Catalytic synthesis of 1,1,1,2-tetrafluoroethane from 1,1,1,2-tetrachloroethane - A mechanistic consideration

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1,1,1,2-Tetrachloroethane and its fluorinated derivatives as well as trichloroethene are fluorinated by hydrogen fluoride in the presence of a pre-conditioned chromia catalyst. The reaction pathways are derived under different conditions. Fluorinated haloalkanes are formed both by dehydrochlorination/hydrofluorination mechanism as well as chlorine/fluorine exchange mechanism. Thus, beside fluorinated alkanes considerable amounts of haloolefins occur in the product mixture. A survey is given on the reaction pathway showing dependence on the reaction conditions. It is discussed with respect to calculated thermodynamic data. Kinetic and mechanistic investigations of the isomerisation reactions of 1,1,2,2-tetrafluoroethane on a CFC-conditioned chromia catalyst are also presented. The desired 1,1,1,2-tetrafluoroethane can be obtained from its symmetric isomer in the presence of a chromia catalyst conditioned exclusively with chlorine-free fluorocarbons. Mechanistic information is obtained by employing DCI which behaves similar to HF during the consecutive isomerisation reaction of 1,1,2,2-tetrafluoroethane. Thus, it is most probable that dehydrohalogenation/hydrohalogenation processes (elimination/addition mechanism) are mainly responsible for the formation of the haloolefins and halocarbons observed on chromia.

Due to their kinetic stability fully halogenated chlorofluorocarbons (CFCs) have a very long atmospheric life time and act therefore, as ozone depleting molecules. The introduction of hydrogen into the molecules provides an easier hydrolysis of the resulting hydrochlorofluorocarbon molecule (HCFCs) which consequently exhibits a strongly lesser ozone depleting potential. The chlorine-free hydrofluorocarbons (HFCs) are considered to be the best alternative for substituting the former CFCs by non-ozone depleting compounds since they exhibit physical properties similar to the widely used CFCs.

Among the new CFC-alternatives 1,1,1,2-tetrafluoroethane (HFC-134a) is the most interesting HFC, used as a refrigerant instead of CCl3F and CCl2F2.

The synthesis of HFC-134a is possible through various pathways. The general procedure is the fluorination of the corresponding chlorocarbons by gaseous hydrogen fluoride. As known from the synthesis of CFCs, the chlorine/fluorine exchange is generally thermodynamically possible, but majority of reactions are kinetically hindered. Therefore it is necessary to use suitable fluorination catalysts, such as fluorides and oxides of trivalent metals (Cr, Al, Fe). Principally there are two different synthetic routes to the desired product:

i) starting from trichloroethylene (TCE)

\[
\text{CCl}_2=\text{CHCl} + 4\text{HF} \rightarrow \text{CF}_3-\text{CH}_2\text{F} + 3\text{HCl}
\]  

(1)  

and

ii) starting from tetrachloroethylene (PCE)

\[
\text{CCl}_2=\text{CCl}_2 + \text{Cl}_2 \rightarrow \text{CCl}_3-\text{CCl}_3
\]

(2)  

\[
\text{CCl}_3-\text{CCl}_3 + 4\text{HF} \rightarrow \text{CF}_3\text{Cl}-\text{CF}_2\text{Cl} + 4\text{HCl}
\]

(3)  

\[
\text{CCl}_3-\text{CCl}_3 + 4\text{HF} \rightarrow \text{CF}_3-\text{CFCl}_2 + 4\text{HCl}
\]

(4)  

followed by replacement of the chlorines in the CFC-114a through catalytic hydrogenolysis

\[
\text{CF}_3-\text{CFCl}_2 + \text{H}_2 \rightarrow \text{CF}_3-\text{CH}_2\text{F} + 2\text{HCl}
\]  

(5)  

Although the conditions of the synthesis are similar to those of the CFC synthesis, there are a number of specific points, which are not yet well understood. Most of the studies\textsuperscript{1-6} concentrated on how the technical process was developed and optimised and suitable catalysts were created. Furthermore, some partial reactions of the system were studied, e.g. by Blanchard \textit{et al.}\textsuperscript{7} who investigated the activity of
various catalysts prepared for the synthesis of CH₂F- CF₃ (HFC-134a) by fluorination of CH₂Cl-CF₃ (HCFC-133a) with hydrogen fluoride. Additionally, Kavanagh et al. studied the fluorination reactions of tetrachloroethene and trichloroethene. They found the addition/elimination mechanism more dominant in the system containing more hydrogen and that the loss of the dehydrochlorination route in the case of perhalogenated haloalkanes shows that hydrogen substitution by chlorine markedly reduces the rate of this process.

