

Description

The present invention relates to the manufacture of 1-chloro-1,1-difluoroethane $\text{CF}_2\text{Cl}-\text{CH}_3$ by a catalytic reaction in the liquid phase of 1,1,1-trichloroethane CCl_3-CH_3 with hydrofluoric acid HF.

5 1-Chloro-1,1-difluoroethane, which is used most especially as an intermediate in the synthesis of 1,1-difluoroethylene $\text{CF}_2=\text{CH}_2$ (itself a monomer of increasing importance for the industrial production of fluorinated polymers), but also as an aerosol propellant, is
10 generally prepared by the reaction of 1,1,1-trichloroethane and hydrofluoric acid in the liquid phase.

According to a known process (Patent DE 2,137,806), the reaction may be performed without a catalyst provided it is carried out at high temperature
15 (110°C) with a large excess of hydrofluoric acid ($\text{HF}/\text{C}_2\text{H}_3\text{Cl}_3$ mole ratio of between 15 and 30). This leads to substantial formation of 1,1,1-trifluoroethane as a by-product, and to a low productivity of 1-chloro-1,1-difluoroethane. In addition, hydrofluoric acid is carried
20 away by the hydrochloric acid formed in this chlorine $\longleftrightarrow$ fluorine exchange reaction, and this necessitates a suitable apparatus (under sufficient pressure) for recovery of this expensive raw material. In the above-mentioned patent, it is stated that the use of acid HSO_3F
25 leads to tar formation, probably due to the chemical instability of this catalyst (oxidation by SO_3).

Other known processes recommend the use of catalysts based on antimony derivatives or molybdenum derivatives (see, for example, Patent DE 2,659,046 and
30 the Japanese publications 74-03965, 76-29404 and 76-39606).

The major drawback of antimony derivatives lies in their rapid deactivation by reduction to a lower valency state at the degree of oxidation Sb^{3+} . The countermeasure
35 which consists in continuously oxidising the catalyst (by means of chlorine) contributes to the formation of heavy compounds (derived from a chlorination of the CH_3 group of 1,1,1-trichloroethane). In addition, the solubility of some catalytic species (SbF_3 , for example) is so low in the
40 reaction medium that it brings about, more often than not,

a physical separation of this species and inefficacy of the action of the chlorine. This results in an irregularity of the chemical reaction and a substantial consumption of catalyst, as well as a sustained corrosion due to the formation of highly acidic compounds which strongly attack the material forming the reactor. Finally, the difficulty in regulating the catalytic activity in a suitable manner leads to substantial formation of 1,1,1-trifluoroethane as an undesirable by-product.

With molybdenum derivatives, the formation of volatile species brings about a loss of catalyst in the gaseous phase of the reactor.

It has now been found that it is possible to remedy these drawbacks and carry out the reaction with a reasonable excess of hydrofluoric acid ($\text{HF}/\text{CH}_3\text{-CCl}_3$, mole ratio of between 2 and 5) by using an acid catalyst which is soluble in the reaction medium and consists of a perfluoroalkanesulphonic acid $\text{CF}_3\text{-(CF}_2)_n\text{-SO}_3\text{H}$, it being possible for n to range from 0 to 7 and preferably being equal to zero (triflic acid $\text{CH}_3\text{-SO}_3\text{H}$).

The catalyst according to the invention is advantageously used in the proportion of 1 to 10 moles per 100 moles of 1,1,1-trichloroethane, and preferably in the proportion of 3 to 5 moles per 100.

The process according to the invention may be carried out in discontinuous or continuous fashion, at a temperature ranging from 80 to 150°C, but preferably in the region of 100 - 110°C.

In discontinuous fashion, the reaction is performed in a closed reactor in which all the reactants are introduced at the beginning of the operation and in which the autogenous pressure increases up to a maximum value.

In continuous fashion, the reactants are introduced by means of a pump into the reaction mixture containing the catalyst, with continuous recovery of the useful compounds (1-chloro-1,1-difluoroethane and hydrochloric acid) and condensation of the heavier compounds (catalyst, hydrofluoric acid, 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane), while the total pressure is

maintained at a specified value by means of a suitable regulating device. The working pressure must be sufficient (at least equal to 15 bars, and preferably between 15 and 20 bars), to enable, on the one hand the hydrochloric acid to be separated by distillation, and on the other hand the reactants to be maintained in the liquid state.

The 1,1-dichloro-1-fluoroethane formed is advantageously recycled and converted to 1-chloro-1,1-difluoroethane.

The examples which follow, in which the percentages stated are expressed in moles, illustrate the invention.

EXAMPLE 1

3.2 g of triflic acid, 71 g of 1,1,1-trichloroethane and 23.3 g of hydrofluoric acid are introduced successively into a stainless steel autoclave (NS 22 S) 800 ml in volume, equipped with a bar magnet stirrer system.

With the stirrer operating at approximately 700 rpm, the reaction mixture is brought to 100°C by means of a heat-transfer fluid circulating through the jacket of the reactor. The autogenous maximum pressure reaches 31.2 bars (equivalent to approximately 32 bars absolute).

