87

KINETICS OF CHLOROFORM FLUORINATION BY HF CATALYZED BY ANTIMONY PENTACHLORIDE

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SUMMARY

It is shown that $SbCl_4F$ can be considered as the main fluorinating agent when HF and $SbCl_5$ are used in fluorination with an $HF/SbCl_5$ ratio of 1:1. A very simple way for preparing $SbCl_4F$ is described in the paper.

Kinetic runs, performed in batches using both $SbCl_4F$ and $HF+SbCl_5$ as fluorinating agents, allowed identification of the reaction pattern for the chloroform fluorination. Fluorination proceeds through four consecutive steps in which the first and the second are fast and reversible reactions, corresponding to the fluorine-chlorine exchange between $HF/SbCl_5$ and $SbCl_4F/CHCl_3$ respectively. The main product, $CHClF_2$ is formed in the third reaction. The last step to CHF_3 is very slow. Assuming the formation of $CHClF_2$ as reference, the relative reaction rates for the steps are: 150/7/1/0.03.

Kinetic equations and parameters obtained by fitting batch runs have also been verified by interpreting experiments performed under steady state conditions. The kinetic model, employed for elaborating both batch and continuous runs, takes into account also the vapour-liquid equilibria for reactant and products. Suggestions are made on the reaction mechanisms.
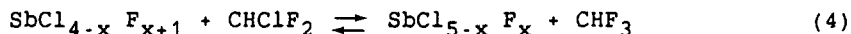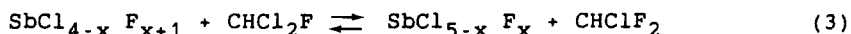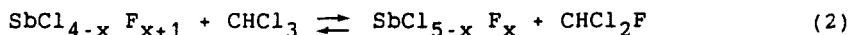
INTRODUCTION

The fluorination of chloroform with hydrogen fluoride catalyzed by $SbCl_5$ is an important reaction for industry in the production of $CHClF_2$, which is employed as a refrigerant and an intermediate for fluoropolymers and perfluoropolyethers [1,2]. Very few papers have been published on the chloride-fluorine exchange reaction in the presence of antimony halides [3,4]. In particular, no paper has been published on the kinetic and mechanistic aspects of the fluorination of chloroform with hydrogen fluoride. This reaction occurs in the liquid phase, at 80-120°C, in the presence of $SbCl_5$. The main reaction products are HCl and $CHClF_2$; $CHCl_2F$ and CHF_3 are also obtained, as by-products, in relatively small amounts. From the literature [4] it is known that $SbCl_5$ reacts with HF by exchanging the halogen according to the following scheme:

$$SbCl_{5-x}F_x + HF \rightleftharpoons SbCl_{4-x}F_{x+1} + HCl \qquad (1)$$
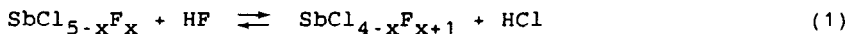
where $0 \leq x < 4$.

Fluorinated antimony compounds could react with $CHCl_3$ according to the following scheme:

$$SbCl_{4-x}F_{x+1} + CHCl_3 \rightleftharpoons SbCl_{5-x}F_x + CHCl_2F \qquad (2)$$

$$SbCl_{4-x}F_{x+1} + CHCl_2F \rightleftharpoons SbCl_{5-x}F_x + CHClF_2 \qquad (3)$$

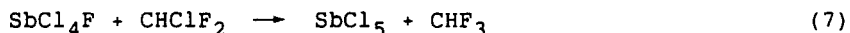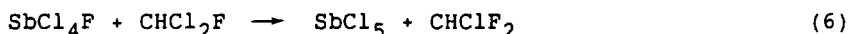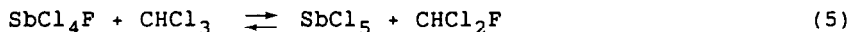$$SbCl_{4-x}F_{x+1} + CHClF_2 \rightleftharpoons SbCl_{5-x}F_x + CHF_3 \qquad (4)$$

The volatility of the reaction products increases strongly with the degree of fluorination [5,6]. Therefore, in industrial continuous reactors, HF and $CHCl_3$ are fed as liquids, while products are withdrawn from the gas phase which is kept at a quite low pressure. In order to optimize the yields of $CHClF_2$, it is necessary to define the kinetic equations involved in the process and to evaluate the fluorinated antimony species which are active in the halide exchange; in practice, it is necessary to assign the correct value to x in reaction (1).

In the case considered the kinetic study needs to take account of the vapor-liquid equilibria of all the chemical

species involved in the reaction, with the exception of the non volatile antimony halides. Reaction rates, in fact, depend on the reagent concentrations, in the liquid phase, which can be strongly affected by the vapour-liquid equilibrium. As will be shown in this paper, when the ratio between HF and $SbCl_5$ is kept equal to 1, $SbCl_4F$ turns out to be the main active species in chloroform fluorination.

We prepared $SbCl_4F$ in a simple and original way and employed it in stoichiometric amounts to separately study the kinetics of the following reactions, performed in a batch reactor, at a fixed temperature of 100°C:

$$SbCl_4F + CHCl_3 \ \rightleftharpoons \ SbCl_5 + CHCl_2F \qquad\qquad (5)$$

$$SbCl_4F + CHCl_2F \ \longrightarrow \ SbCl_5 + CHClF_2 \qquad\qquad (6)$$

$$SbCl_4F + CHClF_2 \ \longrightarrow \ SbCl_5 + CHF_3 \qquad\qquad (7)$$

On the basis of the results obtained, it is possible to define a reliable kinetic pattern for chloroform fluorination, in which reactions (1) and (5) turn out to be equilibrium reactions.

The fluorinating power of $SbCl_4F$ has been compared with that of other fluorinated antimony complexes. Kinetic equations for the reactions (1,5-7) have been derived and the corresponding parameters determined. Kinetic batch runs have been simulated employing a mathematical model in which the evolution with time of the different components is calculated both in the liquid and vapour phases. Kinetic relations and parameters have then been verified by simulating continuous runs, also performed at 100°C, by feeding $CHCl_3$ and HF into a reactor containing known amounts of $SbCl_5$. Continuous runs have also been performed at 85°C and 115°C for evaluating the influence of temperature on the reaction kinetics.