Due to the fact that HFCs tend to undergo dehydrohalogenation reactions, the reaction scheme of HFC production is more complicated than the synthesis of CFC's. There is always a need only for one concrete isomer, therefore the formation of others has to be suppressed. Separation of different isomers is very difficult due to the very similar boiling points of all isomers.

Therefore, this paper focuses on the reaction pathway for the fluorination of 1,1,1,2-tetrachloroethane by hydrogen fluoride to HFC-134a and the mechanistic conditions for the conversion of the undesired symmetric isomer HFC-134 into the desired HFC-134a.

As will be explained later both isomers of tetrachloroethane undergo a dehydrochlorination reaction in the presence of a suitable catalyst. Therefore the formation of HFC-134 is usually performed by starting directly from TCE and not from tetrachloroethane as is shown in Eq. 6.

\[
\begin{align*}
\text{CH}_2\text{Cl}_2\text{CCl}_2 & \xrightarrow{\text{HF}} \text{CH}_2\text{Cl}_2\text{CF} \xrightarrow{\text{HCl}} \text{CH}_2\text{Cl}_2\text{CCl}_2 \\
\text{CH}_2\text{Cl}_2\text{CCl}_2 & \xrightarrow{\text{HF}} \text{CH}_2\text{Cl}_2\text{CCl}_2 \\
\text{CH}_2\text{Cl}_2\text{CCl}_2 & \xrightarrow{\text{HCl}} \text{CH}_2\text{Cl}_2\text{CCl}_2 \\
\text{CH}_2\text{Cl}_2\text{CCl}_2 & \xrightarrow{\text{HF}} \text{CH}_2\text{Cl}_2\text{CF}_3 \\
\text{CH}_2\text{Cl}_2\text{CCl}_2 & \xrightarrow{\text{HCl}} \text{CH}_2\text{Cl}_2\text{CCl}_2 \\
\end{align*}
\]

Materials and Methods

The fluorination reactions with HF have been carried out in a nickel-flow reactor (length 400 mm, inner diameter 7 mm) as described previously. Chromia synthesised by thermal decomposition of ammonium dichromate was used as the catalyst (315-500 µm, specific surface area: 54.6 m²/g). Surface area was determined by the BET method using the surface analyser Micromeritics ASAP 2000.

The solid was calcined at 673 K in a pre-dried nitrogen stream for 3 hours. Then a constant gas flow of CH₂Cl- CCl₂F (residence time 1 second) was passed through the catalyst bed at a given temperature until a constant product composition in the gas phase was observed. The conditioned catalyst was analysed by XRD and XPS.

Each partial reaction was carried out with a fresh conditioned catalyst (500 mg) at various temperatures. The liquid organic compounds were metered by a pump into a vaporiser heated to 573 K and then mixed with HCl and HF, respectively. HCFC-133a was metered by a gas flow controller and the hydrogen halides by a fine needle valve (Monel). The calibration of the HX gas flow was realised by absorbing it in a known quantity of standard sodium hydroxide aqueous solution (0.1 m) followed by titration. The mole ratio for the reaction with HF was 1:4 between the organic phase and HF. The residence time was adjusted to 3 seconds for each reaction with the exception of the reaction of HCFC-133a with hydrogen fluoride (6 seconds).

Quantitative estimation of the organic product distribution was carried out chromatographically with a capillary gas chromatograph (Chromatron MGC-4000, fused silica, 25 m Poraplot Q, detector: FID). The unknown components in the gas mixture were identified by means of GC-FTIR-coupling (PerkinElmer system 2000, fused silica, 25 m Poraplot Q).

For the isomerisation reactions the reactor (Ø 5.1 mm) and the associated equipment (nickel, copper construction) have already been illustrated and described. Different from the hydrofluorination reactions, here for all experiments a pulse technique was used exclusively in order to follow the reactions between the gas phase and the reactive intermediate compounds adsorbed onto the catalyst surface.

