

Reactivity of antimony mixed halides for the fluorination of tetrachlorethene (PCE) in liquid phase

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Abstract

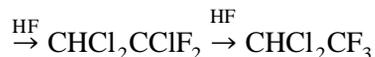
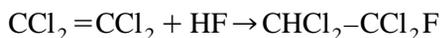
The active species for the liquid phase fluorination of tetrachloroethene (PCE) was produced by in situ reaction between HF and SbCl₅. By comparison with various commercial antimony mixed halides (SbCl₄F, SbCl₃F₂, SbCl₂F₃ and SbClF₄), the active species, produced in situ in our conditions, could be composed by SbCl₄F or/and SbCl₃F₂ or a mixture of both. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fluorination; Tetrachlorethene; Lewis acid; Antimony

1. Introduction

The catalytic fluorination in liquid phase of chloro compounds is currently carried out in liquid hydrogen fluoride in the presence of SbCl₅ [1–3]. This antimony halide is the starting material for the in situ formation of the catalyst.

For example, the preparation of CHCl₂CClF₂ and CHCl₂CF₃ involves the addition of HF on tetrachloroethene followed by a Cl/F exchange.



It has been suggested that the catalyst is an antimony mixed halide SbCl_{5-x}F_x, *n*HF. The

value of *x* depends naturally on the temperature ($1 \leq x \leq 4$) and on the amount of HF [3–9]. It is possible in fact that a mixture of these halides is obtained. The reaction is accompanied by a reduction of Sb(V) into Sb(III). This side reaction is a major drawback because Sb(III) halides are unreactive and, unless an amount of Cl₂ is added continuously, the catalytic activity decreases drastically.

It was, therefore, interesting to use preprepared antimony mixed halides and to compare their activity, their selectivity towards the formation of CF₂ClCHCl₂ and their stability.

2. Experimental

All the experiments were carried out in a 100 ml Teflon autoclave at 90°C in liquid HF at a

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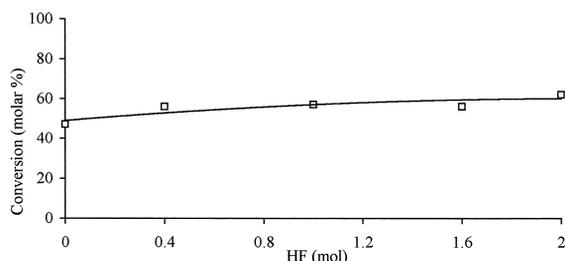


Fig. 1. Influence of the amount of HF for the in situ fluorination of SbCl_5 on the conversion of PCE. $\text{SbCl}_5 = 0.027$ mol; PCE = 0.25 mol, HF = 1.3 mol; $T = 90^\circ\text{C}$, $P = 10$ bar N_2 .

pressure of 10 bar. The catalyst was prepared, prior to reacting PCE with HF. For this, SbCl_5 (0.027 mol) was reacted with HF. After 1 h, the autoclave was cooled down and vented with dry dinitrogen in order to eliminate the HCl and the HF in excess. PCE (0.25 mol), and HF (1.3 mol) were then added. The reaction was carried out for 4 h at 90°C under 10 bar of dinitrogen. We checked that CF_3CHCl_2 was not vented under these conditions. The contents were quenched with 20 ml 6 M H_2SO_4 . The organic phase was dried and analyzed by temperature programmed GC with a BP1 column (40 to 150°C). The products were identified by GC-MS.

Since the reaction was 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. Both Sb species were measured by atomic adsorption. The amount of Sb(III) was determined by oxidation with a KMnO_4 solution. In some cases the residual amount of Cl^- was measured by titration with AgNO_3 in the presence of K_2CrO_4 .

In another series of experiments, the catalyst (SbCl_5 or antimony mixed halides), HF (1.3 mol) and PCE (0.25 mol) were added sequentially and the mixture was heated at 90°C . The reaction was carried out as mentioned above. The different antimony mixed halides (SbFCl_4 , SbCl_3F_2 , SbCl_2F_3 and SbClF_4) were purchased at the Ozarvi-Mahoning (an Elf Atochem North America, Subsidiary) with a purity > 99.5 .

The transformation of $\text{CFCl}_2\text{CHCl}_2$ was also studied under the same conditions (90°C , 10 bar) with preprepared SbCl_5 during 4 h.

3. Results

The catalytic activity of SbCl_5 preprepared with various amounts of HF for the PCE transformation is reported in Fig. 1. No significant effect of the amount of HF on the conversion of PCE could be observed. However, a small increase of the selectivity towards $\text{CHCl}_2\text{CClF}_2$ and a small decrease of $\text{CHCl}_2\text{CCl}_2\text{F}$ and of other products down to 1 mol of HF could be observed (Fig. 2). Below this value, all the performances were constant. A large reduction of Sb(V) into Sb(III) can be noticed.

