FLUORINATION OF HYDROGEN-CONTAINING OLEFINS WITH ELEMENTAL FLUORINE

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SUMMARY

The hydrohalo-olefins cis and trans CHCl=CHCl, CHCl=CCl$_2$, CHCl=CH-CH$_2$Cl and CH$_2$=CCl-CH$_2$Cl have been fluorinated with elemental fluorine to give good yields of hydrohalofluoroalkanes. The best operational conditions for F$_2$ addition to the double bond rather than hydrogen and/or chlorine atom substitution, dimerization and oligomerization of radical intermediates have been studied. Preliminary studies on the reaction of Freon 12 and Freon 22 towards elemental fluorine have also been carried out.

INTRODUCTION

Although the addition of fluorine to double bonds has been extensively reported [1,2,3] the published research is concerned almost exclusively with halogen-containing olefins. Only limited studies deal with reactions of fluorine and olefins containing hydrogen atoms.

In these works [4,5,6] however the conditions are favorable to the substitution reaction and the addition of fluorine to the double bond occurs with only extremely low yields.

RESULTS AND DISCUSSION

A preliminary study on the reaction of Freon 12 and Freon 22 with fluorine has been carried out to find the best reaction conditions to minimize the substitution reaction of hydrogen and/or chlorine. At room temperature Freon 12 reacts with fluorine diluted up to 10% in nitrogen only in a very small percentage (about 2-3%) to give Freon 13. Below 0 °C no reaction occurs. At room temperature with increasing concentration of fluorine in nitrogen, the substitution reaction of chlorine atoms in Freon 12 becomes increasingly important.

With Freon 22 we have noticed, as already foreseen, that the hydrogen atom reacts with fluorine and in some cases the reaction occurs explosively. The products formed by the reaction are Freon 13 and Freon 14.

The study of Freon 22 reactivity towards fluorine has been closely examined to verify which operating parameters to choose in order to control and limit the substitution reaction. The conditions under which the substitutio reaction occurs, or it is negligible, are reported in Table 1, for tests carried out at room temperature. It is evident that the reaction can be controlled by changing the concentration of fluorine and Freon in the nitrogen mixture.

With concentrations of Freon 22 higher than 8 % the substitution reaction occurs at all concentrations of fluorine, while with Freon percentages lower than 7 % the reaction occurs only with fluorine concentrations higher than 14 %. In some cases the substitution reaction takes place immediately, as soon as the reagents mix in the space preceding the reactor. Once the reaction is started, it goes on in an uncontrollable way forming Freon 13 and Freon 14. If a mixture of fluorine in nitrogen is bubbled into Freon 22 at -80 °C, the substitution of hydrogen occurs to a limited extent when working with a high concentration of fluorine.

Once the possibility of controlling the hydrogen and/or chlorine substitution reactions through the concentration of reactants and the reaction temperature was established, the research was focussed on some

TABLE 1

Reaction of fluorine on F_{22} ($CHCIF_2$)

Fluorine (% in N_2)	$CHClF_2$ (% in N_2)	Reaction
6	5.5	NO
	8.5	YES
8	6.0	NO
	11.3	YES
10	7.3	NO
	13.0	YES
11	6.6	NO
	8.4	YES
14	6.6	NO
	9.3	YES
20	6.3	YES
	10.1	YES

hydrohalo-olefins, and particularly on trichloroethylene, _cis_ and _trans_
dichloroethylene, 1,3-dichloropropene and 2,3-dichloropropene. The olefin
was fed in Freon 11 as solvent, since it proved to be inert to fluorine
under our working conditions. The conditions and the product yields are

given in Table 2. It is observed (tests 1 and 3) that for dichloroethylene the cis isomer is more reactive, while the trans one is more selective.

In fact for the same amount of fed fluorine the olefin conversion is greater for the cis isomer, while the yield of the addition product, based on the reacted olefin, is greater for the trans isomer. For the first three tests of Table 2, the composition of the reaction mixture is given in Table 3. The quantity of substitution products and of the dimer is higher for the cis dichloroethylene.

From test 2 it is clear that an increase of fluorine percentage in nitrogen causes a decreased yield of addition product and a relative increase in substitution products present in the reaction mixture, but mostly in an increase of the same products in the outlet gasses from the reactor. As a consequence of the substitution reactions, there is formation of products with lowered boiling point because of an increased number of fluorine atoms in the molecule. These products are therefore stripped from the reaction mixture by the nitrogen stream that dilutes the fluorine. Table 4 gives the identified products in the reaction mixture and in the outlet gasses.

In regard to the temperature effect it has already been noticed that at -59 °C there is a noticeable decrease in the yield of addition product and an increase in the percentage of substitution and dimerization products.

For trichloroethylene the reactivity with fluorine is comparable with the one of cis dichloroethylene. The addition product to double bond, together with the substitution products of chlorine and hydrogen, are obtained in relatively good yields. Products formed by hydrogen and/or chlorine substitution, such as Freon 113, Freon 114 and Freon 123, were identified.