Sample injection was via a gas sample valve to ensure accurate and consistent injection volumes. A second six port valve, situated behind the pulse reactor, was equipped with an external heat-conducting detector, which indicates the presence of the product gas and enables its extremely accurate injection into the GC. The quantitative analysis of the product gas was performed using a capillary gas chromatograph GC-14A from Shimadzu (column Poraplot U, 25 m). All gas lines were heated in order to prevent any condensation of organic products.
The same catalyst as described above, namely, chromia, was used for these measurements. All experiments were carried out using the same amount of catalyst, namely 600 mg. Before starting the reaction, the chromia catalyst was activated.

The DCI used was synthesised by hydrolysing PCl₅ (Merck) with D₂O (Merck). The HFC-134 employed was a product of Fluorochem Limited, the CFC-12 was from Hoechst AG and HCl from Merck.

The MS measurements were carried out using a GC-MS coupling, GC 17A / QP-5000, from Shimadzu and also a MS unit, QMG-421I, from Balzers, respectively.

### Results

#### A. 1,1,1,2-Tetrafluoroethane from trichloroethylene

**Thermodynamics of the reaction system**

In the case of the C₁-haloalkanes for every step of replacement of Cl by F there is a significant negative value in the free reaction enthalpies. Contrary to that the thermodynamic situation in the C₂-haloalkane system is somehow different. A detailed, thermodynamic consideration of the individual reaction steps has not been carried out until now because the thermodynamic data of the interesting halocarbons

<table>
<thead>
<tr>
<th>Educts</th>
<th>Reaction</th>
<th>Products</th>
<th>ΔᵣH° (kJ mol⁻¹)</th>
<th>ΔᵣG°(kJ mol⁻¹) in a closed reaction system</th>
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<tbody>
<tr>
<td>CH₂Cl·CCl₃</td>
<td>Dehydrochlorination</td>
<td>CHCl·CCl₂, CH₂Cl·CCl₂F</td>
<td>33</td>
<td>532 K: 60, 598 K: 60, 673 K: 71</td>
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<tr>
<td></td>
<td>+ HF/-HCl</td>
<td>CH₂Cl·CCl₂F</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrochlorination</td>
<td>CH₂Cl·CCl₃</td>
<td>-33</td>
<td></td>
</tr>
<tr>
<td>CHCl·CCl₂</td>
<td>Hydrofluorination</td>
<td>CH₂Cl·CCl₂F</td>
<td>-17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HF/-HCl</td>
<td>CH₂Cl·CCl₂F</td>
<td>35</td>
<td></td>
</tr>
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<td></td>
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</tr>
<tr>
<td></td>
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<td>CH₂Cl·CCl₂F</td>
<td>-18</td>
<td></td>
</tr>
<tr>
<td>CH₂Cl·CCl₂F</td>
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<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HCl/-HF</td>
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</tr>
<tr>
<td></td>
<td>+ HF/-HCl</td>
<td>CH₂Cl·CCl₃</td>
<td>-17</td>
<td></td>
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<td>CH₂Cl·CClF₂</td>
<td>Dehydrochlorination</td>
<td>CH₂Cl·CCl₂F</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HCl/-HF</td>
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<td></td>
<td>+ HF/-HCl</td>
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<td>-39</td>
<td></td>
</tr>
<tr>
<td>CH₂Cl·CClF₂</td>
<td>Dehydrofluorination</td>
<td>CH₂Cl·CCl₂F</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HCl/-HF</td>
<td>CH₂Cl·CCl₂F</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>CH₂Cl·CF₃</td>
<td>Dehydrofluorination</td>
<td>CH₂Cl·CCl₂F</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ HCl/-HF</td>
<td>CH₂Cl·CCl₂F</td>
<td>64</td>
<td></td>
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</table>
are known only partly\textsuperscript{13-16}. Therefore, first we have calculated the thermodynamic data for the whole 130-series using the computational software "HyperChem" on the basis of a semi-empirical AM1-method\textsuperscript{17,18}. The results are summarised in Table I allowing a partial understanding of the situation in this reaction system. Besides this, a detailed description of the reaction behaviour of every derivative of the 130-series on a chromia catalyst is given in ref.9. In this paper, we summarise the main reaction pathways derived from the above mentioned investigations occurring in the complex reaction system.

