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Kinetics of tetrachloromethane fluorination by hydrogen fluoride in the presence of antimony pentachloride

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Abstract

Contradictory information concerning the kinetics of tetrachloromethane fluorination by anhydrous hydrogen fluoride in the presence of antimony pentachloride has been explained. The present studies were performed using a stainless steel autoclave. The exchange of the first chlorine atom was carried out in the temperature range of 35–95 °C, with the molar ratio of HF/CCl_4 varied within the range of 1.2–1.7 and at a constant molar ratio of $SbCl_5/Cl_2$ equal to 1.9. The degree of conversion of CCl_4 to CCl_3F and the reaction rate constant as a function of temperature fit to an Arrhenius straight line. The Arrhenius constants (pre-exponential factor) and the activation energy were determined. Studies concerning the exchange of the second chlorine atom, i.e. the conversion of CCl_3F to CCl_2F_2 have been performed. The results of kinetic investigations were created in the same way. Based on these results it was found that the Arrhenius equation is fulfilled also in the second stage of the fluorination. The same slope of the straight lines confirms that the fluorination stages proceed according to the same mechanism with the same activation energy but with different pre-exponential factors.

Several kinetic problems associated with the performance of the reactor can be solved on the basis of the equations derived. However, knowledge of CCl_4 conversion as a function of time, temperature, catalyst concentration and the type of the reaction is required for this purpose. Such calculations enable the selection of the optimal process parameters.

Keywords: Kinetics; Fluorination; Chlorofluorocarbons

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1. Introduction

The fluorination of tetrachloromethane by anhydrous hydrogen fluoride in the presence of antimony pentachloride was the principal reaction in the synthesis of chlorofluorocarbons (CFCs): CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) which were utilized previously as refrigerants.

The fluorine–chlorine exchange reaction is of considerable practical importance in the synthesis of hydrochlorofluorocarbons (HCFC) and completely safe hydrofluorocarbons (HFC), e.g. CF_3CH_2F (HFC-134a). The latter compound [1,2] is most often used as a replacement for CFC-11 and -12.

Literature reports concerning the way in which $SbCl_5$ participates in fluorine exchange between HF and CCl_4 provide no intrinsic discrepancy [1–4]. There is convincing evidence, confirming that antimony(V) chlorofluorides with a general formula of $SbCl_{5-n}F_n$ can be used as fluorinating agents. They are formed in the following reaction

$$SbCl_5 + nHF \rightarrow SbCl_{5-n}F_n + nHCl \tag{1}$$

where $n = 1$ to 4.

There is also consistency in the opinions that the reaction of antimony(V) chlorofluoride with CCl_4 proceeds according to the following way

$$SbCl_{4-n}F_{n+1} + CCl_4 \rightarrow SbCl_{5-n}F_n + CCl_3F \tag{2}$$

$$SbCl_{4-n}F_{n+1} + CCl_3F \rightarrow SbCl_{5-n}F_n + CCl_2F_2 \tag{3}$$

$$SbCl_{4-n}F_{n+1} + CCl_2F_2 \rightarrow SbCl_{5-n}F_n + CClF_3 \tag{4}$$

$$SbCl_{4-n}F_{n+1} + CClF_3 \rightarrow SbCl_{5-n}F_n + CF_4 \tag{5}$$

Antimony fluorides were the subject of many studies performed by Kolditz and coworkers [4–7]. Although their objective has been focused mainly on the analytical problems, they shed some light on the process of fluorine exchange between HF and $SbCl_5$. The results confirm that the exchange of fluorine with the first and second chlorine atoms in $SbCl_5$ proceeds readily even at low temperatures (from −70 to −40 °C). Complete exchange of the third atom occurs with a sufficient excess of HF in the temperature range from −40 to 20 °C, whereas the fourth atom is exchanged in the temperature range from −25 to 0 °C. However, the exchange of the last chlorine atom for fluorine does not proceed by this route. The use of even a considerable excess of HF (HF/$SbCl_5$ ~20 mol),

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with annealing carried out for more than 2 h at temperature of 85 °C and distillation of HF, does not lead to the formation SbF_5 but to formation of $SbClF_4{\cdot}HF$. Further distillation of $SbClF_4{\cdot}HF$ causes its decomposition with the evolution of chlorine, and simultaneous reduction of Sb(V) to Sb(III).