After one hour's reaction under these conditions, the mixture is cooled with stirring, this requiring approximately 50 minutes to reach room temperature.

Analysis of the hydracids and the organic compounds of the reaction mixture gives the following results:

- degree of conversion of 1,1,1-trichloroethane = 92.6 %
- degree of conversion of $\text{CH}_3\text{-CCl}_3$

	to $\text{CH}_3\text{-CF}_3$	=	0.07 %
	to $\text{CH}_3\text{-CF}_2\text{Cl}$	=	12.3 %
	to $\text{CH}_3\text{-CFCl}_2$	=	79.2 %
	- ratio $\text{CF}_3\text{-CH}_3/\text{CF}_2\text{Cl-CH}_3$	=	0.6 %

EXAMPLE 2

Example 1 is repeated, but without stirring. The maximum autogenous pressure reaches 31 bars absolute and the following results are obtained:

- 5 - degree of conversion of $\text{CH}_3\text{-CCl}_3$ = 89 %
- degree of conversion of $\text{CH}_3\text{-CCl}_3$
 - to $\text{CH}_3\text{-CF}_3$ = 0.13 %
 - to $\text{CH}_3\text{-CF}_2\text{Cl}$ = 14.5 %
 - to $\text{CH}_3\text{-CFCl}_2$ = 71.7 %
- 10 - ratio $\text{CF}_3\text{-CH}_3/\text{CF}_2\text{Cl-CH}_3$ = 0.9 %

This latter ratio shows that it is preferable to carry out the reaction with stirring.

EXAMPLE 3

15 Example 1 is repeated, but the $\text{HF}/\text{CH}_3\text{-CCl}_3$ mole ratio is modified to bring it to 2.2 to 5, using the following quantities of reactants:

- 2.8 g of triflic acid
- 61.8 g of 1,1,1-trichloroethane
- 46.3 g of hydrofluoric acid

20 In this experiment, carried out under conditions identical to those of Example 1 (stirring at 700 rpm; 100°C), the maximum autogenous pressure reaches 36 bars absolute and the results obtained are as follows:

- degree of conversion of $\text{CH}_3\text{-CCl}_3$ = 93.5 %
- 25 - degree of conversion of $\text{CH}_3\text{-CCl}_3$
 - to $\text{CH}_3\text{-CF}_3$ = 0.4 %
 - to $\text{CH}_3\text{-CF}_2\text{Cl}$ = 37.2 %
 - to $\text{CH}_3\text{-CFCl}_2$ = 52.6 %
- ratio $\text{CH}_3\text{-CF}_3/\text{CH}_3\text{-CF}_2\text{Cl}$ = 1.1 %

30 Comparative experiment no. 1

The procedure is as in Example 1, but without the addition of a catalyst; the quantities of reactants introduced are as follows:

- 35 - 66.8 g of 1,1,1-trichloroethane
- 21.9 g of hydrofluoric acid

The maximum autogenous pressure reaches 27 bars absolute and the following results are obtained:

- degree of conversion of $\text{CH}_3\text{-CCl}_3$ = 81.2 %
- degree of conversion of $\text{CH}_3\text{-CCl}_3$
 - to $\text{CH}_3\text{-CF}_3$ = 0.03 %
 - to $\text{CH}_3\text{-CF}_2\text{Cl}$ = 2.9 %
 - to $\text{CH}_3\text{-CFCl}_2$ = 78.0 %
- ratio of $\text{CH}_3\text{-CF}_3/\text{CH}_3\text{-CF}_2\text{Cl}$ = 1 %

Comparison of the results of this experiment with those obtained in Example 1 shows that the catalyst according to the invention enables the selectivity for $\text{CH}_3\text{-CF}_2\text{Cl}$ to be improved even though the degree of conversion of $\text{CH}_3\text{-CCl}_3$ to $\text{CH}_3\text{-CF}_2\text{Cl}$ is four times as large.

Comparative experiment no. 2

This experiment was carried out in the presence of SbCl_5 as a catalyst and at a temperature of 65°C with the following reactants, introduced in the order shown:

- 6 g of SbCl_5
- 66.8 g of $\text{CH}_3\text{-CCl}_3$
- 21.9 g of HF

The results obtained in one hour and with stirring at 700 rpm (maximum pressure reached : 36 bars absolute) are as follows:

- degree of conversion of $\text{CH}_3\text{-CCl}_3$ = 98.5 %
- degree of conversion of $\text{CH}_3\text{-CCl}_3$
 - to $\text{CH}_3\text{-CF}_3$ = 28.4 %
 - to $\text{CH}_3\text{-CF}_2\text{Cl}$ = 64.4 %
 - to $\text{CH}_3\text{-CFCl}_2$ = 1.7 %
- ratio $\text{CH}_3\text{-CF}_3/\text{CH}_3\text{-CF}_2\text{Cl}$ = 44.1 %

Although carried out at a lower temperature which discourages the formation of $\text{CH}_3\text{-CF}_3$, this experiment clearly shows the influence of the nature of the catalyst on the desired selectivity for $\text{CH}_3\text{-CF}_2\text{Cl}$.