The reaction pathways

A one-step reaction of trichloroethene with hydrogen fluoride according to Eq. (7)
\[
\text{CHCl}=\text{CCl}_2 + 4 \text{HF} \rightarrow \text{CH}_2\text{F-CF}_3 + 3 \text{HCl} \quad (7)
\]
is unknown because no commercial process has been described involving a high degree of conversion. The reason for this is attributed to limitations of the thermodynamic equilibrium of the last step, the conversion of HCFC-133a with HF to HFC-134a.

Hence, the overall process is divided into two steps. Firstly trichloroethene reacts with HF forming HCFC-133a. The second step is the conversion of HCFC-133a to HFC-134a.

Compared to formerly studied reactions of perhalogenated haloalkanes (CFC's) with the reaction system of C2- HCFC's and HFC's, there are at least two principal differences complicating the reactions in the system of hydrogen containing C2- haloalkanes.

The formation of olefins is thermodynamically favourable and leads to unwanted byproducts. On the other hand, it is evident that the common Cl/F exchange as the desirable reaction is thermodynamically not as favourable as in the case of the perhalogenated alkanes. The result is an essentially more complicated reaction system determined by thermodynamic as well as kinetic factors, i.e. by catalyst, temperature, concentrations, and residence time.

On the basis of our experimental results, it is impossible to make a quantitative distinction between the different reactions in this complex reaction system. However, qualitative distinguishing reaction pathways can be given by different strengths of the reaction arrows (Scheme 1).

The reaction Scheme I mainly consists of two different reaction types:

(i) dehydrohalogenation reactions being responsible for the formation of several olefins in this reaction system, and

(ii) a common halogen exchange being mainly responsible for the formation of alkanes with a higher degree of fluorination.

Dehydro-/hydrohalogenations

Dehydrohalogenations, especially dehydrofluorinations, are generally dominant in the HF-free system of the haloalkane/catalyst. Thus, the use of 1,1,1,2-tetrachloroethane as starting material is practically unnecessary because of the trend of HCl elimination. The fluorinated compounds HCFC-131a and

![Scheme I](image-url)

\textbf{Scheme I} — Halogen exchange reactions of 1,1,1,2-tetrachloroethane and its fluorinated derivatives with gaseous HF on conditioned chromia.
HCFC-132b also tend to form olefins by eliminating the hydrogen fluoride.

Trichloroethene will undoubtedly be formed by dehydrohalogenation from 1,1,1,2-tetrachloroethane and HCFC-131a.

CHCl=CF₂ can also be formed using HCFC-132b and HCFC-133a as reactants. In this case the dehydrochlorination for the formation of HCFC-132b should be thermodynamically preferred, but experiments showed that HF elimination from HCFC-133a also occurs at 673 K.

In contrast to the thermodynamics of the equilibrium, the hydrofluorination of trichloroethene giving HCFC-131a leads to polyfluorinated alkanes, especially HCFC-133a. This is a result of the complete course of the consecutive reaction between HCFC-131a and hydrogen fluoride. Under these conditions, only traces of HCFC-132b and no HCFC-131a are formed. Both compounds should be obtained thermodynamically at lower temperatures.

**Common chlorine-fluorine-exchange**

Obviously, dehydrohalogenations will be repressed in the presence of hydrogen fluoride, so that the common chlorine-fluorine exchange will become predominant.

Thus, in the first step, the formation of HFC-134a from CHCl=CCl₂ and HF starts with the hydrofluorination forming CH₂Cl-CCl₂F and continues then mostly with a common Cl/F exchange resulting at least in the formation of CH₂F-CF₃. These results are in complete agreement with the reaction pathway given by Kavanagh et al.⁸. Employing DF for their experiments, they could prove that starting from CHCl=CCl₂ the main part of products consisted of CHDF-CF₃. This is possible only as a result of a common Cl/F exchange.