2. The kinetic model

To our knowledge no paper has been published on the kinetics of fluorine exchange between $SbCl_5$ and HF in the existing literature. Simakov and Korobochko [8] have reported that the HF absorption is accompanied by the chemical reaction, the role of which can be given by the kinetic equation

$$R = k[SbCl_5]^2[HF] \tag{1}$$

where $[SbCl_5]^2$ and [HF] are molar concentrations, k the observed rate constant of reaction, estimated at room temperature as $k = 1 \times 10^3\ dm^6\ mol^{-2}\ s^{-1}$.

From this value it can be concluded that it describes the rate of exchange of the first chlorine atom in $SbCl_5$. However, one cannot evaluate whether further stages of exchange in (1) for $n = 2, 3, 4$ will proceed with the same reaction rate. When the less advantageous variant is assumed and in the reaction (1), only $SbCl_4F$ ($n = 1$) is formed, $SbCl_5$ is regenerated in the reactions (2)–(5) and is almost instantaneously fluorinated to $SbCl_4F$. Thus, as long as HF is present in the reaction, the principal process of CCl_4 fluorination proceeds at a constant concentration of fluorinating agent.

The authors of the papers related to the kinetic aspect [4,9,10] are in agreement that at temperature higher than 20–26 °C the reaction is (Eq. (6)) irreversible

$$SbCl_4F + CCl_4 \rightarrow CCl_3F + SbCl_5 \tag{6}$$

Kolditz and Schultz [7] believed that the effect of temperature can be attributed to the deactivation of $SbCl_4F$. This compound forms a stable complexes $(SbCl_4F)_n{\cdot}SbCl_5$ at low temperatures in which all fluorine atoms are involved in bridge bonds, thereby they cannot participate in the exchange reaction with CCl_4.

The papers discussing the kinetic equation of the reaction lead to contradictory conclusions. The results of studies performed by Chekmarev et al. [9], indicate that the rate of Eq. (6) reaction at the temperature range between 20 and 50 °C can be described by the kinetic equation

$$r = k[SbCl_4F]_2[CCl_4] \tag{2}$$

Kolditz and Schultz [7] claimed that at a temperature range between 0 and 26 °C the following equation is more appropriate

$$r = k[SbCl_4F][CCl_4] \tag{3}$$

Different values of the activation energy obtained by both authors suggest that a change of the reaction mechanism take places with change in temperature.

The reaction between antimony(V) chlorofluorides and CCl_4 was also presented as (7).

$$SbCl_2F_3 + 3CCl_4 \rightarrow 3CCl_3F + SbCl_5 \tag{7}$$

However, the authors have restricted their discussion only to a comparison of the kinetic curves of the reactions (6) and (7). On the basis of the form of Eq. (7) they have assumed that $SbCl_2F_3$ is three times more active than $SbCl_4F$ during the exchange of fluorine. In accordance with this assumption they compared the kinetic curves for solutions with the initial composition: 1 mol $SbCl_4F + nCCl_4$ and 1/3 mol $SbCl_2F_3 + nCCl_4$.