EXPERIMENTAL

Equipment methods and reagents

All the kinetic runs have been performed in the same stainless steel 5 l autoclave, equipped with a magnetic stirrer. Fig. 1 shows the equipment employed.
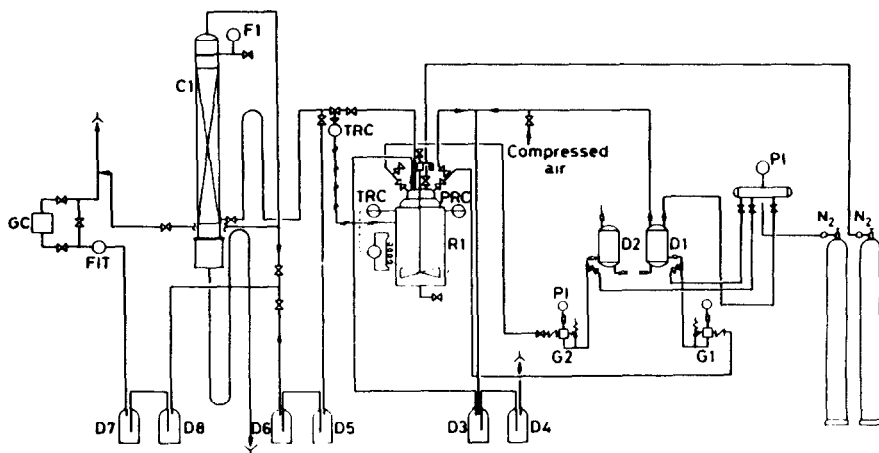
Fig. 1. Diagram of the apparatus employed for the continuous runs.
R1 - Reactor; PRC - Pressure control; TRC - Temperature control; N_2 - Nitrogen bottles; PI - Manometer; D1 - HF reservoir; D_2-$CHCl_3$ reservoir; G1 and G2 - pumps; D3,4,5,6,7,8 - Withdrawing bottles; C1 washing column; GC - on line gas chromatrograph.

In the kinetic runs, performed in batches, weighed amounts of antimony catalysts were fed into the autoclave. Then, the autoclave was heated to the reaction temperature and the reagents were quickly introduced from a nitrogen pressurized bottle. At different reaction times, small amounts of the liquid mixture and of the corresponding vapour phase were withdrawn and analyzed. Organic components of both phases were analyzed gas chromatographically after the elimination of acidity. The chromatographic column was a copper column, 6 m long, diameter 4 mm, filled with 35% by weight of Tergitol NPX 728, supported on particles of 30-60 mesh of Chromosorb P. Helium was employed as carrier gas, at 100°C, with a HWD.

The inorganic part of the liquid phase was also analyzed by determining antimony, inorganic chlorine, and

fluorine. Classical methods were employed for these analyses, that is, iodometry for antimony [7], the Volhard method for chlorine, and the Willard and Winter method [8] for fluorine. Several batch experiments were performed employing different fluorinating complexes of antimony, such as $SbCl_4F$, SbF_3Cl_2, SbF_3, and SbF_5, diluted with $SbCl_5$ in order to get the same ratio Sb/F = 1 in all cases.

Those runs were then compared with each other and with a run performed in the presence of $SbCl_5$ and HF, always keeping Sb/F = 1. $SbCl_4F$ has been prepared by reacting $SbCl_5$, at 0°C, diluted in $C_2Cl_3F_3$ (3:5), with HF, added slowly in stoichiometric amounts. A crystalline precipitate was formed which was filtered, washed with the solvent and dried. The product showed a ratio of F/Sb of 0.95, and a melting point of 82-84°C, which corresponds to literature value for $SbCl_4F$ [9,11]. The possibility of the formation in the precipitate of chemical adducts between $SbCl_5$ and fluorinated complexes containing more than 1 fluorine atom for each antimony atom, is unlikely because when mixing $SbCl_5$ with SbF_3Cl_2, SbF_3, and SbF_5 in order to obtain the ratio Sb/F = 1, the mixture remains liquid at room temperature. This new method for producing $SbCl_4F$ is easier than that reported in literature [9-11] which is based on the reaction between $SbCl_5$ and AsF_3.

In the kinetic runs, performed under steady state conditions, the reagents chloroform and hydrogen fluoride were fed as liquid streams into the autoclave containing the catalyst ($SbCl_5$) and the whole was heated at the reaction temperature. At the outlet of the reactor gaseous reaction products and unreacted reagents were collected at a moderate pressure (6-10 atm).

The non-ideality of the liquid phase has been investigated by determining the infinite dilution coefficient for the subcritical components, $CHCl_3$ and $CHCl_2F$, independently of kinetic runs. The determination has been made by gas chromatography [12] by measuring the retention time of the components in a stainless steel column filled with $SbCl_5$ (7.5% by weight) supported on Teflon (powder of a 160-220 mesh). $SbCl_5$ presaturated with helium has been used as carrier gas. Moreover the overall effect of non-ideality, both in the liquid and gas phases, has directly been evaluated in batch, as the deviation from the Raoult's law. For the supercritical components, vapour pressures have been estimated by extrapolation. The observed deviations from Raoult's law include, of course, the large approximations introduced in the extrapolation.

All the reagents employed were supplied from Montefluos SpA, except for the antimony compounds $SbCl_5$, SbF_3, and SbF_5 provided from Carlo Erba SpA.

The compound $SbCl_2F_3$ was prepared according to the literature [5,9-11, 14-18].

RESULTS

1) <u>Kinetic behaviour of different fluorinated antimony compounds in chloroform fluorination</u>

Kinetic runs of chloroform fluorination with different fluorinated antimony compounds have been performed by adding $SbCl_5$ to the different fluorinated complexes in such amounts to always have F/Sb = 1. Therefore, $SbCl_4F$ has been employed without dilution with $SbCl_5$. The autoclave was normally filled with about 1.5 l of the antimony mixture and heated at 100°C. Then, chloroform was added in such amount to have the molar ratio F/C = 2.

Batch runs have been performed by employing the following substances as fluorinating agents: $SbCl_4F$ alone, 2 $SbCl_5$ + SbF_3Cl_2, $4SbCl_5$ + SbF_5, and 2 $SbCl_5$ + SbF_3. The obtained results are reported in Figs. 2, 3, 4 and 5 respectively.

