*Polish Journal of Chemical Technology, 12, **2**, 1 — 3, 2010, 10.2478/v10026-010-0009-y*

Oxidation of hexafluoropropylene to hexafluoropropylene oxide using oxygen

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A method for pressure oxidation of hexafluoropropylene (HFP) to hexafluoropropylene oxide (HFPO), using oxygen, is presented. Oxidation was achieved in a batch-fed reactor at temperature range between 130 to 170°C. The influence of temperature and kind of solvents, such as 1,2,2-trichloro-1,1,2-trifluoroethane (CFC-113) and carbon tetrachloride on the yield of HFPO and the course of oxidation was investigated in preliminary studies. The maximum HFPO yield of approximately 83% was noticed.

Keywords: hexafluoropropylene, hexafluoropropylene oxide, epoxidation.

INTRODUCTION

Hexafluoropropylene oxide (HFPO) is a valuable monomer that can be oligomerized to prepare intermediates for the synthesis of highly effective nonionic, ionic, and amphoteric surface-active agents. Even small amounts of such compounds cause a significant decrease in the surface tension of water, and, for this reason, these materials are used as components of extinguishing agents[1]. HFPO oligomers are also employed as inert solvents and hydraulic fluids[2]. Higher oligomers are valuable as lubricating oils, showing good thermostability and chemical resistance[3, 4].

To date, HFPO has been produced by oxidation using sodium hypochlorite[5], oxygen under pressure[6] and in a pressure-free method[4], hydrogen peroxide[7], and employing an electrochemical procedure[1]. HFPO can be obtained with high efficiency by epoxidation of HFP with hypochlorite using a phase-transfer catalyst in a system of two phases, water and an organic solvent, in the presence of an inorganic base. Quaternary ammonium, phosphonium, and arsenium salts, and lipophilic reagents complexed with sodium cations, have been used as phase-transfer catalysts. However, such methods are employed only in small-scale preparations[5].

The oxidation of HFP by oxygen in the gaseous phase, in the presence of catalysts such as barium compounds, activated silica gels, metals (Ag, V), supported silica gel, or diatomaceous earth, has also been investigated[4]. Pressure oxidation of HFP using oxygen in the liquid phase shows the greatest promise for commercial production of HFPO[8]. Investigation of HFPO preparation by catalyst-free oxidation using hydrogen peroxide in a water-soluble polar solvent such as acetone or acetonitrile is ongoing[9].

Electrochemical oxidation has also attracted research interest1. An aqueous solution of acetonitrile, or a mixture thereof with acetic acid and a compound improving conductivity ($NaClO_4$), has been used as an electrolyte. The principal oxidation reaction of HFP, using oxygen, proceeds in both the gaseous and liquid phases as shown in Figure 1.

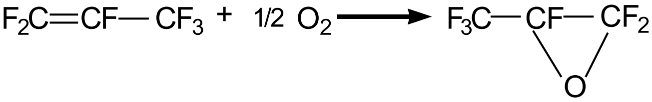

Figure 1. The principal reaction in oxidation of hexafluoropropylene

The reaction mechanism assumes that, after addition of oxygen to the double bond, a biradical is formed involving electrons of both oxygen and carbon[5]. The decomposition and rearrangement of this intermediate, together with decomposition of HFPO, results in the formation of several by-products including trifluoroacetic acid fluoride, carbonyl fluoride, 1-trifluoromethyl-perfluorocyclopropane, tetrafluoroethylene, and perfluorocyclopropane. Carbine is also formed temporarily. Figure 2 shows the relevant chemical equations[10].

The purpose of the present work was to investigate the influence of changes in technological parameters on direct oxidation of HFP using oxygen in a liquid phase under pressure, and to establish optimal parameters for process operation.

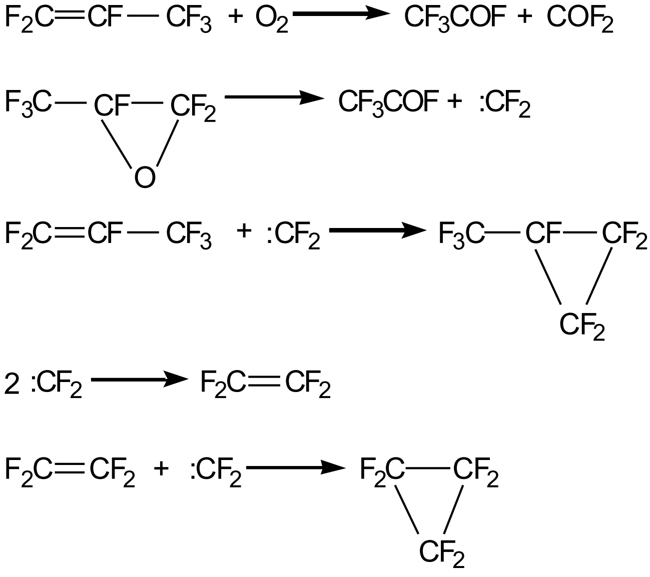

Figure 2. The mechanism of formation of HFPO

EXPERIMENTAL

Raw Materials

HFP was prepared by debromination of 1,2-dibromohexafluoropropane. Oxygen and nitrogen were obtained from Messer-Poland. Carbon tetrachloride (CCl_4), perfluorotributylamine ($[CF_3(CF_2)_3]_3N$), and 1,2,2-

trichloro-1,1,2-trifluoroethane (CFC-113), were obtained from POCh, Poland.