However, the authors did not take into account that the exchange abilities of $SbCl_4F$ and $SbCl_2F_3$ equalize with increase in reaction temperature. By recalculation of the number of moles of CCl_3F formed in the reactions (6) and (7) on 1 mol of $SbCl_{5-n}F_n$ instead of $1/n$ mol, the initial rates of both reaction are the same at 26 °C. The kinetic curve for the reaction (7) is characteristic for a system of irreversible consecutive reactions with the rate constants being identical or very close to each other. Thus, it can be assumed that $SbCl_2F_3$ participates in the three consecutive steps of reactions (2), by exchanging consecutively with CCl_4 by one fluoride atom according to

$$SbCl_2F_3 + CCl_4 \rightarrow CCl_3F + SbCl_3F_2 \tag{8}$$

$$SbCl_3F_2 + CCl_4 \rightarrow CCl_3F + SbCl_4F \tag{9}$$

$$SbCl_4F + CCl_4 \rightarrow CCl_3F + SbCl_5 \tag{6}$$

$$SbCl_2F_3 + 3CCl_4 \rightarrow 3CCl_3F + SbCl_5 \tag{7}$$

Assuming, that the above scheme describes the real reaction mechanism and the rate constants of the reactions (6), (8) and (9) are identical, then for a significant excess of CCl_4, the kinetic equations are linear

$$\left.\begin{aligned}\frac{d[SbCl_2F_3]}{dt} &= -k_{ef}[SbCl_2F_3]\\ \frac{d[SbCl_3F_2]}{dt} &= k_{ef}[SbCl_2F_3] - [SbCl_3F_2]\\ \frac{d[SbCl_4F]}{dt} &= k_{ef}[SbCl_3F_2] - [SbCl_4F]\end{aligned}\right\} \tag{4}$$

where $[SbCl_xF_x]$ is the molar concentration of component, t-reaction time, k_{ef} the effective rate constant of reaction determined as: $k_{ef} = kb$, where k the rate constants of reactions (6), (8), (9), b the initial concentration of CCl_4. The rate of (6) reaction can be given by the equation

$$\frac{d[SbCl_4F]}{dt} = -k_{ef}[SbCl_4F] \tag{5}$$

Denoting by X and Y the yields of reactions (**6**) and (**7**) respectively, and determining them as the ratio of the mole

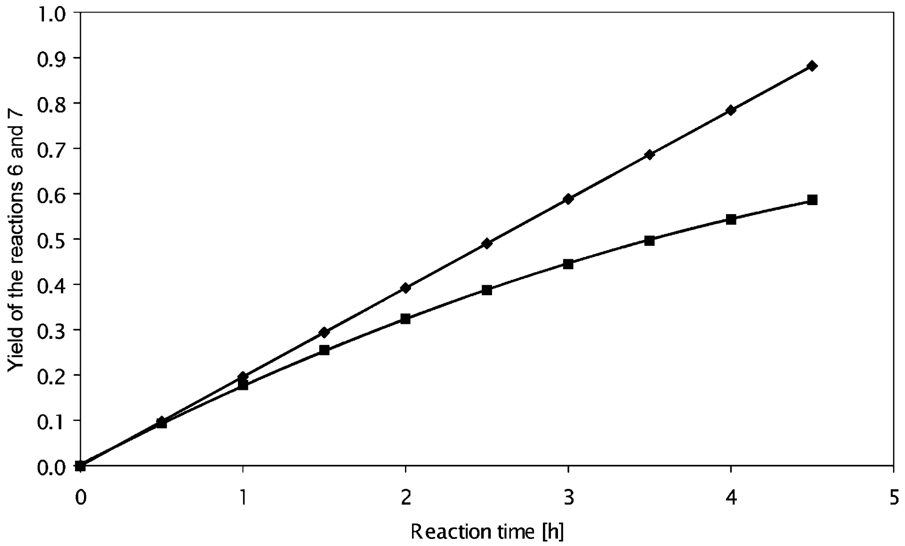

Fig. 1. The yield of CCl_3F in reaction (6) (◆) and (7) (■) as a function of the reaction time.

number of CCl_3F to the initial mole number of $SbCl_{5-n}F_n$, respectively for $n = 1$ and 3, then we can obtain

$$X = 1 - e^{-k_{ef}t} \quad \mathbf{(6)}$$

By the solution of the equation system (**4**) and for a short reaction time, it can be demonstrated that the relationship $Y = f(t)$ is approximately linear

$$Y = k_{ef}t \quad \mathbf{(7)}$$

The results of work performed by Kolditz and Schultz [7] are consistent with this derived equation. The experimental results of Kolditz are presented in Fig. 1 together with the values calculated on the basis of Eqs. (**6**) and (**7**) for $k_{ef} = 0.194\ h^{-1}$.

