Journal of Fluorine Chemistry, *59* (1992) 33–39

Liquid-phase fluorination of 1,1,1-trichloroethane

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(Received October 4, 1991; accepted January 26, 1992)

Abstract

The reaction of HF with $SbCl_5$ at 60 °C and 1 MPa provides antimony mixed halides whose empirical formulae have been determined. The product is a mixture of $SbClF_4$ and $SbClF_2$ solvated by HF and its activity has been measured for the conversion of 1,1,1-trichloroethane (F140a) into mono- and difluorochloroethane (F141b and F142b).

Introduction

The fluorination of 1,1,1-trichloroethane (F140a) to 1,1-dichloro-1-fluoroethane (F141b) and 1-chloro-1,1-difluoroethane (F142b) is effected at 60 °C under 1.0 MPa pressure with anhydrous hydrogen fluoride in the liquid phase in the presence of $SbCl_5$ [1–4]. Some trifluoroethane (F143a) is also formed but only in small yield.

$$\underset{\text{(F140a)}}{CH_3-CCl_3} \xrightarrow[SbCl_5]{HF} \underset{\text{(F141b)}}{CH_3-CCl_2F} + \underset{\text{(F142b)}}{CH_3-CClF_2} + \underset{\text{(F143a)}}{CH_3-CF_3}$$

F141b is, at present, under consideration as a replacement for chlorofluoromethanes as a foam blowing agent and F142b is the starting material for the production of polyvinylidene fluoride.

During the above reaction, there is an exchange of chlorine for fluorine between HF and $SbCl_5$ which results in the formation of antimony mixed halides whose stoichiometry depends upon the reaction conditions [5–8].

$$SbCl_5 + xHF \longrightarrow SbCl_{5-x}F_x + xHCl$$

We have previously reported [9] that the use of a 50:1 molar ratio of hydrogen fluoride to antimony pentachloride at −40 °C results in the formation of $SbCl_5 \cdot 4HF$. This active species converts 1,1,1-trichloroethane with high selectivity to 1,1-dichloro-1-fluoroethane (F141b).

In this communication we report, firstly the catalytic fluorination of 1,1,1-trichloroethane at 60 °C and 1 MPa. Secondly, and in order to obtain some information about the active species, we reasoned that it should be interesting

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0022-1139/92/$5.00

to first react HF with $SbCl_5$ at 60 °C and 1 MPa and then to titrate the F^- and Cl^- ions bonded to the antimony. The antimony mixed halide which was obtained was used for the fluorination of 1,1,1-trichloroethane.

Experimental

All experiments were carried out at 60 °C and 1.0 MPa pressure.

Catalytic fluorination of 1,1,1-trichloroethane

To a 500-ml capacity stainless-steel reactor was added 3.6×10^{-2} mol $SbCl_5$ followed by 0.85 mol 1,1,1-trichloroethane and 0.87 mol liquid HF. The reactor was heated at 60 °C under 1 MPa pressure (N_2). Analysis was performed by on-line gas chromatography at 40 °C using a column packed with CP Sil 5.

Prior to injection, the gaseous mixture was allowed to flow through a column packed with KF in order to eliminate HF.

Preparation and titration of the active species

To the reactor was added 2.35×10^{-2} mol $SbCl_5$ followed by liquid HF. By selection of the amount of liquid HF employed, various molar ratios of hydrogen fluoride to $SbCl_5$ were obtained. After heating at 60 °C for 1 h, excess HF was vented in a stream of dry N_2. To the autoclave was added 120 ml of 6 N H_2SO_4, and this solution was used for the titration of antimony, fluoride and chloride ions.

Atomic absorption spectroscopy provided the total amount of antimony, after calibration of the apparatus with standard solutions of Sb^{5+}. Estimation of Sb^{3+} was effected by titration with potassium permanganate: a sample (20 ml) of the solution was diluted with water and cooled at 0 °C. After 15 min and the subsequent addition of 5 ml concentrated H_2SO_4, 0.1 N potassium permanganate was added dropwise until a stable pink colour was obtained.

Chloride ions were titrated according to Mohr's procedure [10] and fluoride ions were titrated potentiometrically using a lanthanum fluoride electrode [11].

Results

Catalytic fluorination of 1,1.1-trichloroethane

A plot of the variation of the composition of the reaction mixture with time is depicted in Fig. 1. Under the conditions employed the major product was 1-chloro-1,1-difluoroethane (F142b), with 1,1-dichloro-1-fluoroethane (F141b) and 1,1-dichloroethene being the obvious primary products.

