## NMR Study of the Interaction of Tin(II) and Antimony(III) Fluorides with Phosphorus Chlorides

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**Abstract**—Reactions of  $SnF_2$  and  $SbF_3$  with POCl<sub>3</sub> and PCl<sub>5</sub> in acetonitrile were studied by <sup>19</sup>F, <sup>31</sup>P, and <sup>119</sup>Sn NMR. Tetrahedral compounds POF<sub>2</sub>Cl and POF<sub>3</sub> form in the reaction with POCl<sub>3</sub>. Interaction of  $SnF_2$  and  $SbF_3$  with PCl<sub>5</sub> yields higher (in terms of fluorine) octahedral complexes [PF<sub>5</sub> · MeCN] and [PF<sub>6</sub>]<sup>-</sup>. In all cases, fluorine-free phosphorus compounds are found in the acetonitrile solution.

Tin(II) difluoride and antimony(III) trifluoride are fluorine donors in reactions with tin(IV) [1], titanium [2], niobium [3], and tantalum [4] halides. It has been found that their reactions with metal chlorides yield octahedral fluoride and fluorochloride complexes.

Neutral phosphorus(V) fluorochloride compounds have the structure of a trigonal bipyramid; they have been prepared by chlorinating the corresponding phosphorus(III) fluorochlorides [5]. To synthesize higher fluorides, for example, PCIF<sub>4</sub>, the reaction between PCl<sub>2</sub>F<sub>3</sub> and SbF<sub>3</sub> was used in [6]. Mixed octahedral anions of the [PF<sub>n</sub>Cl<sub>6-n</sub>]<sup>-</sup> composition have been prepared by redistributing ligands between PCl<sub>5</sub> and PF<sub>5</sub> in acetonitrile (MeCN). The compositions and structures of the complexes were determined using <sup>19</sup>F and <sup>31</sup>P NMR in [7, 8].

The purpose of this work was to study the interaction of  $SnF_2$  and  $SbF_3$  with POCl<sub>3</sub> and PCl<sub>5</sub> in MeCN and to determine the compositions of the products by <sup>19</sup>F and <sup>31</sup>P NMR.

 $SnF_2$  was prepared according to [9]; reagent grade  $SbF_3$  and  $PCl_5$  and pure grade  $POCl_3$  were used. Acetonitrile was dried by repeated holding over  $P_2O_5$  followed by distillation.

NMR spectra were recorded on a Bruker AC-200 spectrometer at room temperature. Chemical shifts were measured relative to  $CFCl_3$  (<sup>19</sup>F) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P).

It is known that  $SnF_2$  and  $SbF_3$  are poorly soluble in MeCN. This is why solid fluorides were added to acetonitrile solutions of POCl<sub>3</sub> and PCl<sub>5</sub> in the experiments. The initial molar ratio of the reagents  $SnF_2(SbF_3)$  : POCl<sub>3</sub>(PCl<sub>5</sub>) was varied from 1 : 2 to 2 : 1. Reactions were carried out at both room temperature and the temperature of liquid nitrogen. In the latter case, the acetonitrile solutions of POCl<sub>3</sub> or PCl<sub>5</sub> were frozen in liquid nitrogen, solid fluorides were added, and the reaction mixtures were gradually heated. In all cases, fluorides

dissolved under thorough stirring, indicating the onset of the reaction. However, even before full dissolution of fluorides, crystals precipitated. Acetonitrile solutions were removed from undissolved fluorides and new solids and studied by NMR.