Runs have also been carried out in which the fluorinating agent was formed in situ by reacting $SbCl_5$ with HF, keeping the molar ratio F/Sb = 1. In one case, the HCl formed in the reaction was removed by washing with nitrogen before introducing chloroform, while, in another case, chloroform has been added in the presence of HCl. The results of the two cases are reported in Figs 6 and 7. As can be seen, the behaviour of the runs reported in Fig. 2 and 6 are almost identical. This suggests that $SbCl_4F$ is the main fluorinating agent when HF is used with $SbCl_5$ with a molar ratio equal to 1. The presence of HCl has a detrimental effect on the fluorination rate and yield. This can be explained by assuming that the reaction:

$$SbCl_5 + HF \rightleftharpoons SbCl_4F + HCl \tag{8}$$
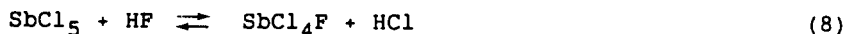
is an equilibrium reaction, with an equilibrium constant near to 1.

From Figs 3 and 4, it can be concluded that more highly fluorinated antimony (V) compounds are not particularly
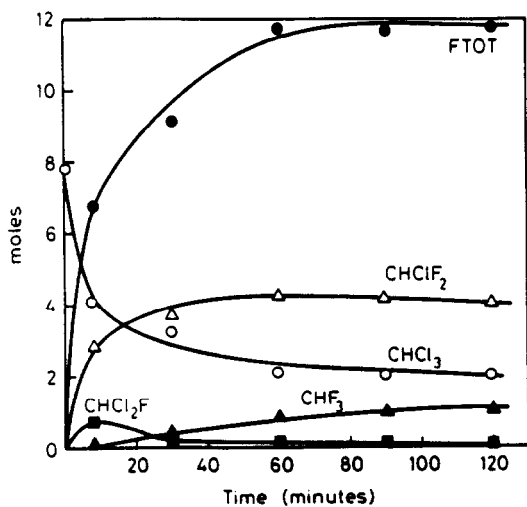
Fig. 2. Kinetic batch run, performed at 100°C, by reacting 15.56 moles of $SbCl_4F$ with 7.97 moles of $CHCl_3$. Continuous curves are calculated.

Fig. 3. Kinetic batch run, performed at 100°C, by reacting 5.46 mole of SbF_3Cl_2, dissolved in 10.92 moles of $SbCl_5$, with 7.86 moles of $CHCl_3$.
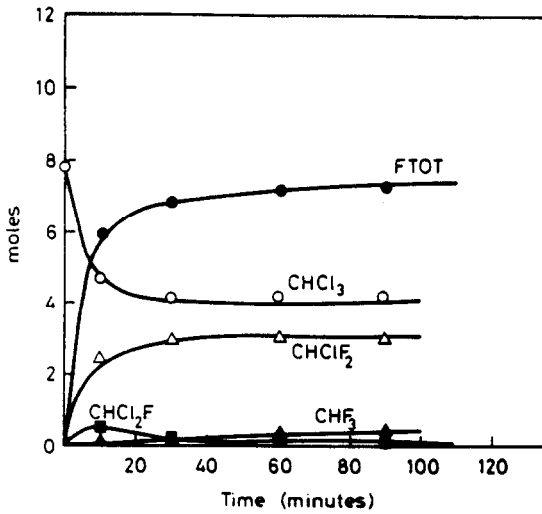
Fig. 4. Kinetic batch run, performed at 100°C, by reacting 3.17 moles of SbF_5, dissolved in 12.7 moles of $SbCl_5$, with 7.88 moles of $CHCl_3$.
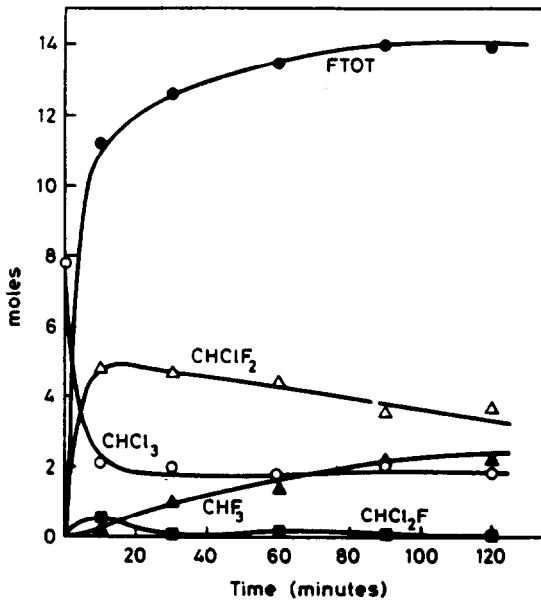
Fig. 5. Kinetic batch run, performed at 100°C, by reacting 5.48 moles of SbF_3, diluted in 10.96 moles of $SbCl_5$, with 7.85 moles of $CHCl_3$.

Fig. 6.   Kinetic batch run, performed at 100°C, by reacting 15.84 moles of $SbCl_5$ with 15.85 moles of HF. The hydrochloric acid formed is removed by washing with nitrogen; then 7.07 moles of $CHCl_3$ were introduced. The run is very similar to that reported in Fig. 2.

Fig.   7.   Kinetic batch run, performed at 100°C, under the same conditions as Fig. 6, but without removing hydrochloric acid.

active, as compared with $SbCl_4F$. Therefore, it is reasonable to consider that SbF_5 and SbF_3Cl_2 when mixed with $SbCl_5$ give other fluorinated species, mainly $SbCl_4F$. On the contrary, SbF_3 mixed with $SbCl_5$ is more active than $SbCl_4F$ as shown in Fig. 5. Since the reaction pattern remains unchanged in this case, we must conclude that the intermediate antimony complexes formed have a greater mobility of fluorine than $SbCl_4F$ or other Sb(V) fluorinated complexes.