Starting with CHCl=CCl₂ and HF, small amounts of HCFC-131a are formed by hydrofluorination contrary to the position of the thermodynamic equilibrium. The halogen exchange on HCFC-131a as well as on HCFC-132b is so fast that the olefin formation, which is favoured thermodynamically will be repressed kinetically. By the formation of HCFC-133a, an energy minimum will be reached, wherefrom the reaction to HFC-134a is thermodynamically as well as kinetically controlled. The equally possible dehydrofluorination of HCFC-133a will be repressed by a sufficient excess of hydrogen fluoride. This HF excess is also required on account of the fact that the free reaction enthalpy of the last step of the consecutive reaction from HCFC-133a to HFC-134a is nearly zero. Therefore, besides using a large excess of HF, higher temperatures as well as long residence times are required to shift the thermodynamic equilibrium in the desired direction. This explains why in the commercial process only small conversion yields are obtained leading to complicated isolation and recycling processes.

Hence it is established that the practical synthesis of HFC-134a from trichloroethene with hydrogen fluoride is only possible because the formation of HCFC-133a is strongly favoured thermodynamically. It is also a fact that the formation of the thermodynamically favoured olefins in the presence of HF is repressed as opposed to the further reaction of HCFC-131a and HCFC-132b.

**B. Isomerisation reactions of HFC-134 to HFC-134a**

In the technical process of HFC-134a synthesis always changing amounts of the undesired symmetric HFC-134 are formed. Moreover, according the PCE-route symmetric 114 can be formed as shown by Eq. 3. Hydrogenolysis reactions of this symmetric CFC can deliver the symmetric HFC-134. For both reasons we focused our interest on the mechanism and kinetics of this isomerisation reactions.

The kinetic investigations on conditioned, chlorine-free chromia catalysts¹⁹ prove an isomerisation equilibrium according to Eq. (8).

$$\text{CHF}_2\text{-CHF}_2 \rightarrow \text{CH}_2\text{F} - \text{CF}_3 \quad \Delta G° = -9.8 \text{kJ/mol} \quad (8)$$

This equilibrium tends to the right in accordance with the thermodynamic calculations.

The reactions occurring in the reaction system are represented by the following equations. In the first step HFC-134 undergoes a dehydrofluorination reaction forming considerable amounts of TFE and HF

$$\text{CHF}_2\text{-CHF}_2 \rightarrow \text{CHF}=\text{CF}_2 + \text{HF} \quad (9)$$

Starting from trifluoroethylene (TFE) we always found the formation of the asymmetric isomer HFC-134a and with traces of the symmetric HFC-134.

$$\text{CHF}=\text{CF}_2 + \text{HF} \rightarrow \text{CH}_2\text{F}-\text{CF}_3 \quad (10)$$

$$\text{CHF}=\text{CF}_2 + \text{HF} \rightarrow \text{CHF}_2\text{-CHF}_2 \text{ (traces)} \quad (11)$$

As already shown in the absence of HF, HFC-134a tends to a partial splitting of HF being the back reaction of Eq. (10).

$$\text{CH}_2\text{F}-\text{CF}_3 \xrightarrow{\tau} \text{CHF}=\text{CF}_2 + \text{HF} \quad (12)$$
Two different kinetic models were established in order to describe the consecutive reaction system kinetically. The first one considers dehydrofluorination of HFC-134 to be irreversible (cf. Eq. 13).

\[
\begin{align*}
\text{CHF}_2\text{CHF}_2 & \xrightarrow{k_1} \text{CHF} = \text{CF}_2 + \text{HF} & \xrightarrow{k_3} & \text{CH}_2\text{F} \text{CF}_3 \\
\end{align*}
\]

The second one considers also the first reaction step as a reversible equilibrium (cf. Eq. 14).

\[
\begin{align*}
\text{CHF}_2\text{CHF}_2 & \xleftrightarrow{k_1^*} \text{CHF} = \text{CF}_2 + \text{HF} & \xleftrightarrow{k_2^*} & \text{CH}_2\text{F} \text{CF}_3 \\
\end{align*}
\]

As can be derived from Fig. 1, model 2 fits the experimentally determined kinetic lines much better than model 1. Consequently, model 2 is assumed to be the representative for the reaction pathway of the isomerisation of HFC-134.

The reaction scheme becomes more complicated if chlorine containing halocarbons are used for the activation process of the chromia which is used as the catalyst. As shown previously, in this case besides HF very small quantities of strongly adsorbed HCl will be formed giving a more complex product spectrum. A series of chlorinated derivatives of the three main components of the isomerisation equilibrium (CHF2-CHF2, CF2=CHF and CF3-CH2F) are formed while passing the first view pulses of HFC-134 over such a catalyst. In Table 2 the main products are summarised which could be clearly identified by GC-MS. Because not all of these representatives were not accessible, the necessary correction coefficients could not be precisely determined, thus making a quantitative determination impossible. Consequently, only the changes of the relative peak areas of all compounds are listed, indicating semi-quantitatively the general development with every new pulse of HFC-134.