According to the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra, after reacting  $SnF_2$  and  $SbF_3$  with POCl\_3, the main compounds in solutions are POCl<sub>3</sub>, POF<sub>2</sub>Cl, and a small quantity of POF<sub>3</sub> (parameters of the <sup>19</sup>F and <sup>31</sup>P NMR spectra are given in the table). In addition, the  $[PF_6]^-$  ion appears in the solution (<sup>31</sup>P NMR spectrum: septet with  $\delta = -143.3$  ppm and  $J_{{}^{31}P-{}^{19}F} = 709$  Hz,  ${}^{19}F$  spectrum: doublet with  $\delta = -71.4$  ppm and  $J_{{}^{31}P_{-}{}^{19}F} = 709$  Hz). The  $[PF_6]^-$  ion seems to form due to the admixture of PCl<sub>5</sub> in POCl<sub>3</sub>. The low-intensity doublet at -19.5 ppm with  $J_{{}^{31}\mathrm{P}_{-}{}^{19}\mathrm{F}}$  = 1186 Hz also appears in the  ${}^{19}\mathrm{F}$  NMR spectrum (no corresponding signal being observed in the <sup>31</sup>P spectrum). The <sup>19</sup>F spectra show no signals of fluorine atoms bonded to  $Sn(\hat{I})$ . At the same time, single signals appear in the <sup>119</sup>Sn NMR spectra in the –690 to –760 ppm range. This indicates that the solutions contain polymeric cationic Sn(II) complexes with bridging fluorine atoms.

When  $\text{SbF}_3$  was used as a fluorinating agent, a wide signal was observed at -86 ppm in the <sup>19</sup>F spectra, in addition to the signals of fluoride phosphorus compounds, and was assigned to the Sb(III) fluorine-containing compounds.

In the reaction of SnF<sub>2</sub> with PCl<sub>5</sub> (SnF<sub>2</sub> : PCl<sub>5</sub> = 1 : 2 in MeCN), PF<sub>5</sub> · MeCN predominantly forms in the solution (<sup>31</sup>P NMR spectrum: sextet with  $\delta$  = -141.2 ppm and  $J_{^{31}P_{-}^{^{19}F}}$  = 777Hz, <sup>19</sup>F NMR spectrum: doublet at -59.3 ppm with  $J_{^{31}P_{-}^{^{19}F}}$  = 778 Hz). The shape of the



Fig. 1. The (a)  ${}^{31}$ P and (b)  ${}^{19}$ F spectra of the products of interaction between SnF<sub>2</sub> and PCl<sub>5</sub> in acetonitrile.

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spectra indicates that the fluorine atoms in the  $PF_5$  · MeCN complex are equivalent.

In addition, signals at 6.4 and 220.5 ppm are observed in the <sup>31</sup>P NMR spectrum. It is known that  $[PCl_6]^-$  and  $[PCl_4]^+$  ionic forms occur in solutions of phosphorus pentachloride [10]. According to [8, 11],  $[PCl_4]^+$  reacts with MeCN to yield phosphonitrile compounds producing <sup>31</sup>P signals at 82 and 2.5 ppm. These compounds tend to eliminate PCl<sub>3</sub>, whose signal is observed in the weakest field (217 ppm) [8, 12]. Therefore, the signal at 220.5 ppm is assigned to PCl<sub>3</sub> and the signal at 6.4 ppm should be assigned to the product of the reaction between  $[PCl_4]^+$  and MeCN or to POCl<sub>3</sub> present in PCl<sub>5</sub> as an admixture or produced in hydrolysis.

An increase in the solid SnF<sub>2</sub> : PCl<sub>5</sub> initial ratio in acetonitrile up to 1 : 1 causes changes in the <sup>19</sup>F and <sup>31</sup>P NMR spectra of the solutions (figure). In addition to the signals at 220.7 and 6.6 ppm, the <sup>31</sup>P NMR spectrum shows a septet at –143.3 ppm with  $J_{^{31}P_{-}^{19}F} = 709$  Hz assigned to the [PF<sub>6</sub>]<sup>-</sup> anion and two low-intensity quartets at  $\delta = -33.9$  ppm with  $J_{^{31}P_{-}^{19}F} = 1068$  Hz (POF<sub>3</sub>) and at 104.1 ppm with  $J_{^{31}P_{-}^{19}F} = 1398$  Hz. The latter multiplet signal was assigned to PF<sub>3</sub> on the basis of the values of the chemical shift and spin–spin coupling constant. These multiplet signals correlate with doublets at  $\delta = -71.4$  ppm with  $J_{^{31}P_{-}^{19}F} = 707$  Hz ([PF<sub>6</sub>]<sup>-</sup>), at -87.6 ppm with  $J_{^{31}P_{-}^{19}F} = 1068$  Hz (POF<sub>3</sub>), and at -36.4 ppm with  $J_{^{31}P_{-}^{19}F} = 1404$  Hz (PF<sub>3</sub>) in the <sup>19</sup>F NMR spectrum.