To identify the active species for the fluorination of PCE under our conditions, the reactivity of various commercial antimony mixed halides (SbFCl_4 , SbCl_3F_2 , SbCl_2F_3 and SbClF_4) was tested for the transformation of the PCE. The catalytic activity of these antimony mixed halides was compared in Table 1 to the in situ SbCl_5 preprepared with HF and to SbCl_5 without prefluorination. First, the prefluorination of SbCl_5 increases the total conversion and the selectivity towards $\text{CF}_2\text{ClCHCl}_2$. Similar conversion and selectivities are obtained with prefluorinated SbCl_5 , SbCl_4F and SbCl_3F_2 . The great activity and selectivity towards fluorina-

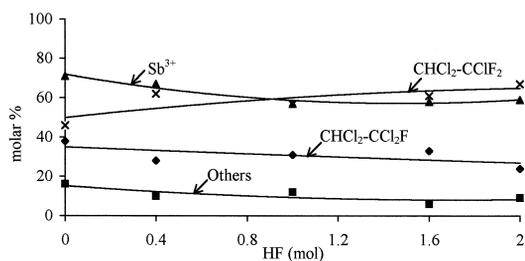


Fig. 2. Influence of the amount of HF in the in situ fluorination of SbCl_5 on the different selectivities and on the reduction of Sb(V) . $\text{SbCl}_5 = 0.027$ mol; PCE = 0.25 mol, HF = 1.3 mol; $T = 90^\circ\text{C}$, $P = 10$ bar N_2 . Others: CCl_3CCl_3 , $\text{CCl}_3\text{CCl}_2\text{F}$, $\text{CCl}_3\text{CCl}_2\text{H}$, $\text{CCl}_2\text{FCCl}_2\text{F}$.

Table 1
Catalytic activity of different antimony mixed halides compared to SbCl_5 (with and without prefluorination)

Catalyst	Conversion (molar %)	$\text{CHCl}_2\text{-CClF}_2$ (molar %)	$\text{CHCl}_2\text{-CCl}_2\text{F}$ (molar %)	Others ^a (molar %)	Sb^{3+} (molar %)
SbCl_5	47	46	38	16	71
without prefluorination					
SbCl_5 prefluorinated	57	57	31	12	60
SbCl_4F	58	54	33	13	72
SbCl_3F_2	52	53	37	10	64
SbCl_2F_3	70	67	25	8	60
SbClF_4	70	66	26	8	40

$T = 90^\circ\text{C}$. $P = 10$ bar of N_2 . Catalyst = 0.027 mol. PCE = 0.25 mol. HF = 1.2 mol.

^a CCl_3CCl_3 , $\text{CCl}_3\text{CCl}_2\text{F}$, $\text{CCl}_3\text{CCl}_2\text{H}$, $\text{CCl}_2\text{FCCl}_2\text{F}$.

Table 2
Fluorination of $\text{CFCl}_2\text{CHCl}_2$ with SbCl_5

Catalyst	Sb(III) after reaction (molar %)	Conversion (molar %)	$\text{CCl}_2 = \text{CCl}_2$ (molar %)	$\text{CF}_2\text{ClCHCl}_2$ (molar %)	Others ^a (molar %)
SbCl_5	27	98	0.3	97.7	2

$\text{SbCl}_5 = 0.0135$ mol, HF = 0.3 mol. $\text{CFCl}_2\text{CHCl}_2 = 0.0625$ mol. HF = 0.3 mol. $T = 90^\circ\text{C}$. $P = 10$ bar N_2 .

^a CCl_3CCl_3 , $\text{CCl}_3\text{CCl}_2\text{F}$, $\text{CCl}_3\text{CCl}_2\text{H}$, $\text{CCl}_2\text{FCCl}_2\text{F}$.

tion can be observed with the antimony mixed halides which contain a high degree of fluorination (SbCl_2F_3 and SbClF_4). In every case, a significant reduction of Sb(V) into Sb(III) occurs.

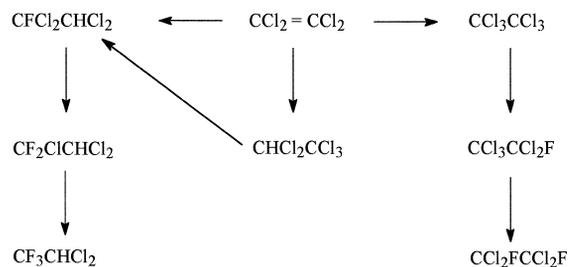
The reactivity of prepared SbCl_5 under the same conditions ($T = 90^\circ\text{C}$) was also tested for the $\text{CFCl}_2\text{CHCl}_2$ fluorination which involved only a Cl/F exchange (Table 2). After 4 h of reaction, the conversion of $\text{CFCl}_2\text{CHCl}_2$ is 98%, the main product being $\text{CF}_2\text{ClCHCl}_2$. A reduction of Sb(V) into Sb(III) can be also noticed.