As a result of removing this adsorbed hydrogen chloride from the solid the pure isomerisation reaction becomes more and more dominant, a fact which can be seen from the strong increase of HFC-134, HFC-134a and TCE concentrations.

Obviously, the adsorbed HCl takes part in the catalysed halogen exchange reactions with a series of different aliphatic and olefinic fluorocarbons in a way very similar to HF formation during the isomerisation reactions. Consequently, HCl was used as an internal detector atom to follow the reaction mech-

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**Table II**—Product distribution depending on the pulse number of HFC-134 employed (T = 673K; catalyst: chromia activated with CFC-12, pulse volume: 2 mlsTP)

<table>
<thead>
<tr>
<th>Pulse number</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF2-CHF2</td>
<td>-</td>
<td>0.05</td>
<td>8</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>CH2F-CF3</td>
<td>0.1</td>
<td>13</td>
<td>79</td>
<td>78</td>
<td>62</td>
</tr>
<tr>
<td>CH2Cl-CF3</td>
<td>0.04</td>
<td>62</td>
<td>13</td>
<td>3</td>
<td>0.7</td>
</tr>
<tr>
<td>CHCl2-CHF2</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CH2Cl-CCl2</td>
<td>-</td>
<td>0.08</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CHF-CF2</td>
<td>0.8</td>
<td>0.7</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>CHCl-CFCl</td>
<td>0.8</td>
<td>3</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CHF=CCl2</td>
<td>99</td>
<td>21</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CHCl=CCl2</td>
<td>99</td>
<td>21</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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**Fig. 1**—Fitting of the experimentally determined data with the kinetic model 1 and model 2 (lines - calculated according the models; points - experimental data)
nism of the isomerisation reaction. More over, instead of HCl deuterium chloride, DCI, was employed allowing us to follow the reaction pathway occurring here in more detail.

A D for H exchange occurs on fresh chromia surfaces only to a very small extent via surface hydroxyl groups and becomes unimportant after fluorination of the chromia surface (due to the removal of these hydroxyl groups) as proved by Kijowski et al.\(^1\). Consequently, a D for H exchange can most probably be excluded under the conditions used which is also in agreement with the results of Kavanagh et al.\(^2\), who employed deuterohalides for mechanistic investigations of the synthesis of HCFC-133a starting with trichloroethylene.

Our main goal was to find out the reaction processes of this complex reaction system. In principle two possible reaction mechanisms could result in the observed product spectrum:

i) dehydrohalogenation/hydrohalogenation reactions (elimination/addition mechanism)

ii) consecutive substitution reactions (chlorine/fluorine exchange)

From the experimental results one can decide on the reaction pathways. If only these halogen exchange reactions occur, all compounds should contain hydrogen only. If elimination/addition reactions are dominant, deuterium should be incorporated into the organic compounds.

The ion chromatogram (Fig.2) showed clearly the same product distribution which was obtained in the case of hydrogen chloride (Table II). But the advantage now is the appearance of a wide range of deuterated products. On the basis of the qualitative and quantitative (H to D ratio) distribution of these deuterated products it is now possible to get a deeper understanding about the real processes of this complex reaction system. In Scheme II, the reaction pathways are given which we believe are responsible for the formation of all the products observed. In Scheme II we differentiate between three probabilities: such reactions which we are sure will occur (unbroken line), the ones which will probably occur (broken lines) and the ones which are unlikely (dotted lines).