A further increase in the solid  $SnF_2$ : PCl<sub>5</sub> ratio in acetonitrile is followed by a decrease in the intensity of the signal at 220.6 ppm and an increase in the intensity of the [PF<sub>6</sub>]<sup>-</sup> signal in the <sup>31</sup>P NMR spectrum. The spectrum also contains signals due to POF<sub>3</sub> and PF<sub>3</sub>. The character of the <sup>19</sup>F spectra agrees with the <sup>31</sup>P NMR spectra. In addition to the aforementioned signals, the <sup>31</sup>P NMR spectrum contains two low-intensity triplets at  $\delta = -5.0$  ppm with  $J_{{}^{31}P_{-}{}^{19}F} = 1124$  Hz and at 5.9 ppm with  $J_{{}^{31}P_{-}{}^{19}F} = 1119$  Hz. They correlate with the two low-intensity doublets at -64.3 ppm with  $J_{{}^{31}P_{-}{}^{19}F}$  = 1121 Hz and at -63.7 ppm with  $J_{{}^{31}P_{-}{}^{19}F} = 1121$  Hz in the <sup>19</sup>F NMR spectrum. The shape of the spectra, chemical shifts, and spin-spin coupling constants allow one to assign these signals to the *cis*- and *trans*-[ $PF_2Cl_3 \cdot MeCN$ ] complexes. The <sup>119</sup>Sn spectra of the solutions show single signals in the -680 to -690 ppm region assigned to the polymeric tin(II) fluorine-containing cations.

According to the <sup>19</sup>F and <sup>31</sup>P NMR spectra, the interaction of SbF<sub>3</sub> with PCl<sub>5</sub> in acetonitrile does not differ from the reaction of SnF<sub>2</sub> with PCl<sub>5</sub>. In this case,  $[PF_6]^$ and  $[PF_5 \cdot MeCN]$  are also the main products in the s.

<sup>19</sup>F and <sup>31</sup>P NMR spectra of  $POF_nCl_{3-n}$  compounds in acetonitrile

Com- pound	δ( <sup>19</sup> F), ppm	$J_{{}^{31}\mathrm{P}-{}^{19}\mathrm{F}},\mathrm{Hz}$	δ( <sup>31</sup> P), ppm	$J_{{}^{31}\mathrm{P}-{}^{19}\mathrm{F}}$ , Hz
POCl <sub>3</sub>			5.9	
POF <sub>2</sub> Cl	-82.2	986	-22.9	984
POF <sub>3</sub>	-87.8	1064	-33.6	1068

Therefore, when  $SnF_2$  and  $SbF_3$  are used as fluorine donors in the reaction with  $POCl_3$ ,  $POF_2Cl$  and  $POF_3$ are mainly formed. The above fluorides react with  $PCl_5$ in acetonitrile to yield higher phosphorus complexes  $[PF_6]^-$  and  $[PF_5 \cdot MeCN]$ . No mixed fluorochloride complex anions of the  $[PF_nCl_{6-n}]^-$  composition were found. The reaction of  $SnF_2$  and  $SbF_3$  with  $POCl_3$  and  $PCl_5$  in MeCN under the indicated conditions does not result in the complete conversion of phosphorus chloride forms into fluorochloride or fluoride forms. In all cases, the NMR spectra show signals due to the fluorine-free phosphorus compounds.

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