The proposed kinetic scheme indicates that in each elementary reaction one chlorine atom undergoes exchange, according to reaction (2). The rate of the first stage of reaction describes the kinetic equation

$$r_n = k[SbCl_{5-n}F_n][CCl_4] \quad \mathbf{(8)}$$

with the reaction rate constant k independent of n.

Our studies reported here permit the explanation of literature reports concerning the kinetics and mechanism of this complex process.

3. Results and discussion

3.1. The exchange reaction of fluorine between antimony(V) chlorofluorides and CCl_4 (reaction (2))

The kinetic constant of reaction was calculated with the assumption, that the reaction is second order and proceeds in the liquid phase, thus

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad \mathbf{(9)}$$

where a is initial concentration of HF, b the initial concentration of CCl_4, x the concentration of CCl_3F after time t.

The average reaction rate constants for particular temperatures from the range under investigation are summarized in Table 1. Due to the excess of hydrogen fluoride it can be expected that under the conditions investigated, the rate of conversion of CCl_4 to CCl_3F is dependent only on the CCl_4 concentration and the initial concentration of $SbCl_5$, i.e. the kinetic equation is fulfilled

$$r = kc_{SbX}[CCl_4] \quad \mathbf{(10)}$$

This equation is valid when the total amount of $SbCl_5$ will be transformed into the active form, i.e. when $SbCl_5 = 0$.

Taking into consideration the rate of reaction given by

$$r = \frac{-d[CCl_4]}{dt} \quad \mathbf{(11)}$$

after the integration of Eqs. (10) and (11) we can obtain

$$\alpha = 1 - e^{-kc_{SbX}t} \quad \mathbf{(12)}$$

Table 1
The kinetic constants of reaction in CCl_4 fluorination to CCl_3F

Number	Temperature (°C)	Kinetic constant of reaction $k \times 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)
1	0	0.33[a]
2	13	0.69[a]
3	26	1.67 ± 0.39[a]
4	35	4.22 ± 0.39
5	45	4.47 ± 0.46
6	55	8.51 ± 0.71
7	65	15.3 ± 2.2
8	75	27.0 ± 3.5
9	85	34.3 ± 4.9
10	95	36.4 ± 5.6

[a] Based on literature data.

where α is the degree of CCl_4 conversion. This equation can be written in a more convenient form for testing as

$$-\ln(1-\alpha) = kc_{\mathrm{SbX}}t \qquad \textbf{(13)}$$

Because of the uncertainly in the rate constant shown in Eq. (**9**), testing of Eq. (**13**) separately for individual measurements will give a wide scatter of results and it would not be possible to show unequivocally that Eq. (**13**) correctly describes the kinetics of transformation of CCl_4 to CCl_3F. For this reason it was verified that

- the reaction rate constants calculated on the basis of Eq. (**13**) comply with the Arrhenius equation;
- the values of the constants determined from this equation (pre-exponential factor and the activation energy) are consistent with the literature data.

The calculation were carried out in the following way:

- the concentration of c_{SbX} catalyst was evaluated;
- for each measuring point (α, t) the value of reaction rate constant, k, was calculated from Eq. (**13**);
- at each temperature after several reaction times, the value of the constant, k, was averaged and the standard deviation was calculated.

These magnitudes are summarized in Table 1 and they were compared with literature data [7]. In order to determine the catalyst concentration, the volume of the liquid phase was calculated. It was assumed that the volume is an additive function

$$v = \sum_i n_i V_i \qquad \textbf{(14)}$$

where n_i is the number of mole component i of the liquid phase, V_i molar volume of component i. The molar volume of particular components was calculated from the equation

$$V_i = \frac{M_i}{d_i} \qquad \textbf{(15)}$$

where M_i is the molecular weigh of component i, d_i the density of component i (HF, CCl_4, CCl_3F, $SbCl_5$, $SbClF_4$).

