

# Catalytic liquid phase fluorinations with Sb–Ti mixed halides

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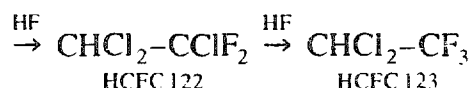
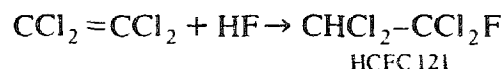
## Abstract

An efficient catalytic system for the liquid phase fluorination of tetrachlorethene (PCE) was achieved by utilization of a Ti–Sb mixed halide. The best results were obtained with a prefluorinated catalyst.

*Keywords:* Fluorination; Tetrachlorethene; Lewis acid; Chlorides; Antimony; Titanium

## 1. Introduction

The addition of HF to chloroalkenes and the subsequent F for Cl exchange is a possible route to CFC alternatives [1–3]. For example, the fluorination of tetrachlorethene (PCE) is the first step of a multistage process which results in the formation of hydrochlorofluorocarbons (HCFC).



The heavily chlorinated double bond does not react with HF under ordinary conditions. When this reaction occurs it takes place by a nucleophilic addition mechanism [4] and a catalyst, traditionally a Lewis acid, is required. For that purpose, TaCl<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, SbCl<sub>5</sub> have been used at temperatures between 90°C and 150°C [3,5–8].

Since SbCl<sub>5</sub> is a strong halogen acceptor, we reasoned that its association with another halide would increase the acidity and would provide an efficient catalyst under mild conditions. Of particular interest is a TiCl<sub>4</sub>–SbCl<sub>5</sub> mixture which gives, at room temperature, TiCl<sub>3</sub><sup>+</sup>, SbCl<sub>6</sub><sup>–</sup> [9] and could be an attractive candidate. It was expected that its reaction with HF would give a SbCl<sub>x</sub>F<sub>y</sub>·nHF species associated with TiF<sub>4</sub>. This system would behave as a F<sup>–</sup> pool and would also activate the unreactive double bond.

## 2. Experimental part

All the experiments were carried out at 90°C in liquid HF. A 100 ml autoclave was charged with 0.05 mol SbCl<sub>5</sub> or 0.05 mol SbCl<sub>5</sub>–TiCl<sub>4</sub> mixture. Then PCE 0.25 mol and HF were added sequentially and the mixture was heated at 90°C. After appropriate reaction time, usually 4 h the autoclave was cooled to 30°C and vented with dry dinitrogen. We have checked that the HCFC 123 is not vented in these condi-

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Table 1  
Catalytic activity of some Sb–Ti mixtures

Catalyst <sup>a</sup>	Conversion <sup>b</sup> (%)	HCFC 122	HCFC 121	Other <sup>c</sup>
SbCl <sub>5</sub>	47	20	48	32
SbCl <sub>5</sub> –TiCl <sub>4</sub> 7:1	61	23	46	31
SbCl <sub>5</sub> –TiCl <sub>4</sub> 5:1	64	33.5	39.5	37
SbCl <sub>5</sub> –TiCl <sub>4</sub> 3:1	62	35.5	38	36.5
SbCl <sub>5</sub> –TiCl <sub>4</sub> 1:1	22	5.5	58	36.5
TiCl <sub>4</sub>	0	0	0	0

<sup>a</sup> Molar composition.

<sup>b</sup> PCE: 0.25 mol catalyst; 0.05 mol HF; *T*: 90°C.

<sup>c</sup> CCl<sub>3</sub>–CCl<sub>3</sub>, CCl<sub>2</sub>F–CCl<sub>2</sub>F, CHCl<sub>2</sub>–CCl<sub>3</sub>.

tions. The contents were quenched with 50 ml 6 M H<sub>2</sub>SO<sub>4</sub>. The organic phase was dried and analyzed by temperature programmed GC with a BP1 column (40°C to 150°C). Products were identified by GC–MS.

Since the reaction is accompanied by a partial reduction of Sb(V) into Sb(III), the amounts of these two species were determined by titration of the aqueous phase. Atomic adsorption was used for measuring both Sb species. The

amount of Sb(III) was determined by oxidation with KMnO<sub>4</sub> solution. In some instances the residual amount of Cl<sup>–</sup> was measured by titration with AgNO<sub>3</sub> in the presence of K<sub>2</sub>CrO<sub>4</sub>.

In another series of experiments the catalyst was prepared prior to reacting PCE with HF. For that purpose, SbCl<sub>5</sub>, 0.05 mol or SbCl<sub>5</sub>–TiCl<sub>4</sub> mixtures 0.05 mol were reacted with HF at 90°C. After 1 h the autoclave was cooled, and vented with dry dinitrogen in order to eliminate HCl and excess HF. Then PCE, 0.25 mol, and HF were added. The reaction was carried out as mentioned above.

