO₂H with an excess of SnCl₄ in CH₂Cl₂.

The reaction between Me₂PO₂H and SnCl₄ depends on the molar ratio of the reactants. Refluxing Me₂PO₂H and SnCl₄ in CH₂Cl₂ in a molar ratio of 2:1 leads to the evolution of HCl without precipitation of Cl₂Sn(O₂PMe₂)₂. The reaction between Me₂PO₂H and metal chlorides with Lewis acid character such as AlCl₃, TiCl₄, SnCl₄ and SbCl₅ could arise from nucleophilic attack by the terminal oxygen of the acid at the metal atom which would tend to weaken the metal chlorine bond and facilitate HCl evolution.

Vibrational Spectra

The infrared and Raman frequencies of Al(O₂PMe₂)₃, Me₂Sn(O₂PMe₂)₂ and the IR absorptions of Cl₂Sn(O₂PMe₂)₂, with the relative intensities and assignments, are shown in Table I. The bands arising from vibrations of the O₂PMe₂ groups are assigned by comparing the vibrational spectra of the given compounds with that for NaO₂PMe₂ [8], Cl₂Ti(O₂PMe₂)₂ and Cl₂Sb(O₂PMe₂)₂ [1].
It is well known that \( \nu(PO_2) \) frequencies appear between 1200 and 1000 cm\(^{-1} \) for bidentate \( O_2PMMe_2 \) groups, while monodentately linked \( O_2PMMe_2 \) groups give the absorptions \( \nu(P=O) > 1200 \text{ cm}^{-1} \) and \( \nu(P-O) < 1000 \text{ cm}^{-1} \).

The vibrational spectra of \( Al(O_2PMMe_2)_3 \), \( Me_2Sn(O_2PMMe_2)_2 \) and \( Cl_2Sn(O_2PMMe_2)_2 \) show \( \nu(PO_2) \) absorptions between 1200 and 1000 cm\(^{-1} \), which indicate bidentate \( O_2PMMe_2 \) groups. This behaviour and the physical properties of the compounds such as the insolubility in common organic solvents are consistent with the expected polymeric structure of \( Al(O_2PMMe_2)_3 \), \( Me_2Sn(O_2PMMe_2)_2 \) and \( Cl_2Sn(O_2PMMe_2)_2 \), in which the metal atoms are joined by \( O-P-O \) bridges. As a result of such bridges, the polymeric structure contains \( M_2O_4P_2 \) (\( M = Al, Sn \)) eight-membered rings, and the metal atoms are hexa-coordinated. The coupling of \( \nu(PO_2) \) vibrations in the eight-membered ring causes the appearance of four stretching frequencies, which are to be interpreted as in- and out-of-phase vibrations \( \nu_x(PO_2) \) and the \( \nu_y(PO_2) \). In eight-membered rings with high symmetry (C\(_{2h}\), D\(_{2h}\)) these vibrations obey the mutual exclusion rule, which allows a direct statement about the ring geometry. A \( Sb_2O_4P_2 \) eight-membered ring with C\(_{2h}\) symmetry has been found in \( (Cl_4Sb_02PMMe_2)_2 \) [1].

The appearance of three very strong \( \nu(PO_2) \) bands at 1177, 1157 and 1082 cm\(^{-1} \) in the IR spectrum of \( Al(O_2PMMe_2)_3 \) is consistent with \( Al_2O_4P_2 \) eight-membered rings and gives additional evidence for bridge-bonded \( O_2PMMe_2 \) groups. The IR
The IR spectrum of Me₂Sn(O₂PMe₂)₂ similarly shows three \( \nu(PO) \) absorptions at 1135, 1079, and 1037 \( \text{cm}^{-1} \) with a shoulder at 1165 \( \text{cm}^{-1} \).

The IR spectrum of Me₂Sn(O₂PMe₂)₂ contains two very strong \( \nu(PO) \) bands at 1107 and 1039 \( \text{cm}^{-1} \), but the appearance of three bands at 1086, 1050 and 1040 \( \text{cm}^{-1} \) in the Raman spectrum did not confirm a centrosymmetric Sn₂O₄P₂ eight-membered ring geometry. In the SnC₂ absorption range, Me₂Sn(O₂PMe₂)₂ shows only one band at 578 \( \text{cm}^{-1} \) in the IR spectrum due to \( \nu_\text{as}(SnC₂) \) and one band at 514 \( \text{cm}^{-1} \) in the Raman spectrum due to \( \nu(SnC₂) \). Consequently, the tin methyl groups are in a trans-octahedral position and a sheet-like polymeric structure can be suggested for Me₂Sn(O₂PMe₂)₂.

Similar structures have been found in Me₂Sn(O₂PMe₂)₂ [9], Me₂Sn(O₂PF₂)₂ [10] and R₂Sn(O₂PH₂)₂ [11]. The band at 300 \( \text{cm}^{-1} \) in the IR spectrum of Cl₄Sn(O₂PMe₂)₂ is attributed to \( \nu(SnCl₂) \). A comparison of the IR spectra of Me₂Sn(O₂PMe₂)₂ and Cl₂Sn(O₂PMe₂)₂ supports the assignments given for \( \nu(SnC₂) \) and \( \nu(SnCl₂) \).

For Al(O₂PMe₂)₃, the band at 523 \( \text{cm}^{-1} \) (IR) and the line 515 \( \text{cm}^{-1} \) (Raman) are ascribed to \( \nu(A106) \), since no \( O₂PMe₂ \) fundamental vibrations are expected in this region.

**Experimental**

The IR spectra were obtained with a Perkin-Elmer 577 spectrophotometer equipped with CsI window; Nujol or Hostaflon mulls were used. Raman spectra were recorded with a Cary 83, Al(O₂PMe₂)₃, and a Cary 82, Me₂Sn(O₂PMe₂)₂ with argon laser excitation (\( \lambda \) 514.5 nm). Me₂PO₂H [12] and Me₂SnS [13] were prepared by published methods. The experiments were carried out under anhydrous conditions. Commercial AlCl₃ was purified by sublimation before use.