For dichloropropenes studied in the tests 6, 7, 8 and 9, the best yields have been obtained with 1,3-dichloropropene, the less polar of the two propenes examined. Together with the addition product of fluorine to the double bond, the other main compound obtained is $CHClF-CF_2-CH_2Cl$, formed from the substitution of the hydrogen atom in position two. In the case of

TABLE 2

| | % Olefin in Solution | | Fluorine (mole) | $\frac{F_2\ \text{flowed}}{F_2\ \text{theor.}}$ | Reaction Time hr. | Rate of F_2 addn. g/hr | Reaction Temp. °C | Molar ratio N_2/F_2 | Yield of addition product A | Yield of addition product B | Olefin Conversion |
	Starting	Final									
1) CHCl=CHCl cis+	12.82	8.5%	1.03	45.4%	8	4.89	-75°C	13:1	54%	46%	53%
2) CHCl=CHCl trans+	12.82	7.55	1.5	66%	8'	7.12	-75°C	9:1	49%	58%	56%
3) CHCl=CHCl trans+	12.82	12.32	0.97	42.7%	7.5	4.91	-75°C	13:1	54%	73.5%	32%
4) CHCl=CHCl cis	12.0	2.67	0.89	61%	6	5.63	-59°C	12:1	30%	23%	78%
5) CHCl=CCl$_2$	12.7	2.45	0.87	76.7%	7	4.75	-75°C	13:1	45%	41.5%	81%
6) CH$_2$=CCl-CH$_2$Cl	14.2	1.2	0.42	93%	2.5	6.38	-73°C	10:1	28%	29.5%	91%
7) CH$_2$=CCl-CH$_2$Cl	14.2	6	0.26	57.7%	1.5	6.6	-72°C	10:1	26%	25.6%	59%
8) CHCl=CH-CH$_2$Cl	14.2	1	0.42	93%	2.5	6.38	-70°C	10:1	42%	42.5%	93.2%
9) CHCl=CH-CH$_2$Cl	14.2	6	0.25	55.5%	1.5	6.33	-70°C	10:1	47%	44%	59%

A -based on total amount of fluorine added

B -based on olefin reacted

+ olefin was added after 4 hours

TABLE 3
Composition of reaction products

	run 1 CHCl=CHCl cis	run 2 CHCl=CHCl trans	run 3 CHCl=CHCl trans
CHF_2-CF_2Cl	0.37%	/	/
$CHClF-CHF_2$	5.14%	4.56%	3.61%
$CHClF-CHClF$	70.2%	69.6%	73.0%
Dimer	20.0%	13.5%	13.7%
Other Products	4.3%	11.8%	9.6%

TABLE 4
Identified Products

	Solution	b.p.
F124a	CHF_2-CF_2Cl	-10.2°C
F114	CF_2Cl-CF_2Cl	3.6°C
F133	$CHF_2-CHFCl$	17.0°C
F123a	$CHFCl-CF_2Cl$	28.2°C
F132	$CHFCl-CHFCl$	59.0°C
	Gas Outlet	
F125	CF_3-CHF_2	-48.5°C
F115	CF_3-CF_2Cl	-38.7°C
F134	CHF_2-CHF_2	-19.7°C
F124	CHF_2-CF_2Cl	-10.2°C
F133	$CHF_2-CHFCl$	17.0°C

2,3-dichloropropene, the substitution of hydrogen atom occurs in position three and $CH_2F-CClF-CHClF$ is formed. In the reaction mixture the presence of products such as $CH_2=CCl-CHClF$, $CH_2=CCl-CHF_2$, $CHCl=CH-CHClF$ and $CHCl=CH-CHF_2$ was also observed. These compounds retaining the double bond rise from substitution of hydrogen and/or chlorine in position 3.

Moreover the whole series of the products resulting from reactions of further substitution and/or from cracking has been observed. The available experimental data are in accordance with a free radical reaction mechanism and the use of catalysts such as $SbCl_3$ and $SbCl_5$ do not have any effect.

CONCLUSIONS

The tests carried out allowed us to verify that it is possible to add fluorine to the double bond of hydrohalo-olefins with good yields for the addition products. The competitive substitution reactions as well as the dimerization can be limited by controlling the reaction conditions. We would point out the importance of temperature and fluorine concentration in the nitrogen flow as well as of olefin concentration in the reaction mixture as affects the final composition of the products. We suggest working with an olefin concentration of about 15% and to keep the concentration at a fixed value as long as the test runs with a continuous feeding of fresh olefin. Stirring of the reaction mixture is important so as to ensure good heat transfer. It has been found that the most important factor for the selectivity of the reaction is the temperature and it seems that working at a temperature lower than -70 °C is important.

EXPERIMENTAL

Two kinds of reactor have been used according to the temperature at which the reactivity with fluorine of various compounds was to be studied. When the experiments were carried out at a temperature higher than the boiling point of the compound to be tested, this was mixed with fluorine diluted in nitrogen and fed into a 500 ml copper tubular reactor fitted

with copper chips. The reactor had an external thermostatic jacket inside which a thermostatic fluid was circulating. The internal temperature of the reactor was measured with a thermocouple.

For the reaction carried out at temperatures below the boiling point of the compound to be experimented the fluorine diluted in nitrogen was bubbled into the liquid or into the mixture of Freon and olefin in a cylindrical reactor held in a dewar containing trichloroethylene cooled with an immersion cooler. The 1000 ml reactor, made of teflon or glass, was equipped with a paddle stirrer.

The GLC determinations were carried out with a Shimadzu GC-8APT Chromatograph using He as a carrier gas and a copper column (4 mm x 6 mt) packed with OS 200/50 on Chromosorb.

The identification of the reaction products was carried out with a ITD Perkin-Elmer Mass Spectrometer.

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