2) <u>Kinetics of chloroform fluorination, performed with pure $SbCl_4F$ as fluorinating agent, in batch conditions</u>

On the basis of the results reported above, where $SbCl_4F$ was recognized as the main fluorinating agent when HF and $SbCl_5$ are mixed with the molar ratio Sb/F = 1, kinetic runs have been performed in batch conditions, employing the following substances as reagents: $SbCl_4F$ and $CHCl_3$, $CHCl_2F$, or $CHClF_2$. The results obtained have already been described for $CHCl_3$ in Fig. 2. In the other cases, runs have been performed similarly and also at 100°C: the results are in Figs 8 and 9. From Fig. 8, it can be seen that the reaction between $CHCl_2F$ and $SbCl_4F$ quickly reaches equilibrium with the formation of chloroform. On the contrary, in the case of $CHClF_2$, only CHF_3 is formed. Therefore, reaction (5) is a reversible reaction, while reactions (6) and (7) are irreversible.

3) <u>Kinetics of chloroform fluorination in a continuous flow reactor</u>

Runs have been performed at three different temperatures: 85, 100, and 115°C. The results obtained together with the operative conditions are summarized in Table 1. As can be seen, the composition of the vapour stream from the reactor is little affected by temperature. The pressure has been kept at 6.5-13 atm to allow easy access to gas phase products. The concentration of CHF_3 is not completely reproducible in some runs because of analytical difficulties arising at very low concentration levels of this compound.

Under all conditions reaction (5) resulted in equilibrium. In particular, the vapour concentrations of $CHCl_3$, $CHCl_2F$, HF, and HCl agree satisfactorily in all cases with the thermodynamic equilibrium constants determined from literature data [21-22].
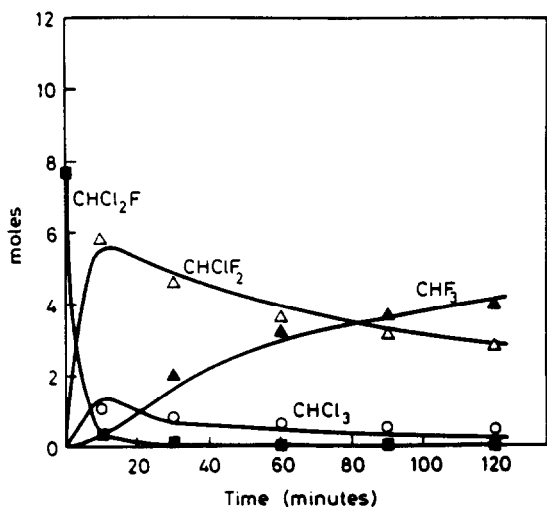
Fig. 8. Kinetic batch run, performed at 100°C, by reacting 15.46 moles of SbCl$_4$F with 7.73 moles of CHCl$_2$F. Continuous curves are calculated.
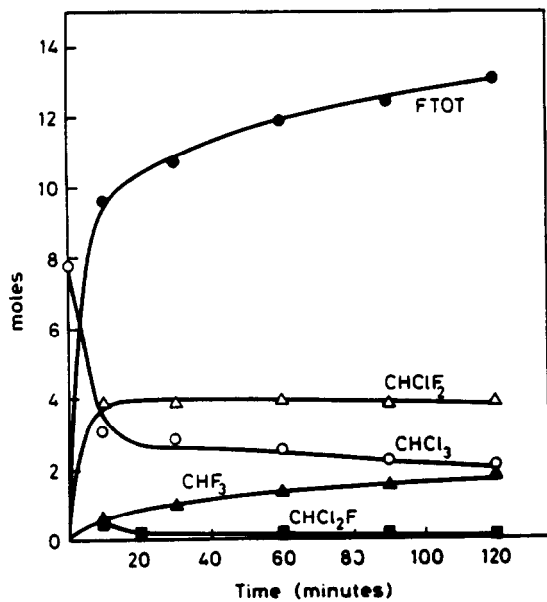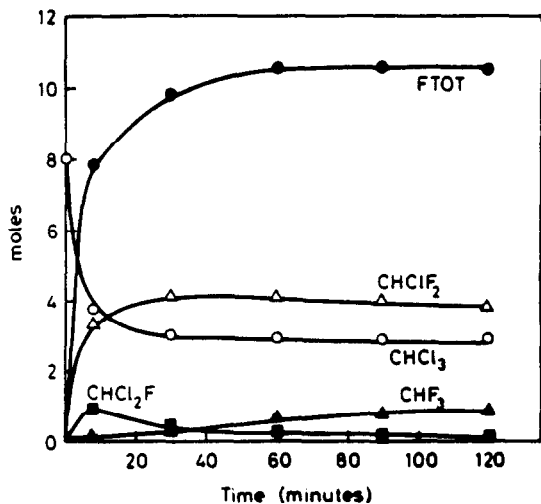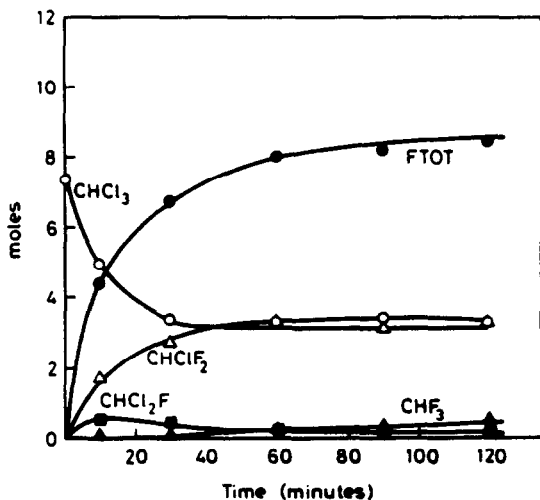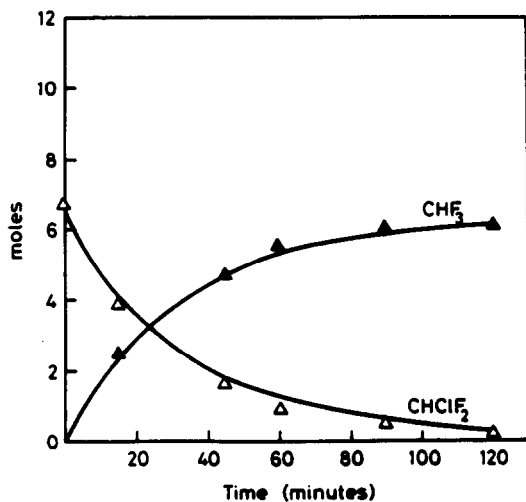

Fig. 9. Kinetic batch run, performed at 100°C, by reacting 15.76 moles of SbCl$_4$F with 6.80 moles of CHClF$_2$. Continuous curves are calculated.