### 3. Results

The catalytic activity of some Sb–Ti mixtures is reported in Table 1. The addition of TiCl<sub>4</sub> to SbCl<sub>5</sub> increases the conversion and the best Sb:Ti molar ratio is approximately 5:1. As far as selectivities are concerned the fluorination competes with a hydrochlorination and a chlorination of PCE. The first reaction results from HCl formed in situ, the second is due to a

Table 2  
Preparation of the active species using various amounts of HF

Catalyst <sup>a</sup>	HF (mol) <sup>b</sup>	Conversion <sup>c</sup> (%)	HCFC 121	HCFC 122	Other <sup>d</sup>	Sb(III)
SbCl <sub>5</sub>	1.3	28	34.6	60	5.4	63
SbCl <sub>5</sub> –TiCl <sub>4</sub> 3:1	0.1	42.1	55.6	26.5	17.8	39
	1.0	77.4	19.6	64.1	16.3	94
	1.3	79	19.3	71.3	9.3	62
	2.0	68.5	21.4	72.8	5.8	69
	2.6	48	27.8	59.8	12.4	43
SbCl <sub>5</sub> –TiCl <sub>4</sub> 1:1	0.08	32.2	54.3	27.2	18.5	60
	0.7	56.3	31.5	58	10.5	62
	1.25	67.0	23.5	70	6.5	68
	1.60	66	22.7	70	7.3	60
	2.20	49	35	55	9.7	53
	2.30	45	33	57	10	55
TiCl <sub>4</sub>	1.3	0				

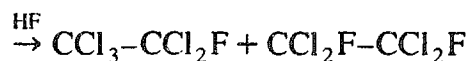
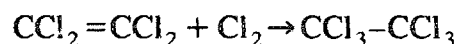
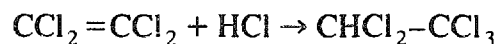
<sup>a</sup> Molar ratio.

<sup>b</sup> Amount of HF used for the preparation of the active species (90°C, 1 h).

<sup>c</sup> Catalyst: 0.05 mol; PCE: 0.25 mol; HF: 1.3 mol; *T*: 90°C; 4 h.

<sup>d</sup> CCl<sub>3</sub>–CCl<sub>3</sub>, CCl<sub>2</sub>F–CCl<sub>2</sub>F, CHCl<sub>2</sub>–CCl<sub>3</sub>.

reduction of Sb(V) into Sb(III). During the reaction a subsequent F for Cl exchange occurs (Table 1).



In order to improve the selectivity, another series of experiments was performed with preprepared catalysts. For that purpose, two mixed Sb–Ti halides were selected and various amounts of HF were used for the preparation of the active species (Table 2). The catalytic fluorinations of PCE were carried out with identical amounts of HF.

Chloride ion titrations were carried out with Ti–Sb mixtures of molar compositions 3:1. When an amount of HF greater than 1.6 mol is used for the preparation of the active species its empirical formula is  $\text{TiF}_4 - \text{SbClF}_4 - \text{SbCl}_2\text{F}$ . We checked that in our experimental conditions the  $\text{TiCl}_4 - \text{SbCl}_3$  mixture is inactive.

#### 4. Discussion

The addition of  $\text{TiCl}_4$  to  $\text{SbCl}_5$  provides a catalyst which is active for the fluorination of PCE. The best molar composition is Sb–Ti = 3:1 (Fig. 1). The greatest selectivity for fluorination

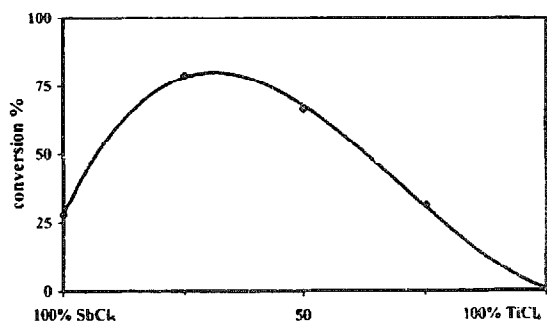


Fig. 1. Conversions of PCE as molar composition of the mixed halide. All catalysts were prepared by reacting 1.3 mol HF with a 0.05 mol Sb–Ti mixture at 90°C for 1 h. Catalytic experiments were carried out as indicated in Table 2.

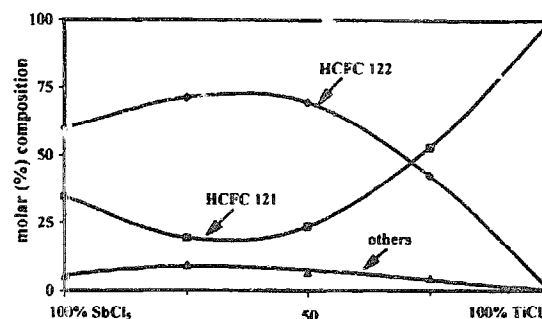


Fig. 2. Selectivity with molar composition of the halide mixed. All catalysts were prepared by reacting 1.3 HF with a 0.05 mol Sb:Ti mixture at 90°C for 1 h. Catalytic experiments were carried out as indicated in Table 2.

(which corresponds to  $\text{CF}_2\text{Cl} - \text{CHCl}_2$  formation) was also observed with this ratio (Fig. 2). The best conversions are obtained when the catalyst is preprepared for that purpose; the amount of HF is a key factor. It appears that the best HF:Sb–Ti molar ratio is approximately 26:1. This result suggests that the majority of chloride ions in the starting halide must be substituted by fluoride ions in order to increase the acidity of the catalyst.

We tentatively suggest that the catalytic system consists of a Ti–Sb mixed halide and a Sb halide, the former being the  $\text{F}^-$  pool which is necessary for the F/Cl exchange [10,11]. This optimum activity would also be in relation with the catalyst mixtures solubility.

The reaction is accompanied by a reduction of Sb(V) to Sb(III), which corresponds to a loss of catalyst activity since Sb(III) is inactive. This reduction may result from a wall effect of the stainless steel reactor and/or loss of chlorine from the antimony active species [12]. We are currently investigating the mechanism(s) of this reduction.

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