The numbers of moles of the respective reagents were calculated with the following assumptions:

- the reaction between $SbCl_5$ and HF proceeds instantaneously and the total amount of $SbCl_5$ is transformed to $SbClF_4$;
- introduction of Cl_2 and formation of HCl occur in the gaseous phase;
- the pressure in the reactor is so high that the remaining components, i.e. HF, CCl_4, CCl_3F and $SbClF_4$ are in the liquid phase.

From the mass balance calculation the catalyst concentrations c_{SbX} are

$$c_{\mathrm{SbX}} = \frac{1}{0.968 + 1.891(m/\alpha) - 0.19} \qquad \textbf{(16)}$$

c_{SbX} is the catalyst concentration (mol dm^{-3}), m the mass of mixture of CCl_4, $SbCl_5$, Cl_2 (g); α the degree of CCl_4 conversion.

The catalyst concentrations in the particular tests calculated from Eq. (**16**) vary from 0.8 to 0.9 mol dm^{-3}. Taking into account simplifications, the average value of $c_{\mathrm{SbX}} = 0.85$ mol dm^{-3} was assumed.

Based on the results summarized in Table 1, Fig. 2, line 1 was plotted as

$$\ln k = f\left(\frac{1}{T}\right) \qquad \textbf{(17)}$$

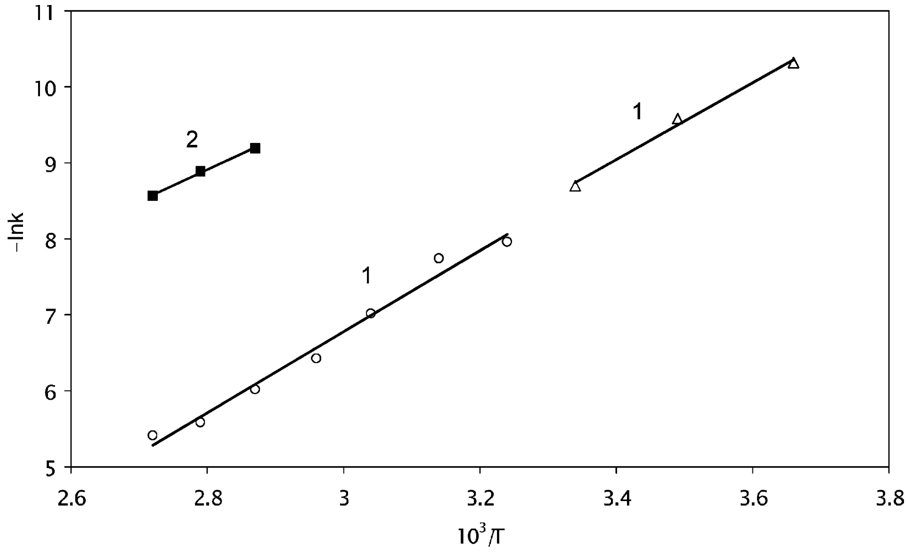

Fig. 2. Verification of the Arrhenius equation for the reaction $CCl_4 \rightarrow CCl_3F$ (1) and $CCl_3F \rightarrow CCl_2F_2$ (2) (△), (■) the result of our studies; (○) data from work of Kolditz and Schultz.

This chart convincingly validates the assumed mechanism of CCl_4 fluorination. Most of the data points form a straight line according to Arrhenius equation

$$\ln k = \ln k_0 - \frac{E}{RT} \qquad \textbf{(18)}$$

These results are consistent with those obtained by Kolditz et al. (Fig. 2, long line 1) [7]. The constants of the Arrhenius equation determined from the graph are: pre-exponential factor $k_0 = 2.08 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, and the activation energy $E = 46\ \mathrm{kJ\ mol^{-1}}$.