TABLE 1

Compositions obtained by chemical analysis at the outlet of the continuous reactor in the chloroform fluorination. Operative conditions are also reported for any single run in the table. Compositions obtained by calculation are also reported for comparison.

	T (°C)	P (atm)	W (kg)	F (moles/h)	$R= z_1/z_2$	z_1 (HF)	z_2 (CHCl$_3$)	y_1 (HF)	y_2 (CHCl$_3$)	y_3 (HCl)	y_4 (A21)	y_5 (A22)	y_6 (A23)
Exp.	100	10.0	3.642	89.22	1.96	0.662	0.338	0.097	0.034	0.564	0.058	0.23	0.015
calc.								0.109	0.030	0.552	0.069	0.23	0.007
Exp.	100	10.5	3.108	90.70	2.01	0.668	0.332	0.107	0.031	0.560	0.057	0.231	0.014
calc.								0.125	0.027	0.540	0.072	0.225	0.007
Exp.	100	10.0	3.211	90.05	1.99	0.665	0.334	0.095	0.031	0.570	0.054	0.232	0.017
calc.								0.122	0.029	0.540	0.075	0.224	0.007
Exp.	115	13.0	2.52	89.3	1.96	0.662	0.338	0.107	0.033	0.560	0.063	0.228	0.011
calc.								0.120	0.033	0.540	0.075	0.224	0.007
Exp.	115	13.8	4.22	89.4	1.96	0.663	0.337	0.106	0.033	0.556	0.064	0.228	0.012
calc.								0.092	0.032	0.571	0.052	0.241	0.012
Exp.	115	13.8	3.869	96.2	2.19	0.686	0.313	0.105	0.016	0.581	0.037	0.236	0.024
calc.								0.138	0.019	0.54	0.050	0.232	0.012
Exp.	85	8	3.295	89.8	1.98	0.664	0.35	0.106	0.031	0.56	0.062	0.231	0.011
calc.								0.134	0.027	0.53	0.092	0.212	0.005
Exp.	85	7.3	4.224	68.3	1.45	0.392	0.408	0.061	0.066	0.531	0.155	0.184	0.0023
calc.								0.038	0.091	0.55	0.085	0.226	0.0055

4) Liquid-vapour equilibrium of reactants and products

Due to the high vapour pressures of both fluorinated reactants and products, the kinetic study needs definition of the liquid-vapour equilibrium partitions for each of the species involved. Partition constants $k_i = y_i/x_i$ have been evaluated from liquid and vapour phase compositions obtained by chemical analysis during batch experiments.

For the subcritical species, $CHCl_3$ and $CHCl_2F$, the average deviation from the Raoult's law have been evaluated using $\bar{\varphi_i}$ coefficients as shown in Table 2, and derived from the relation:

$$k_i = y_i/x_i = p^{\cdot}_i/P \quad \bar{\varphi_i} \tag{9}$$

Independent experiments have been performed for these subcritical species in order to assess the non ideality in $SbCl_5$ solutions by determining coefficients at infinite dilutions γ_∞. For this purpose, experiments have been carried out at different temperatures, by gas-chromatography. Table 2 shows the results for γ_∞ values at different temperatures. Values at 100°C have been obtained by extrapolation. These values, compared with those obtained by deviation from Raoult's law for the same species show that non-ideality is confined to the vapour phase.

Vapour pressures have been calculated by Antoine's relations and Antoine's constants are also reported in Table 2 for the different components.

For the supercritical components such as $CHClF_2$, CHF_3 and HCl vapour pressures have been extrapolated where necessary. The $\bar{\varphi_i}$ coefficient, therefore, also contains extrapolation errors. In the continuous experiments performed at fairly low pressures (6-12 atm) ideality in both the liquid and gas behaviour has been assumed.

The non-ideality of HF and HCl, which are involved in association equilibria with $SbCl_5$ can be defined from the experimental equilibrium constant of reaction (8), the fitting of batch experiments, and from the thermodynamic equilibrium constant of the reaction:

$$CHCl_{3(V)} + HF_{(V)} \rightleftarrows CHCl_2F_{(V)} + HCl_{(V)} \tag{10}$$
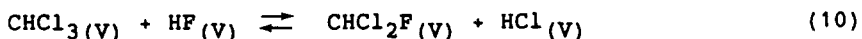
calculated from literature data [21,22], and strictly complied with from the vapour phase compositions measured in the continuous runs.

100

TABLE 2

Vapour-liquid equilibrium parameters as activity coefficient at infinite dilution γ^∞, average deviation of Raoult law in the batch runs, Antoine parameters [23,24] . The asterisked values have been obtained by extrapolation.

COMPONENTS	Temper. (°C)	γ^∞	$\bar{\varphi}$	A	B	C
$CHCl_3$	34	2.23				
	48	1.82				
	68	1.73				
	100	0.95*	2	7.44502	1486.455	264.538
$CHCl_2F$	34	1.17				
	48	1.15				
	68	1.08				
	100	1.03*	2.2	7.17231	1105.42	248.671
$CHClF_2$	100	-	3.5	7.24077	947.577	258.186
CHF_3	100	-	20	7.13058	718.089	251.137
HF	-	-	-	17.6958	3404.49	15.06
HCl	-	-	-	16.5040	1714.25	-14.45

TABLE 3

Kinetic and equilibrium parameters employed in fitting experimental runs both in continuous and batch conditions.

