Catalytic activity of various Lewis acids in the phosphorylation of primary polyfluoroalkanols with phosphoryl chloride*

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The catalytic activity of $SnCl_2$, $SnCl_4$, $SbCl_3$, $SbCl_5$, and $BiCl_3$ in the reaction of 2,2,3,3,4,4,4-heptafluorobutanol with POCl₃ was studied. The mechanism of this reaction is discussed. Strong Lewis acids were found to be less active catalysts.

Key words: catalytic phosphorylation, electrophilic catalysis, Lewis acids, polyfluoroalkanols.

Metal chlorides are known to catalyze the phosphorylation of polyfluoroalkanols with pentavalent phosphorus oxoacid chlorides.¹⁻⁴ It has been assumed that the reaction includes the coordination of metal chloride to the phosphoryl group, which facilitates nucleophilic substitution at the phosphorus atom.^{2,5,6} Hence, we could expect that the catalysis is the more efficient the stronger acceptor properties of the salts employed as catalysts. However, the synthesis of tris(2,2,3,3,4,4,4-heptafluorobutyl) phosphate in the presence of Group I and II metal salts has revealed that the salts of cations with lower charge or larger radius, *i.e.*, weak Lewis acids, are more active catalysts, *viz.*, LiClO₄ > Mg(ClO₄)₂; LiOCOCF₃ > Mg(OCOCF₃)₂; and Ca(ClO₄)₂ > Mg(ClO₄)₂.^{7,8}

To avoid possible specific influence of the salt anion and establish whether this effect is of general character, we studied systematically the catalytic activity of a series of metal chlorides in the reaction of 2,2,3,3,4,4,4-heptafluorobutanol (HFB) with POCl₃. We found that the catalytic activity of stronger Lewis acids similarly depends on the acceptor properties. Thus, metal chlorides (stronger Lewis acids) were found to be less active catalysts than comparable, weaker Lewis acids. For example, for some pairs of Group IV and V metal salts comparable in solubility under the reaction conditions, the following order of catalytic activity is observed: $SnCl_2 > SnCl_4$; $SbCl_3 > SbCl_5$; $BiCl_3 > SbCl_3$. The catalytic activity was assessed from the time required for the reaction to be completed (Table 1).

Thus, the inverse dependence of the salt catalytic activity on its acceptor properties, observed in this reac-

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tion, may be of general character. This dependence can be explained if the catalytic cycle is considered as a twostage process following the simplified scheme:

where MCl_n is the metal chloride, n = 2-5, >POCl is the phosphorus acid chloride, $R = C_3F_7CH_2$, >P(O)OR is the phosphate, and L denotes other ligands that are not involved in this catalytic cycle.

First, the dissolution of metal chloride in the reaction mixture gives a complex of POCl₃ with the catalyst (1), where the metal is O-coordinated to the phosphoryl group (cf. Ref. 9-13). Then, the thus coordinated phosphoryl chloride reacts with an alcohol to give a complex of phosphate (reaction product) with catalyst (2) (stage (1)). An exchange of the phosphoryl ligands in the metal coordination sphere in stage (2) yields the complex of the initial substrate and the catalyst 1, which exists in equilibrium with complex 2. Insofar as the phosphoryl group in phosphate is more basic than in acid chloride,

Table 1. Efficiency of Group IV and V metal chlorides as catalysts for the reaction of 2,2,3,3,4,4,4-heptafluorobutanol with POCl₃

Catalyst	Reaction time/h	Yield (%)
SnClo	3.0	88.2
SnCl	13.2	81.3
SbCl	23.0	90.6
SPCI	62.0	85.4
BiCl	9.7	87.5

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^{**} All the catalysts studied (except for SnCl₂) formed homogeneous solutions in the reaction mixture. Despite its uncomplete solubility, SnCl₂ was, however, more effective than the wellsoluble SnCl₄.

the equilibrium should be shifted toward complex 2 because the alkoxy substituent exhibits weaker electronwithdrawing properties than chlorine (e.g., for $C_{1}F_{7}CH_{2}O, \sigma^{\Phi} = 0.5$ (see Ref. 14), and for Cl, $\sigma^{\Phi} =$ 0.93 (see Ref. 15)). That is why the replacement of the ester ligand by acid chloride (stage (2)) may occur very slowly, which is controlled only by a greater or less pronounced tendency toward ligand exchange in the inner coordination sphere. It is thereby known that the phosphoryl ligand exchange in the metal coordination sphere occurs more easily in the case of weaker Lewis acids.¹⁶⁻¹⁸ The results obtained, namely, the higher catalytic activity of some weak Lewis acids, suggest that the rate-limiting stage of the reaction under discussion is the stage of ligand exchange (stage (2)) rather than the stage of nucleophilic substitution at the phosphorus atom in complex 1 (in this case, strong Lewis acids would be more efficient).

Experimental

Phosphorus oxochloride was twice purified by distillation, b.p. 107 °C. Heptafluorobutanol was distilled over conc. H_2SO_4 and then P_2O_5 , b.p. 96 °C. Tin dichloride was recrystallized from dilute HCl in the presence of metallic tin granules and dehydrated by slow heating to 150 °C in a flow of dry hydrogen chloride. Tin tetrachloride (b.p. 114 °C) and antimony pentachloride (b.p. 51 °C/7 Torr) were distilled in an atmosphere of dry argon. Antimony trichloride and bismuth trichloride (high-purity grade) were used without additional purification.

The catalytic phosphorylation of 1, 1-dihydroperfluorobutanol with phosphorus oxochloride (general procedure). A mixture of HFB (17.0 g, 0.085 mol), phosphorus oxochloride (3.8 g, 0.025 mol), and a catalyst (2 mmol) was refluxed at 160 °C (bath temperature). The reflux condenser was equipped with a bubble counter (filled with conc. H₂SO₄). Refluxing was continued until HCl ceased to evolve. The excess of polyfluoroalkanol and HCl were removed in vacuo at <100 °C (bath temperature), and the residue was distilled in vacuo to yield tris(2,2,3,3,4,4,4-heptafluorobutyl) phosphate, b.p. 78– 80 °C (0.5 Torr), n_D^{20} 1.3105 (cf. Ref. 1). The catalyst, time for completion of the reaction, and product yield are given in Table 1.

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