3.2. Exchange reaction of fluorine between antimony(V) chlorofluorides and CCl_3F (reaction (3))

The second stage of CCl_4 fluorination (reaction (3)) is practically not recognised. It is known from the literature [3,7] that the exchange of the second fluorine atom proceeds with significantly more difficulty than the first. From the literature also, the only reaction product of CCl_4 with $SbCl_4F$ (reaction (2)) at atmospheric pressure and temperature below the boiling point of CCl_4 (76.6 °C) is CCl_3F. It was found that a small amount of CCl_2F_2 occurs at temperature 77 °C after several hours of the reaction [7].

The results of the kinetic studies of CCl_3F fluorination were created similarly to the results of the first stage (fluorination of CCl_4). The following parameters were calculated: the catalyst concentration ($c_{\mathrm{SbX}} = 0.9\ \mathrm{mol\ dm^{-3}}$), the reaction rate constant, assuming that the second stage proceeds in excess of hydrogen fluoride according to the same mechanism as the first. Thereby, the rate of R-3 reaction can be described by the kinetic equation

$$r = kc_{\mathrm{SbX}}[\mathrm{CCl_3F}] \qquad \textbf{(19)}$$

The results of calculations of the reaction rate constants and the degrees of conversions are summarized in Table 2.

After the calculation of the averages, the following values of the rate constants were obtained:

$$k_{95\,^\circ\mathrm{C}} = 2.49 \pm 0.73 \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$k_{85\,^\circ\mathrm{C}} = 1.39 \pm 0.26 \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$k_{75\,^\circ\mathrm{C}} = 1.20 \pm 0.41 \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

Table 2
Rate constants and degree of CCl_3F conversion to CCl_2F_2

Temperature (°C)	Reaction time (min)	Degree of conversion (%)	Rate constant $k \times 10^4$ ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$)
75	13	11.8	1.79
	16	13.4	1.40
	19	13.5	1.41
85	10	10.1	1.97
	13	10.0	1.66
	16	10.9	0.83
	19	10.6	1.09
95	10	11.3	2.22
	13	13.7	2.03
	16	15.2	1.91
	19	16.1	1.81

The results are presented in Fig. 2 (line 2). From this figure results that the Arrhenius equation is also fulfilled for reaction (3) (stage 2). The same slope of the straight line may indicate that both stages of CCl_4 fluorination proceed according to the same mechanism with the activation energy $E = 46\ \mathrm{kJ\ mol^{-1}}$. The pre-exponential factor of reaction (3) is significantly smaller and amounts to $k_0 = 8.01 \times 10^{-12}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

As a result of the rapid reaction of $SbCl_5$ with HF, a mixture of $SbCl_{5-n}F_n$ ($1 \le n \le 4$) is formed, the composition of which is dependent on both temperature and the amount of HF. In previous work [7,11] it has been concluded that $SbCl_4F$ and $SbCl_2F_3$ play a significant role in the replacement of chlorine in CCl_4 and consecutive chlorofluorocarbons. Our studies reveal that the rate of replacement of the first chlorine atom in CCl_4 does not depend on the value of n in $SbCl_{5-n}F_n$. At significantly high temperature, this compound is $SbClF_4$. Thus the course of fluorination can be presented as follows:

$$\mathrm{CCl_4 + SbClF_4 \rightarrow CCl_3F + SbCl_2F_3} \qquad (10)$$

$$\mathrm{CCl_3F + SbClF_4 \rightarrow CCl_2F_2 + SbCl_2F_3} \qquad (11)$$

$$\mathrm{SbCl_2F_3 + HF \rightarrow SbClF_4 + HCl} \qquad (12)$$

Reaction (12) proceeds so rapidly that the total amount of $SbCl_5$ introduced occurs in the active form as $SbClF_4$, i.e.

$$[\mathrm{SbClF_4}] = [\mathrm{SbCl_5}]_0 = c_{\mathrm{SbX}} \qquad \textbf{(20)}$$