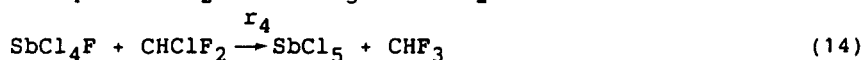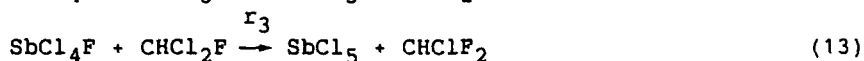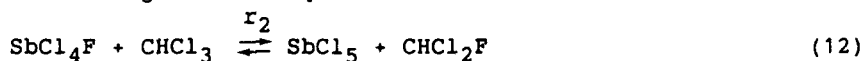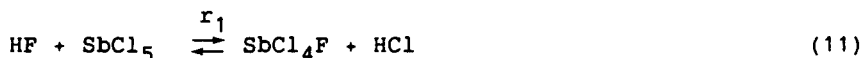| T (°C)	$\overline{k}_e$ (experimental)	k_e (theoretical)	k_{e1}	k_{e2}	k_1 $(\frac{cm^3}{mole/h})$	k_2 $(\frac{cm^3}{mole/h})$	k_3 $(\frac{cm^3}{mole/h})$	k_4 $(\frac{cm^3}{mole/h})$
100	11.7	11.55	~0.45	~0.152	~3.6x10^5	~3.2x10^4	4680±250	175±15
85	13.9	13.37	-	~0.267	-	-	2660+140	101±10
115	10.7	10.09	-	~0.09	-	-	7884+380	295±28

Table 3 compares experimental equilibrium constant values of reaction (10) (obtained from the data of Table 1), with thermodynamic values calculated from literature data [21,22]. Both sets of values agree very well.

5) **Reaction pattern; kinetic model for the fitting of batch experiments; determination of parameters**

The following observations can be drawn from batch experiments:

a) The evolution of the various species involved shows a pattern of consecutive reactions.

b) Monofluorinated and trifluorinated derivatives of chloroform are always present in small concentrations, the first as a reaction intermediate and the latter owing to its slow rate of formation.

c) The monofluorinated species is formed as a consequence of a reaction which quickly reaches equilibrium.

d) $SbCl_4F$ is mainly responsible for fluorination when the molar ratio F/Sb does not exceed the unity.

e) The reaction producing $SbCl_4F$ quickly reaches equilibrium.

On the basis of such evidence, we can write the following reaction schemes:

$$HF + SbCl_5 \underset{}{\overset{r_1}{\rightleftharpoons}} SbCl_4F + HCl \qquad\qquad (11)$$

$$SbCl_4F + CHCl_3 \underset{}{\overset{r_2}{\rightleftharpoons}} SbCl_5 + CHCl_2F \qquad\qquad (12)$$

$$SbCl_4F + CHCl_2F \overset{r_3}{\longrightarrow} SbCl_5 + CHClF_2 \qquad\qquad (13)$$

$$SbCl_4F + CHClF_2 \overset{r_4}{\longrightarrow} SbCl_5 + CHF_3 \qquad\qquad (14)$$

We assumed second order kinetics for all the reactions for reasons which will be discussed later.

Ascribing index 1 to HF, 2($CHCl_3$), 3(HCl), 4($CHCl_2F$), 5($CHClF_2$), 6(CHF_3), 7($SbCl_5$), 8($SbCl_4F$), we can write:

$$r_1 = k_1 \, C_1 \, C_7 \, \left(1 - \frac{1}{K_{e_1}} \frac{C_3 \, C_8}{C_1 \, C_7}\right) \qquad\qquad (15)$$

$$r_2 = k_2 \, C_2 \, C_8 \, \left(1 - \frac{1}{K_{e_2}} \frac{C_4 \, C_7}{C_2 \, C_8}\right) \qquad\qquad (16)$$

$$r_3 = k_3 \, C_4 \, C_8 \qquad\qquad (17)$$

$$r_4 = k_4 \, C_5 \, C_8 \qquad\qquad (18)$$

The rates of formation and disappearance of different species are given by:

$$dC_1/dt = - dC_3/dt = - r_1 \tag{19}$$

$$dC_7/dt = - dC_8/dt = - r_1 + (r_2+r_3+r_4) \tag{20}$$

$$dC_2/dt = - r_2 \tag{21}$$

$$dC_4/dt = r_2 - r_3 \tag{22}$$

$$dC_5/dt = r_3 - r_4 \tag{23}$$

$$dC_6/dt = r_4 \tag{24}$$

Equations (19-24) need to be integrated as concentrations in reaction rate expressions are affected by the liquid-vapour phase partition which depends continuously on the changing liquid composition with time. Liquid volume and total pressure are also time dependent.

In order to account for the liquid-vapour partition, we have to solve a system made up of the following equations:

$$x_i = \frac{n_{il}}{n_{totl}} = \frac{n_{iv}}{n_{totv}} \cdot \frac{P}{P_i^o \varphi_i} \qquad i = 1, NCV \tag{25}$$

$$n_{Ti} = n_{il} + n_{iv} \qquad i = 1, NCV \tag{26}$$

$$n_{totl} = (n_7^o + n_8^o) + \sum_{i=1}^{NCV} i \ n_{il} \tag{27}$$

$$n_{totv} = \sum_{i=1}^{NCV} i \ n_{iv} \tag{28}$$

Two further equations must be added, to determine volume and pressure:

$$v_l = \sum_{i=1}^{NCV} i \ \frac{n_{il} \ PM_i}{\rho_i} \tag{29}$$

$$P = \sum_{i=1}^{NCV} i \ P_i = \frac{n_{totv} \ RT}{v_R - v_l} \tag{30}$$

This system of non linear algebric equations has been solved by the Newton-Raphson method, while the integration of differential equations (19-24) was made by the Runge-Kutta method.

To simulate batch experiments in practice, starting from the known initial conditions, the differential equations (19-24) were integrated and, following each integration step, the liquid-vapour partition as well as the liquid volume and the total pressure was recalculated by solving the system of algebric equations (25-30).

Kinetic constants k_2, k_3, k_4, and the equilibrium constant k_{e2}, were determined at 100°C by fitting batch experiments such as those of Figs 2, 8 and 9.

The partition constants, k_i, and average deviation from ideality, $\overline{\phi}_i$, were obtained from chemically assessed liquid-vapour compositions.

Using these parameters, the experiment of Fig. 7, containing HCl and HF, was also fitted by a rough evaluation of the kinetic constant k_1 and equilibrium constant k_{e1}.

Fittings obtained for the different experiments are reported in the corresponding Figures, while the employed parameters are listed in Table 3.

Tables 4 and 5 report, as examples, equilibrium liquid-vapour compositions for the experiments of Fig. 2 and Fig. 9, respectively, and the corresponding values obtained by calculation. The comparison between the two sets of values is satisfactory.

6) Check of the kinetic model and parameters in continuous runs. Determination of the influence of temperature.