Analysis and reactivity of the active species

In Fig. 2, the amounts of antimony, fluoride and chloride ions in the aqueous solution obtained by hydrolysis of the $SbCl_xF_y$ species (see Ex-

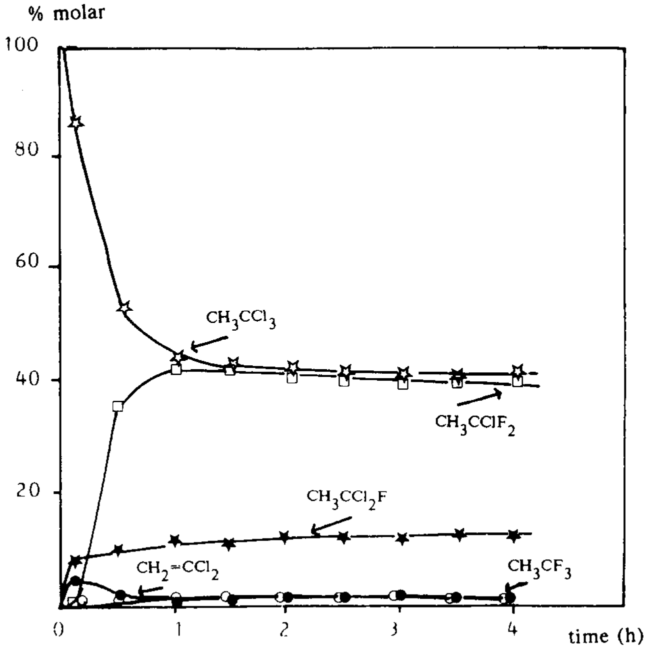


Fig. 1. Catalytic fluorination of 1,1,1-trichloroethane. Variation in the composition of the organic phase with time. Temp. = 60 °C; pressure = 1 MPa; $SbCl_5$ (initial conc.) = 0.036 mol; 1,1,1-trichloroethane (initial conc.) = 0.85 mol; HF:$SbCl_5$ (molar ratio) = 25.

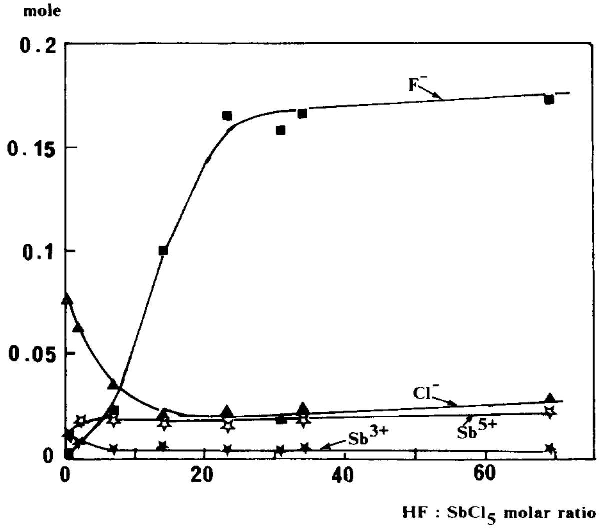


Fig. 2. Plot of the composition of the inorganic phase versus the HF:$SbCl_5$ molar ratio.

perimental Section) have been plotted for various initial molar ratios of hydrogen fluoride to $SbCl_5$. In the absence of HF and at 65 °C, $SbCl_5$ partly decomposes into $SbCl_3$ (48%), but as soon as the amount of HF increases Sb^{5+} is stabilized and above an initial molar ratio HF:$SbCl_5$ of *c.* 10:1, 90% of the initial Sb^{5+} is capable of being recovered.

In addition, the extent of chloride ion substitution in $SbCl_5$ by fluoride ions also increases with the initial HF:$SbCl_5$ ratio. Above a molar ratio of 25:1 the composition of the active species remains constant. According to data arising from titrations, its empirical formula may be written as ($0.9SbClF_4$, $0.1SbClF_2$)$\cdot$4HF. However, because of their instability, it was not possible to isolate these antimony mixed halide and undertake spectroscopic studies.

Stoichiometric fluorination of 1,1,1-trichloroethane

The active species was prepared as above by reacting liquid HF with $SbCl_5$ (2.35×10^{-2} mol) at 60 °C and 1 MPa for 1 h. The initial molar ratio of hydrogen fluoride to antimony pentachloride was 25:1. The unreacted HF was vented and 1 mol of 1,1,1-trichloroethane (F140a) was added to the autoclave. As soon as the composition of the gaseous phase remained constant (as shown by GC analysis), 100 ml of 6 N H_2SO_4 was added and the aqueous phase recovered for analysis of the total antimony, Sb^{3+}, Cl^- and F^- ions. Analytical data relating to the composition of the inorganic phase before and after reaction is reported in Table 1.

The results recorded in this table deserve some comment. All of the antimony was not recovered, which is not surprising since, in addition to the mono- and difluorinated compounds (F141b and F142b), some other by-products were isolated after rotary evaporation of the organic phase to dryness [12]. Analysis of these reactor tars whose composition is very complex is, at present, under investigation, but a preliminary qualitative examination by atomic absorption spectroscopy has shown the presence of antimony. Chloride ion balance is presumably not satisfied since some HCl (approximately 50%) was vented with the gaseous phase and because Cl_2 which was formed during the reduction of Sb^{5+} to Sb^{3+} could not be detected by the analytical methods employed. Finally, it is worth mentioning that at the end of the reaction 85% of the initial Sb^{5+} had been reduced to Sb^{3+}.