4. Discussion

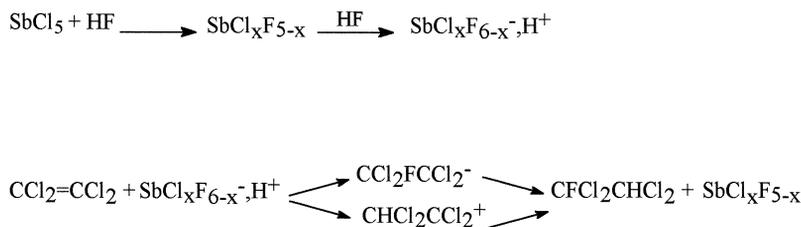
The fluorination of PCE with HF– SbCl_5 involved two reactions: the addition of HF and the Cl/F exchange to produce $\text{ClF}_2\text{CCHCl}_2$ and $\text{Cl}_2\text{FCCHCl}_2$. Other products resulting from the addition of Cl_2 and of HCl on $\text{CCl}_2 = \text{CCl}_2$ were observed. HCl was formed ‘in situ’ during the Cl/F exchange and Cl_2 was produced by the reduction of Sb(V) into Sb(III). All the

products are presented in the Scheme 1. Different mechanisms (electrophilic and nucleophilic) could be involved for both reactions (the addition of HF and the Cl/F exchange) [3,7,10,11]. But in our conditions, we could not separated these two mechanisms.

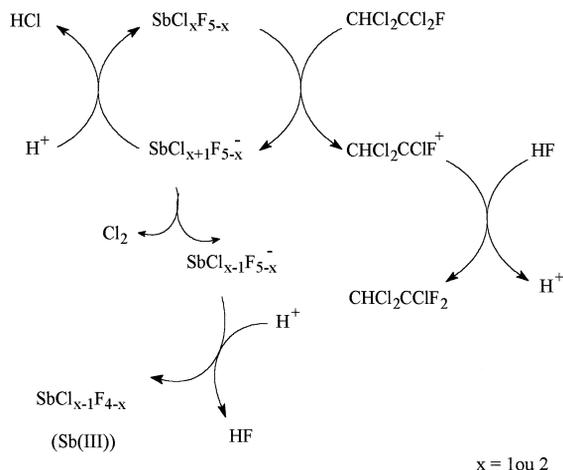
Under these conditions (90°C , 10 bar), the amount of HF during the fluorination of SbCl_5 did not really modify the selectivity towards fluorination and the conversion of PCE. The main product corresponds to the formation of $\text{CF}_2\text{ClCHCl}_2$. A significant selectivity towards fluorination was observed with a high degree of fluorination of antimony (SbCl_2F_3 and SbClF_4). This corresponds also to the decrease of the



Scheme 1. Transformation of PCE with HF– SbCl_5 .



Scheme 2. Change of the catalyst during the reaction of addition of HF on PCE.



Scheme 3. Catalytic cycle of the reduction of Sb(V).

selectivity of the chlorinated products. The prepared catalyst of SbCl_5 with HF has similar performances to the antimony mixed halides SbCl_4F and SbCl_3F_2 . It could be supposed that when HF reacts in situ with SbCl_5 , a formation of these antimony mixed halides or a mixture occurs.

A significant reduction of Sb(V) into Sb(III) can be observed whatever the composition of catalyst. This reduction corresponds to a loss of catalyst activity since Sb(III) is inactive. It could result from a loss of chlorine from the antimony active species. This reduction can also be observed with the fluorination of $\text{CHCl}_2\text{CFCl}_2$ which involves only the Cl/F exchange. The

addition of HF to $\text{CCl}_2=\text{CCl}_2$, which involved a electrophilic or a nucleophilic mechanism, does not seem to reduce Sb(V) (Scheme 2). The catalyst would be regenerated after the addition of HF, without having suffered any reduction. We suggest that the reduction of Sb(V) could occur as described in this cycle (Scheme 3). This catalytic cycle explains the formation of Cl_2 from antimony mixed halides. The addition of Cl_2 to $\text{CCl}_2=\text{CCl}_2$ favours the Sb(V) reduction. It would be difficult to obtain a good fluorinating activity and a good selectivity towards fluorination without a reduction of Sb(V).

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