Oxidation Procedure and Analytical Methods

The main instrumentation for oxidation of HFP is a reactor (volume 1.310 cm^3) featuring a condenser in the upper level. The reactor was electrically heated, with manual regulation, and the feed voltage was controlled by an autotransformator. The reactor was equipped with temperature detectors and a manometer was installed at the top. The apparatus permitted addition of precise levels of olefins and oxygen, and featured an absorption system and a cryostat containing a cold trap, to obtain reaction products.

An appropriate amount of aprotic solvent was introduced to leak-proof the reactor. The reactor was operated in the temperature range 130…170°C, and an inert gas (nitrogen) was introduced to generate overpressure. Gaseous substrates (HFP and oxygen) were introduced at specified velocities. HFP was added to the reactor when the temperature was 70…90°C. Perfluoroolefin was added at a level greater than that of oxygen. Samples for analysis were obtained from three different sites during the chemical process. Products were collected from the reactor outlet (thus before absorption), after absorption but before outdropping, and in the outlet of the cold trap. Cryostat temperature was -45°C and total reaction time was 1…3 h.

Fluoride ion levels in the eluate were determined potentiometrically after absorption of the gaseous products of oxidation. An Orion 4 STAR apparatus fitted with a fluoride electrode (model Orion 9609 B) was used for measurement.

Quantitative analysis of HFPO and the gaseous products of HFP oxidation was performed chromatographically using a Chrom 5 apparatus equipped with a thermal conductivity detector. The concentrations of gaseous HFP, HFPO, and trifluoroacetic acid fluoride were determined. A stainless steel column (2.5 m × 0.4 cm) packed with silica gel ASTM-E of 80/100 mesh was used. Other detection conditions were as follows: carrier gas H_2 = 20 cm^3/min, oven temperature = 150°C and injection level = 100 μL.

RESULTS AND DISCUSSION

The influence of temperature on HFPO yield, in the range 130…170°C (i.e. in the reaction zone), was explored under the following conditions: HFP 115 g (0.766 mol), oxygen 9 dm^3 (0.4 mol), carbon tetrachloride 2,042 g (1,310 cm^3), and reaction time 3 h. Oxygen was added in three aliquots (each of 3 dm^3) at 60 min intervals. The results are listed in Table 1.

It was found that, above 170°C, the epoxy oxides formed were unstable and decomposed into by-products. At temperatures below ca. 155°C, epoxidation of HFP to HFPO was not seen.

Table 1. The influence of temperature on HFPO yield

Reaction time [min]	Reactor temperature [°C]			pressure [bar]	yield [%]
	top	middle	bottom		
20	126	136	145	34.5	–
40	145	151	157	35.5	–
60	152	157	162	36.0	–
80	158	162	166	37.0	8.5
100	160	164	167	36.0	21.3
120	160	164	169	36.2	30.1
140	161	166	170	36.4	41.0
160	158	164	170	36.6	48.6
180	170	172	174	36.8	43.9

The influence of three solvents on the oxidation of HFP to HFPO was also investigated. The experimental parameters were a reaction time of 3 h, a temperature of 160…170°C, a molar ratio of HFP/O_2 of 1:1.05, and three oxygen aliquots each of 3 dm^3. The data obtained are listed in Table 2.

The best results were obtained with use of the solvent 1,2,2-trichloro-1,1,2-trifluoroethane (CFC-113), with an HFPO yield of approximately 83%. The lowest yield (44%) was obtained when carbon tetrachloride was employed. This is attributable to the low solubility of both oxide and HFP in this solvent.

CONCLUSIONS

Temperature plays the most significant role in oxidation of HFP to HFPO. To obtain HFPO in good yield it is necessary to conduct the oxidation reaction in the temperature range 160…170°C. Yield can be improved by the use of an appropriate aprotic solvent. The best solvent for oxidation of HFP was 1,2,2-trichloro-1,1,2-trifluoroethane (CFC-113), which afforded the product in 83% yield.

Synthesis of HFPO is both complicated and time-consuming. The oxidation reaction can be very violent if the oxygen feed level is too fast. The selection of appropriate process parameters including temperature and molar ratio of HFP/O_2 render the temperature controllable and limit formation of by-products.

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Table 2. The influence of solvent type on HFPO yield

Type of solvent	solvent	HFP		O2		Temperature [?C]	Yield [%]
	[cm^3]	[g]	[moles]	[dm^3]	[moles]		
CCl_4	1.310	115	0.766	9	0.4	163	44
$[CF_3(CF_2)_3]_3N$	1.310	115	0.766	9	0.4	165	59
CFC-113	1.310	115	0.766	9	0.4	167	83

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