Special attention is paid to the ratio of H to D in the compounds as this sometimes allows prediction of the different ways possible for the formation of a product. For all compounds, therefore the content of deuterium or hydrogen is given in relative values in brackets in such a way that the major product is adjusted to one.\(^1\)

As can be seen in Scheme 2, the initial reaction is the dehydrofluorination of HFC-134, forming TCE and HF as intermediates as has already been described\(^1\). HF can react with TCE according the Markovnikov rule, forming HFC-134a. Most probably parallel to this, HF undergoes a halogen exchange with DCI forming DF and HC. Consequently, in the reaction system we have the following hydrogen halides to consider: HF, DF, HCl, and DCI. HFC-134 alone clearly eliminates HF but does not undergo any kind of halogen exchange (mono-chlorinated products are missing). The formation of deuterated representatives of HFC-134a can be explained either by the deuterofluorination of TFE (addition of DF) or by the fluorination (Cl/F ex-
change) of C(H,D)2Cl-CF3, which itself can be formed by the deuterofluorination of C(H,D)Cl=CF2. The latter olefin can be formed by the chlorination of TFE. However, in principle, this reaction cycle can proceed in the opposite direction. Even the D/H-ratio does not allow one to draw a clear line between both processes. But from former investigations of the catalysed synthesis of HFC-13422 there is clear evidence that the fluorine/chlorine exchange reaction of TFE (forming C(H,D)Cl=CF2) is a minor reaction. An additional argument is that deuterated TFE was never observed. It is less probable to assume a very higher reactivity of CDF=CF2 in comparison to CHF=CF2. Consequently, the presence of nearly equal amounts of CHCl=CF2 and CDCl=CF2 can only be explained by formation via HFC-133a.

It is conspicuous that the asymmetric isomers of HCFC-132 are the major components. This can be explained both by the (H,D)Cl addition mechanism according to the Markovnikov rule (starting from C(H,D)Cl=CF2) as well as by a fluorine/chlorine exchange reaction starting from HCFC-133a.

In both the cases the hydrogen/deuterium ratio observed in HFC-132a can originate from the starting compounds. Moreover, considering the concentrations of the isomers of HCFC-132 observed in practice one would conclude that the reaction according to the Markovnikov rule is dominant for the (H,D)F addition of C(H,D)Cl=CF2 or the exchange reaction of HCFC-133a, respectively. However, as the concentrations of the possible isomers of the olefin C2(H,D)ClF are the same, both reaction processes, Markovnikov and anti-Markovnikov, have to be recognised in the same manner. Moreover, it is somewhat surprising that the H/D ratio decreases from 1 in all isomers of HCFC-132 to 0.8 in the case of both isomers of dichloromonofluoroethylene. In the case of an ordinary F/Cl exchange between C(H,D)Cl=CF2 and (H,D)Cl this ratio remains constant as well as in the case of elimination reactions of HCFC-132. However, in the latter case it should be
possible that HF elimination is slightly dominant over DF elimination due to the kinetic isotope effect. Consequently, the formation of the stable end product of this reaction scheme, TCE, cannot be formed by an ordinary fluorine/chlorine exchange because of the further remarkable change of the H/D ratio. As this ratio decreases from 0.8 in the case of dichloromonofluoroethylene to 0.3 in the case of TCE, again the only plausible explanation is a (H,D)Cl addition of the olefin, forming HCFC-131. The latter is known to be extremely unstable in the presence of a suitable catalyst and cannot therefore be detected in the product mixture. Consequently, the unstable intermediate undergoes a very fast (H,D)F elimination forming the stable end product, TCE. Again, the only explanation for the decrease of the H/D ratio is the kinetic isotope effect favouring the elimination of HF.

Finally it can be stated that the industrially desirable HFC-134a can be obtained from the symmetric isomer HFC-134 in the presence of a chromia catalyst conditioned exclusively with chlorine-free fluorocarbons. Independently if HF or HCl was used, in all cases exclusively trihalogenoethylenes and tetrahalogenoethanes, respectively, were found, which represent the same general product distributions as in the system of pure HFC-134 isomerisation. Probably, HF acts in a similar way as found for HCl, the advantage by employing HCl or DCI, respectively, is that different chlorinated derivatives are detectable. Hence, a very complex reaction system could be precisely separated. In the case of exclusively fluorinated compounds this differentiation is impossible unless $^{18}$F-labelled HF is used.

By employing pulse techniques in combination with deuterium isotopes, this complex reaction pattern of side reactions could be precisely solved.

As mentioned at the very beginning, it is desirable to produce HFC-134a by dehydrohalogenating CFC-113a. In principle it is also possible to start from CFC-113 and isomerise the hydrogenated product, HFC-134, later. As our results reveal, in this case chlorine-free catalysts have to be used in order to avoid all the side reactions discussed in this paper.

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References