CLAIMS

1. Process for manufacturing 1-chloro-1,1-difluoroethane in the liquid phase by the action of hydrofluoric acid on 1,1,1-trichloroethane, characterized in that a perfluoroalkanesulphonic acid $\text{CF}_3-(\text{CF}_2)_n-\text{SO}_3\text{H}$, n being an integer ranging from 0 to 7, is used as a catalyst.
2. Process according to Claim 1, in which the catalyst is triflic acid.
3. Process according to Claim 1 or 2, in which 1 to 10 moles of catalyst per 100 moles of 1,1,1-trichloroethane, and preferably 3 to 5 moles per 100, are used.
4. Process according to one of Claims 1 to 3, in which the reaction is performed at a temperature ranging from 80 to 150°C, and preferably between approximately 100 and 110°C.
5. Process according to one of Claims 1 to 4, in which the $\text{HF}/\text{CH}_3-\text{CCl}_3$ mole ratio is between 2 and 5.
6. Process according to one of Claims 1 to 5, in which the total pressure is between 15 and 50 bars.
7. Process according to one of Claims 1 to 6, in which the reaction is performed with stirring.
8. Process according to one of Claims 1 to 7, in which the reaction is performed in discontinuous fashion under the autogenous pressure of the reaction mixture.
9. Process according to one of Claims 1 to 7, in which the reaction is performed in continuous fashion under a pressure of between 15 and 20 bars.
10. Process according to one of Claims 1 to 9, in which the 1,1-dichloro-1-fluoroethane formed is recycled.



As printed

Patentansprüche

1. Verfahren zur Herstellung von 1-Chlor-1,1-difluorethan durch Einwirken von Fluorwasserstoffsäure auf 1,1,1-Trichlorethan in der Flüssigphase, dadurch gekennzeichnet, daß man als Katalysator eine Perfluoroalkansulfonsäure, $\text{CF}_3-(\text{CF}_2)_n-\text{SO}_3\text{H}$, worin n eine ganze Zahl von 0 bis 7 ist, einsetzt.

2. Verfahren nach Anspruch 1, in dem der Katalysator Trifluormethansulfonsäure ist.

3. Verfahren nach Anspruch 1 oder 2, in dem man 1 bis 10 mol Katalysator pro 100 mol und vorzugsweise 3 bis 5 mol pro 100 mol 1,1,1-Trichloroethan einsetzt.

4. Verfahren nach einem der Ansprüche 1 bis 3, in dem die Umsetzung bei einer Temperatur von 80°C bis 150°C und vorzugsweise zwischen etwa 100°C und 110°C durchgeführt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, in dem das Molverhältnis $\text{HF}/\text{CH}_3-\text{CCl}_3$ zwischen 2 und 5 beträgt.

6. Verfahren nach einem der Ansprüche 1 bis 5, in dem der Gesamtdruck zwischen 15 und 50 bar beträgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, in dem man unter Rühren arbeitet.

8. Verfahren nach einem der Ansprüche 1 bis 7, in dem man diskontinuierlich bei dem autogenen Druck des Reaktionsgemisches arbeitet.

9. Verfahren nach einem der Ansprüche 1 bis 7, in dem man kontinuierlich bei einem Druck zwischen 15 und 20 bar arbeitet.

10. Verfahren nach einem der Ansprüche 1 bis 9, in dem das gebildete 1,1-Dichlor-1-fluorethan in den Kreislauf zurückgeführt wird.

Claims

1. Process for manufacturing 1-chloro-1,1-difluoroethane in the liquid phase by the action of hydrofluoric acid on 1,1,1-trichloroethane, characterized in that a perfluoroalkanesulphonic acid $\text{CF}_3-(\text{CF}_2)_n-\text{SO}_3\text{H}$, n being an integer ranging from 0 to 7, is used as a catalyst.

2. Process according to Claim 1, in which the catalyst is triflic acid.

3. Process according to Claim 1 or 2, in which 1 to 10 moles of catalyst per 100 moles of 1,1,1-trichloroethane, and preferably 3 to 5 moles per 100, are used.

4. Process according to Claims 1 to 3, in which the reaction is performed at a temperature ranging from 80 to 150°C, and preferably between approximately 100 and 110°C.

5. Process according to one of Claims 1 to 4, in which the $\text{HF}/\text{CH}_3-\text{CCl}_3$ mole ratio is between 2 and 5.

6. Process according to one of Claims 1 to 5, in which the total pressure is between 15 and 50 bars.

7. Process according to one of Claims 1 to 6, in which the reaction is performed with stirring.

8. Process according to one of Claims 1 to 7, in which the reaction is performed in discontinuous fashion under the autogenous pressure of the reaction mixture.

9. Process according to one of Claims 1 to 7, in which the reaction is performed in continuous fashion under a pressure of between 15 and 20 bars.

10. Process according to one of Claims 1 to 9, in which the 1,1-dichloro-1-fluoroethane formed is recycled.