The rates reactions (10) and (11) which determine the first and the second stage of CCl_4 fluorination can be described by the following kinetic equations:

$$r_{\mathrm{I}} = k_{\mathrm{I}}c_{\mathrm{sbx}}[\mathrm{CCl_4}] \qquad \textbf{(21)}$$

$$r_{\mathrm{II}} = k_{\mathrm{II}}c_{\mathrm{SbX}}[\mathrm{CCl_4}] \qquad \textbf{(22)}$$

The reaction rate constants fulfill the Arrhenius equation

$$k = k_0\,\mathrm{e}^{-E/RT} \qquad \textbf{(23)}$$

The activation energies of both reactions are the same and the pre-exponential factors are given by, respectively

$$k_{0\mathrm{I}} = 2.08 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$$k_{0\mathrm{II}} = 8.00 \times 10^2\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

Based on Eqs. (**20**)–(**23**) any kinetic problem associated the operation of the reactor for the synthesis may be solved. In the case of a closed batch reactor, a fundamental kinetic approach leads to the solution of the system of equations

$$\left.\begin{aligned} \frac{\mathrm{d}[\mathrm{CCl_4}]}{\mathrm{d}t} &= -kc_{\mathrm{SbX}}[\mathrm{CCl_4}] \\ \frac{\mathrm{d}[\mathrm{CCl_3F}]}{\mathrm{d}t} &= kc_{\mathrm{SbX}}[\mathrm{CCl_4}] - k_{\mathrm{II}}c_{\mathrm{SbX}}[\mathrm{CCl_3F}] \\ \frac{\mathrm{d}[\mathrm{CCl_2F_2}]}{\mathrm{d}t} &= k_{\mathrm{II}}c_{\mathrm{SbX}}[\mathrm{CCl_3F}] \end{aligned}\right\} \qquad \textbf{(24)}$$

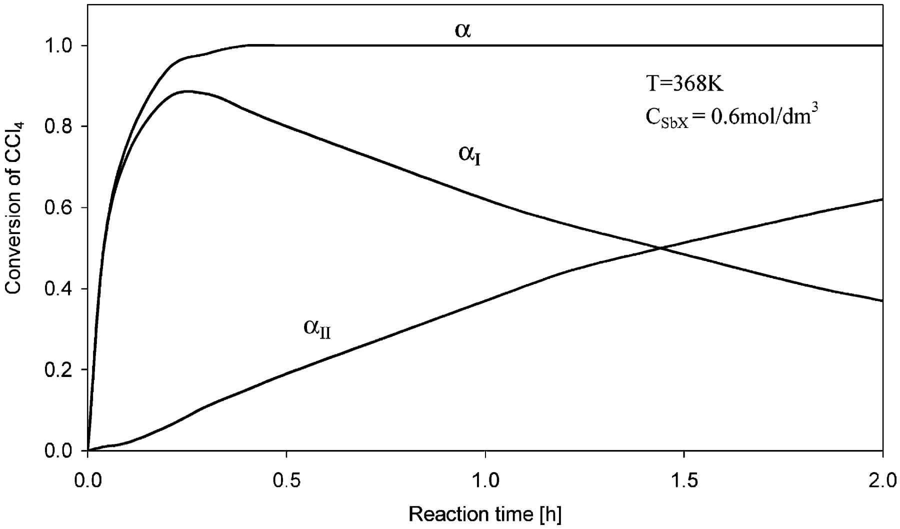

Fig. 3. The degree of CCl_4 conversion as a function of the time: α_I, degree of CCl_4 conversion to CCl_3F; α_{II}, degree of CCl_4 conversion to CCl_2F_2; α, total conversion.

