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Preparation and Properties of Antimony(III) Polyfluoroalkoxides

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Abstract—Reaction of polyfluorinated alcohols with antimony(III) oxide has resulted in thermally and hydrolytically stable polyfluoroalkoxides. Higher conversion has been observed in the case of alcohols with longer perfluorinated alkyl chain.

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Search for new efficient catalysts for polycondensation of terephthalic acid with ethylene glycol has been described in many publications (see [1, 2] and references therein). However, application of fluorine-containing catalysts in PETF production has been scarcely reported so far [1]. This is at least partially due to the low thermal and hydrolytic stability of arsenic, titanium, led, cobalt, manganese, tantalum, magnesium, and antimony fluorides and oxofluorides as well as of potassium, sodium, and lithium trifluorostannates. The instability of listed compounds complicates their industrial applications in polycondensation and dimethylterephthalate transesterification with ethylene glycol. Yet poly- and perfluorinated compounds are promising catalysts and modifiers of polymer materials. Even at low concentration (10^{-3} to 5 wt %), the fluorine-containing compounds can significantly improve the thermo-, photo-, wear-, and hydrolytic resistance of heterochain polymers [3–10].

This work was aimed to prepare alkoxides via reaction of Sb_2O_3 with polyfluorinated alcohols of the type $H(CF_2CF_2)_nCH_2OH$ (n = 1–3) and to determine their thermal and hydrolytic stability. The reaction occurred via the following scheme.

$$Sb_2O_3 \xrightarrow[-H_2O]{H(CF_2CF_2)_nCH_2OH} Sb[OCH_2(CF_2CF_2)_nH]_3,$$

$$n = 1\text{–}3.$$

It was found that the alcohol conversion increased 1.5 times with increasing length of polyfluoroalkyl chain in the alcohol (see table). That was apparently due to the accumulation in the alcohol molecules of fluorine atoms having a pronounced $-I$ effect that leads to increased alcohol acidity facilitating its interaction with amphoteric Sb_2O_3. The amount of released water coincided with the calculated value thus supporting the above scheme.

The X-ray photoelectron spectroscopy data confirmed that the isolated products were mixtures of polyfluorinated alkoxides (99.7–99.9 wt %) and metal antimony (0.1–0.3 wt %). That was in line with the published data: partial reduction of Sb_2O_3, antimony(III) acetate, or antimony(III) glycolate to metal antimony was previously described in [1, 2]. Such process is undesirable, as admixture of metal antimony leads to grayish color of the polymer products. However, the antimony content in the case of prepared polyfluorinated alkoxides was by 26–41% lower than that in the case of Sb_2O_3 and $Sb(OCH_2CH_2OH)_3$ catalysts. In the course of industrial polyester production, the $Sb(III) \rightarrow Sb^0$ reaction is induced by acetaldehyde, one of the main products of polymer degradation [2]. In

Influence of the polyfluorinated alcohol structure on its conversion in reaction with Sb_2O_3

Alcohol	Conversion, %
$n = 1$	44.2
$n = 2$	58.6
$n = 3$	65.4

this work, metal antimony probably formed via the interaction of Sb(III) with the alcohol dehydrofluorination products.

IR spectra of the prepared antimony(III) polyfluorinated alkoxides did not show any signs of destruction after 2 h incubation at 280°C in air. After 4 h of incubation, the $\nu_{C=C}$ (1665–1643 cm^{-1}) and ν_{O-H} (3335–3116 cm^{-1}) bands were observed in the products spectra. The prepared fluoroorganic derivatives of antimony(III) were insoluble in water, aqueous alkali, aqueous acids, or aqueous ammonia. Their decay was observed upon boiling in 5 wt % aqueous sodium hydroxide (2 h, 150°C).

To conclude, we succeeded to prepare thermally and hydrolytically stable antimony(III) polyfluoroalkoxides via the reaction of polyfluorinated alcohols with Sb_2O_3; metal Sb was identified as the reaction side product.

EXPERIMENTAL

The alkoxides were prepared from polyfluorinated alcohols (GaloPolimer) and Sb_2O_3 (Campine, particle size < 45 μm, DIN 50049/3.1B).

IR spectra of the prepared compounds were recorded with Nicolet-6700 spectrometer. Antimony content was determined with XSAM-800 X-ray photoelectron spectrometer (Mg anode, MgK_α irradiation energy of 1253.6 eV). Sb_2O_3 suspension in the polyfluorinated alcohol was homogenized using Prolabo ultrasound bath.

Alkoxides preparation *(general procedure).* Sb_2O_3 and the polyfluorinated alcohol (1 : 6, mol/mol) were loaded to a glass flask, and the mixture was treated with ultrasound at 40 kHz and 180°C during 6 h. After that, the mother liquor was decanted and distilled; the fractions of water and unreacted alcohol were collected. Unreacted Sb_2O_3 was separated by washing with 20% aqueous sodium hydroxide. The product was washed sequentially with ethanol and diethyl ether, and dried over anhydrous calcium chloride. Antimony(III) polyfluoroalkoxides (C_3–C_7) were white-pink pastes.

Tris(1,1,3-trihydroperfluoropropoxide)antimony. IR spectrum, ν, cm^{-1}: 2914–2986 (C–H), 1168–1198 (C–F), 423–802 (Sb–O).

Tris(1,1,5-trihydroperfluoropentoxide)antimony. IR spectrum, ν, cm^{-1}: 2926–2990 (C–H), 1170–1176 (C–F), 409–794 (Sb–O).

Tris(1,1,7-trihydroperfluoroheptoxide)antimony. IR spectrum, ν, cm^{-1}: 2926–2990 (C–H), 1171–1174 (C–F), 416–801 (Sb–O).

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