Continuous runs have been performed using the same autoclave at 100°C, and at 85 and 115°C, respectively. The results obtained are reported in Table 1. They have been interpreted by applying the following equations:

a) Fluorine balance: $FR/(FR+1) = y_1+y_4+2y_5+3y_6$ (31)

b) Carbon balance: $1/(FR+1) = y_2+y_4+y_5+y_6$ (32)

c) Hydrochloric acid balance: $y_3 = y_4+2y_5+3y_6$ (33)

d) $CHClF_2$ balance: $Fy_5 = v_1r_3 - Fy_6$ (34)

e) CHF_3 balance: $Fy_6 = v_1r_4$ (35)

TABLE 4

Compositions of vapour and liquid phase in equilibrium at different reaction times.
Data obtained by the analysis of samples withdrawn in the batch run reported in Fig. 2.
Compositions obtained by calculation are also reported for comparison.

Time (m')	Conditions		% weight						P (atm)
			$CHCl_3$	$CHCl_2F$	$CHClF_2$	CHF_3	$SbCl_4F$	$SbCl_5$	
8	Liq.	Exp.	9.17	0.74	2.99	0.035	46.90	40.08	
		Calc.	9.11	1.43	3.23	0.010	44.71	40.61	
	Vap.	Exp.	7.31	7.9	79.20	5.10			24
		Calc.	8.24	7.2	78.40	6.10			19
30	Liq.	Exp.	7.36	0.46	3.99	0.07	35.5	52.60	
		Calc.	6.71	0.48	4.66	0.05	29.1	57.43	
	Vap.	Exp.	4.15	5.79	74.11	15.9			25
		Calc.	4.05	1.61	75.33	19.0			29
60	Liq.	Exp.	5.17	0.19	3.06	0.04	35.65	55.34	
		Calc.	5.58	0.25	4.88	0.09	20.94	66.26	
	Vap.	Exp.	2.29	3.47	71.6	21.87			34
		Calc.	2.88	0.70	67.5	28.84			39
90	Liq.	Exp.	5.19	0.31	3.45	0.02	28.9	62.1	
		Calc.	5.05	0.16	4.80	0.12	16.49	66.26	
	Vap.	Exp.	2.58	2.87	68.9	25.6			34
		Calc.	2.75	0.44	62.23	34.9			39
120	Liq.	Exp.	5.10	0.21	3.58	0.05	26.07	64.92	
		Calc.	4.74	0.12	4.66	0.14	13.56	74.33	
	Vap.	Exp.	3.01	2.81	67.11	27.06			35
		Calc.	2.22	0.33	58.41	39.02			39

TABLE 5

Compositions of vapour and liquid phase in
equilibrium at different reaction times. Data obtained
by the analysis of samples withdrawn in the batch run
reported in Fig. 9. Compositions obtained by calculat-
ion are also reported for comparison.

Time	Conditions		% Weight		P(atm)
			A22	A23	
15	Liq.	Sper.	2.6	0.44	
		Calc.	4.6	0.25	
	Vap.	Sper.	57.6	41.8	55
		Calc.	46.4	53.39	54
45	Liq.	Sper.	1.17	0.29	
		Calc.	1.97	0.39	
	Vap.	Sper.	23.12	76.87	63
		Calc.	18.72	81.28	59
60	Liq.	Sper.	0.33	0.07	
		Calc.	1.36	0.42	
	Vap.	Sper.	14.4	85.2	63
		Calc.	13.0	86.92	63
90	Liq.	Sper.	0.37	0.43	
		Calc.	0.70	0.44	
	Vap.	Sper.	6.4	93.31	65
		Calc.	6.8	93.17	66
120	Liq.	Sper.	0.15	0.35	
		Calc.	0.37	0.45	
	Vap.	Sper.	4.07	95.7	65
		Calc.	3.77	96.2	67

where

$$r_3 = \frac{K_3}{k_{e_2}} \left(\frac{n_{totl}}{v_1}\right)^2 x_7 \; P \; \frac{y_4^2}{y_2} \; \frac{P_2^\circ}{P_4^{\circ 2}} \tag{36}$$

$$r_4 = \frac{k_4}{k_{e_2}} \left(\frac{n_{totl}}{v_1}\right)^2 x_7 \; P \; \frac{y_4 y_5}{y_2} \; \frac{P_2^\circ}{P_4^\circ \; P_5^\circ} \tag{37}$$

The species $CHCl_2F$ has been assumed to be at thermodynamic equilibrium in the gas phase for all runs, and, therefore:

f) Equilibrium of reaction (10) $\quad k_e = \dfrac{y_3\, y_4}{y_2\, y_1}$ (38)

Three further equations are then necessary for evaluating x_7, n_{totl}, and v_1:

g) $x_7 \left(1 + \dfrac{1}{k_{e_2}}\, \dfrac{y_4}{y_2}\, \dfrac{p_2^o}{p_4^o}\right) - 1 + P \displaystyle\sum_{i=1}^{NCV} i\, \dfrac{y_i}{p_i^o} = 0$ (39)

h) $n_{totl}\left(1 - P \displaystyle\sum_{i=1}^{NCV} i\, \dfrac{y_i}{p_i^o}\right) - n_7^o = 0$ (40)

i) $v_1 - n_{totl}\left[x_7\left(\dfrac{PM_7}{\rho_7} + \dfrac{1}{k_{e_2}}\, \dfrac{y_4}{y_2}\, \dfrac{p_2^o}{p_4^o}\, \dfrac{PM_8}{\rho_8}\right) + \right.$

$\left. + P \displaystyle\sum_{i=1}^{NCV} i\, \dfrac{y_i}{p_i^o}\, \dfrac{PM_i}{\rho_i} \right]$ (41)

This system has been solved using the Newton-Raphson method. The runs performed at 100°C have been simulated employing the parameters reported in Table 3 previously obtained from batch runs. In Table 1 experimental data are compared with the calculated ones. The agreement is satisfactory for all the components, except, sometimes, for CHF_3. However, in this case, the disagreement can be attributed to the analysis because this component is present at very low levels.