TABLE 1

Analysis of the inorganic phase after hydrolysis

Composition of the inorganic phase	Before reaction (mmol)	After reaction (mmol)
Sb_{total}	23.5	19.7
Sb^{3+}	2.5	16.8
Cl^-	22.0	95.0
F^-	166.0	3.17

TABLE 2

Conversion of 1,1,1-trichloroethane by means of $SbCl_5 \cdot 4HF$ at −40 °C and $SbClF_4 \cdot 4HF$ at 60 °C

Extent of conversion of CH_3CCl_3 (F140a) (mol%)	Active species employed	Reaction temp. (°C)	Selectivity		
			CH_3CCl_2F (F141b)	CH_3CClF_2 (F142b)	CH_3CF_3 (F143a)
6.0	$SbCl_5 \cdot 4HF$[a]	−40	100	0	0
–	$SbClF_4 \cdot 4HF$[b]	−40	–	–	–
9.9	$SbClF_4 \cdot 4HF$[b]	60	39.5	57.5	3.0

[a] Prepared by method reported in ref. 9.
[b] Prepared as reported in this communication.

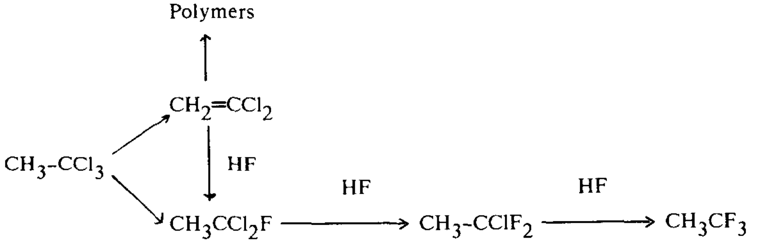
The reactivity of this antimony mixed halide $SbClF_4 \cdot 4HF$ at 0 °C and 60 °C is reported in Table 2 and compared with that of $SbCl_5 \cdot 4HF$ prepared according to the method previously reported [9].

Discussion

The catalytic reaction of 1,1,1-trichloroethane and HF in the presence of $SbCl_5$ at 60 °C and 1 MPa pressure leads to the formation of mono- and difluoro compounds. The same result has been observed when the reaction was carried out with $SbClF_4 \cdot 4HF$ prepared by reacting HF with $SbCl_5$ prior to the addition of 1,1,1-trichloroethane, but in this case the reaction was stoichiometric. In both cases the major product was the difluoro derivative (F142b).

As far as the mechanism is concerned, it can be deduced from Fig. 1 that the primary products are the monofluoro compound (F141b) and the dichloro olefin $CH_2{=}CCl_2$. This latter compound [13] reacts with HF to give $CH_3{-}CCl_2F$ (F141b) and/or polymerizes. Such oligomerization gives rise to the purple material which is always formed in those fluorinations.

In the initial stage of the fluorination two competitive reactions exist, i.e. substitution and elimination, but the former is predominant:



When the reaction was carried out using $SbClF_4 \cdot 4HF$ under the same conditions (60 °C, 1 MPa), predominance of the difluoro compound was now observed. It is suggested that the active species in the catalytic reaction is this mixed antimony halide solvated by polymeric HF. A similar result was obtained at −40 °C [9] but under these conditions the active species was shown to be $SbCl_5 \cdot 4HF$. It is worth mentioning that under both low and high temperature conditions the fluorinating species appears to be polymeric hydrogen fluoride [14] bonded to antimony. According to recently published data [15], even at very high temperatures of *c.* 427 °C, the entering fluorine species is the terminal atom of an HF oligomer.

As far as the reactivity of this fluorinating species is concerned, $SbCl_5 \cdot 4HF$ is more active than $SbClF_4 \cdot 4HF$ since this compound is quite inactive at −40 °C, suggesting that the reactivity of $(HF)_n$ bonded to Sb^{5+} depends on the number of fluorine atoms in the antimony halide. It is assumed that in all experiments conducted at low and high temperatures, 10% of the active species, corresponding to the Sb^{3+} mixed halide, is inactive [16, 17].

The selectivity is better at low temperature since the first carbon–chlorine bond in 1,1,1-trichloroethane is the easiest to break. The energy of this carbon–chlorine bond increases with the number of fluorine atoms bonded to the carbon [18] and hence a higher temperature is necessary for further substitution.

Conclusions

The reaction of HF with $SbCl_5$ provides antimony mixed halides whose composition depends upon the reaction temperature and the molar ratio of HF to $SbCl_5$ in the system. At low temperatures, $SbCl_5 \cdot 4HF$ is obtained, whereas at about 60 °C substitution of chlorine ions occurs which results in the formation of $SbClF_4 \cdot 4HF$ as the major product.

Acknowledgement

The authors thank the Atochem Company for financial support of this work.

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