The solution of system (**24**) for the isothermal process can be presented in the analytical form

$$\alpha_I = \frac{k_I}{k_I - k_{II}}(e^{-k_{II}c_{SbX}t} - e^{-kc_{SbX}t}) \quad \textbf{(25)}$$

$$\alpha_{II} = 1 + \frac{k_{II}}{k_I - k_{II}} e^{-kc_{SbX}t} - \frac{k_I}{k_I - k_{II}} e^{-k_{II}c_{SbX}t} \quad \textbf{(26)}$$

$$\alpha = 1 - e^{-k \cdot_{SbX}t} \quad \textbf{(27)}$$

where α is the total conversion of CCl_4; α_I, α_{II} the conversion of CCl_4 to CCl_3F and CCl_2F_2, respectively.

The results of calculation for the conditions: temperature 95 °C, catalyst concentration 0.6 mol dm^{-3} (the closed, batch reactor) are presented in Fig. 3. Such the calculations for various catalyst concentrations, different types of the reactor, enable the optimal selection of the process parameters.

4. Experimental

4.1. Raw materials

Hydrogen fluoride from a steel cylinder, purity 99.9 wt.%, was the product of Lubon Chemical Works, Poland. Tetrachloromethane, purity 99.9 wt.%, after distillation was obtained from Anwil, Poland. Antimony pentachloride, purity ≥99 wt.%, from Fluka. Dichlorine from a steel cylinder, purity 99.9 wt.% was the product "Rokita" Chemical Works, Poland. Chlorofluorocarbons, CCl_3F, CCl_2F_2; purity 99.8 wt.% were obtained in Department of Organic Technology, Technical University of Szczecin.

4.2. Apparatus and procedure

All studies have been performed in a 7 cm^3 stainless steel autoclave which was charged by means of a syringe with a mixture of CCl_4 or CCl_3F with the catalyst $SbCl_5$ and dichlorine. The molar ratio of $SbCl_5/Cl_2$ was constant. After weighing, the autoclave was cooled to ca. −10 °C, anhydrous hydrogen fluoride was introduced, and its amount determined by weighing. The autoclaves were placed in a shaker and were then submerged in oil bath. After a defined time the autoclaves were taken out, cooled in a water bath with ice and were unloaded. The gaseous content of the reactor was discharged to a polyethylene tank under the water surface using a needle valve. Above the tank was placed a polyethylene absorber, which was sprinkled by cooled water. When the flow of gases was terminated while the needle valve was kept open, water was sucked into the autoclave. The autoclave was opened, the content was discharged to reflux from the absorber and the concentration of the F^- ion was determined potentiometricly. Measurements were performed with ion-selective electrode in OP-108 apparatus (Radelkis). Cl_2 concentration was determined by iodometric titration. CCl_4 and CFCs were determined by gas chromatography. The mass balance of the F^- ion and organic raw material was performed.

4.3. Gas chromatography conditions

A Chrom 5 apparatus equipped with 2.5 m × 4 mm steel column packed with Porapak Q (80–100 mesh) was employed. The apparatus was equipped with a flame ionization detector (FID) with N_2 flow rate 20 $cm^3\ min^{-1}$ (carrier gas), air flow rate 300 $cm^3\ min^{-1}$, H_2 flow rate 30 $cm^3\ min^{-1}$. The temperature were: thermostat 170 °C, detector and sample injector 250 °C.

4.4. General procedure for the synthesis

Experiments were carried out at a temperature range between 35 and 95 °C with variation of the temperature in 10 °C intervals, at a molar ratio of HF/CCl_4 varied over a range of 1.7−1.2. The composition of raw material was as follows: CCl_4, 82 wt.%; $SbCl_5$, 16 wt.%; Cl_2, 2 wt.%. The degree of conversion of CCl_4 to CCl_3F was calculated using the following definition

$$\alpha = \frac{n^0_{HF} - n_{HF}}{n^0_{CCl_4}} \times 100\% \qquad \mathbf{(28)}$$

where n^0_{HF} and n_{HF} the number of moles of hydrogen fluoride before and after the reaction, $n^0_{CCl_4}$: the number of moles of CCl_4 before the reaction.

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