In Table 1, experimental and calculated data obtained are also reported at 85° and 115°C. By observing the experimental data at different temperatures, it is seen that

temperature has little effect on reaction rates. This can be explained by observing that in the proposed kinetic model, the kinetic constants, k_3 and k_4 are always divided by the equilibrium constant, k_{e2}. Assuming the apparent activation energy in the reactions (13,14) to be about zero it must be concluded that the effective activation energy of these reactions and the enthalpy change of reaction (12) are equal but opposite in sign. Therefore, we have assumed 10 kcal/mole for the activation energy of the mentioned reactions, in agreement with the values suggested by Kolditz and Schultz [3] for the CCl_4 fluorine-chlorine exchange reaction. Consequently, the enthalpy of reaction (12) has been assumed as - 10 kcal/mole. The comparison between calculated and experimental data for the continuous runs at 85 and 115°C reported in Table 1, is satisfactory considering the simplifications introduced.

We have not observed deactivating complexes to be formed between $SbCl_5$ and $SbCl_4F$. Such complexes have been observed in the literature [3], but at very low temperatures (0-20°C).

Continuous runs have confirmed that reactions (11) and (12) occur very quickly. Also reaction (13) is fast enough to be affected by convective flow, at the highest flow rates of the reagents. On the other hand, with the described kinetic model, a strong increase in flow rates slightly affects the gaseous stream composition by a small increase of $CHCl_2F$ and HF and a small decrease of $CHClF_2$. The ratio between the initial reaction rates for reactions 11 to 14, by assuming reaction (13) as reference, is 150,7, 1, and 0.03.
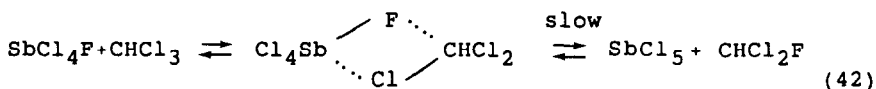

DISCUSSION AND CONCLUSIONS

By comparing the kinetic behaviour of $SbCl_4F$ in the fluorination of $CHCl_3$, with that obtained by dissolving HF in $SbCl_5$ with HCl stripping (Figs 2 and 6) it is reasonable to conclude that, in the temperature range 85-115°C, $SbCl_4F$ is the main fluorinating agent. On the other hand Kolditz and Schultz [3] also indicated $SbCl_4F$ as a fluorine carrier in CCl_4 fluorination. SbF_3Cl_2 gives fluorination activity similar to that of $SbCl_4F$, while SbF_5 is less active. It is reasonable to think that the above compounds exchange part of the fluorine with $SbCl_5$ giving mixtures of fluorinated antimony complexes. However, in the case of SbF_5 it seems that part of the fluorine is not available for fluorination.

According to Kolditz and Schultz [3], fluorine blocked in Sb---F---Sb-type bridges is not important in the halogen

exchange reaction. The formation of these bridges is probably favoured in the case of SbF_5. According to Dejnicke and Weidlein [10] active fluorine is located on the apex of the trigonal bipyramid, that is as in the structure of $SbCl_4F$. This fluorine would easily be ionizable. It is difficult to explain the increase in activity observed for SbF_3 + $SbCl_5$. However, as the reaction pattern is always the same, the problem of different activities must be reduced to the fluorine mobility of the complexes formed.

The different activity in fluorine-chlorine exchange for $CHCl_3$, $CHCl_2F$ and $CHClF_2$ can be explained as formation of fluorine bridges is more favoured over those of chlorine [3]. Therefore, in the case of $CHCl_3$, only the following mechanism would be possible:

$$SbCl_4F + CHCl_3 \; \rightleftharpoons \; Cl_4Sb \overset{F}{\underset{Cl}{\diagdown\!\diagup}} CHCl_2 \; \overset{slow}{\rightleftharpoons} \; SbCl_5 + CHCl_2F \tag{42}$$

In the other cases, $SbCl_4F$ can be involved in unfruitful equilibria giving intermediates as:

$$Cl_4Sb \overset{F}{\underset{F}{\diagdown\!\diagup}} CHCl_2 \qquad \text{or} \qquad Cl_4Sb \overset{F}{\underset{F}{\diagdown\!\diagup}} CHFCl \tag{43}$$
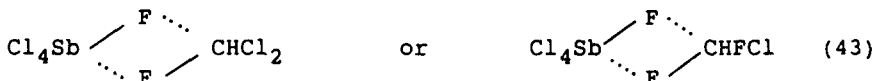
that are much more favoured than the fluorine-chlorine bridge, shown in scheme (42). Therefore, the probability of reactive intermediate formation and reaction strongly decreases with the degree of fluorination of the compound.

Reaction scheme (42) can be considered as a nucleophilic substitution, S_{N2}, in accordance with a second order kinetic law.

The presence of HF does not change such conclusions, because reaction (11) is very fast and quickly furnishes the $SbCl_4F$ necessary for further reactions.

LIST OF SYMBOLS

C	=	concentration (moles/cm^3)
F	=	molar flow rate (moles/h)
FR	=	$CHCl_3$/HF molar feed rate
FTOT	=	total eschanged fluorine
K	=	vapour-liquid partition coefficient
k_1	=	kinetic constant of reaction (11)
k_2	=	kinetic constant of reaction (12)
k_3	=	kinetic constant of reaction (13)
k_4	=	kinetic constant of reaction (14)
k_e	=	equilibrium constant of reaction (10)
k_{e1}	=	equilibrium constant of reaction (11)
k_{e2}	=	equilibrium constant of reaction (12)
n	=	number of moles
NCT	=	total number of components
NCV	=	total number of components in vapour phase
P	=	total pressure
p°	=	vapour pressure (atm)
p	=	partial pressure (atm)
PM	=	molecular weight
R	=	constant of gases (cm^{3}atm/K mole)
t	=	time (h)
T	=	absolute temperature
V	=	volume (cm^3)
x	=	molar fraction in the liquid phase
y	=	molar fraction in the vapour phase
$\bar{\varphi}_i$	=	average coefficient of the Raoult's law deviation
ρ	=	liquid density (g/cm^3)

Indexes

i	=	number related to the components (1=HF, 2=$CHCl_3$, 3=HCl, 4=$CHCl_2F$, 5=$CHClF_2$, 6=CHF_3, 7=$SbCl_5$, 8=$SbCl_4F$)
tot	=	total related to a single phase
T	=	total related to both phases
l	=	liquid
V	=	vapour
R	=	reactor

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