Hexafluoropropylene Oxide (HFPO)

Fluorointermediates

Properties, Uses, Storage, and Handling

Product Information

Introduction

Hexafluoropropylene oxide (HFPO) is a versatile fluorointermediate that can be used in the synthesis of fluoromonomers and fluoropolymers and to add fluorine functionality to a variety of organic precursors. Perfluorinated vinyl ethers utilized in the production of commercial fluoropolymers are produced using HFPO as the key intermediate. In addition, the commercial perfluorinated Krytox™ lubricant has HFPO as the monomer unit.

Properties

HFPO supplied by Chemours has a minimum purity of 98.6 wt% (Table 1). When impurities are detected, they generally consist of hexafluoropropene (HFP). HFP is the key chemical precursor to HFPO, which is synthesized in an oxidation process. This product may also contain a very low level of hexafluoroacetene (HFA). The HFA isomer is generated by a metal catalyzed mechanism that can be initiated by improper storage and handling methods. See Storage section and the Safety Data Sheet (SDS) for more information.

Physical properties of HFPO are given in Table 2. HFPO is a nonflammable gas that is stored as a pressurized liquid. The vapor pressure equilibrium curve for HFPO is included in Figure 1.

Table 1. Product Data

Property	Unit	Minimum	Maximum
Organic Purity—HFPO	wt%	98.6	—
HFP	wt%	—	1.0

Figure 1. HFPO Vapor Pressure, est.

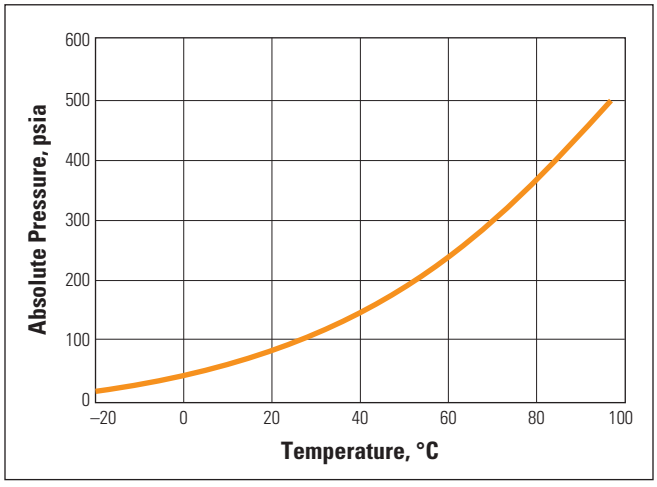

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Table 2. Physical Properties

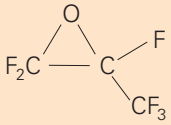
Property	Unit	Typical Value
Chemical Name	—	Oxirane, Trifluoro (Trifluoromethyl)
CAS Number	—	428-59-1
EINECS Number	—	207-050-4
Chemical Formula	—	
Molecular Weight	—	166
Boiling Point at 1 atm	°C (°F)	-27 (-17)
Vapor Pressure at 25 °C (77 °F)	kPa-abs (psia)	660 (96)
Melting Point	°C (°F)	-144 (-227)
Liquid Density at 25 °C (77 °F)	kg/m^3 (lb/ft^3)	1300 (81.2)
Vapor Heat Capacity at 25 °C (77 °F)	J/mol·K	138
Liquid Heat Capacity at 25 °C (77 °F)	J/mol·K	172 (estimated)
Heat of Vaporization at NBP	kJ/mol	21.8
Critical Temperature	°C (°F)	86 (186.8)
Critical Pressure	kPa·abs (psia)	2896 (420)
Critical Density	g/cc	0.59
Flammability Limits	vol%	None

Figure 2. Infrared Spectrum of Hexafluoropropylene Oxide Vapor at 3.5 kPa in a 10-cm cell

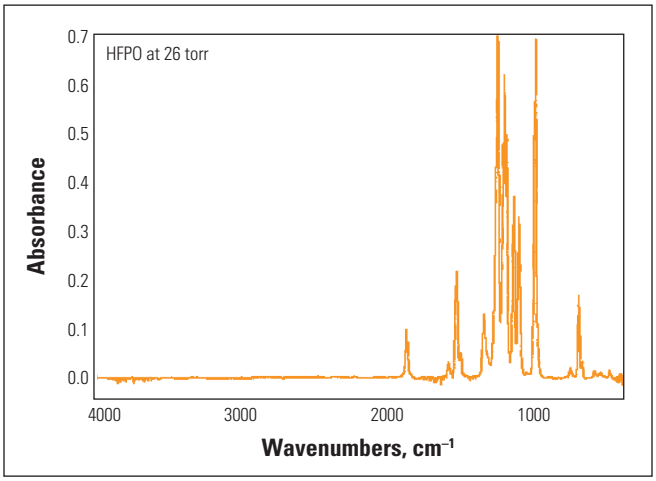
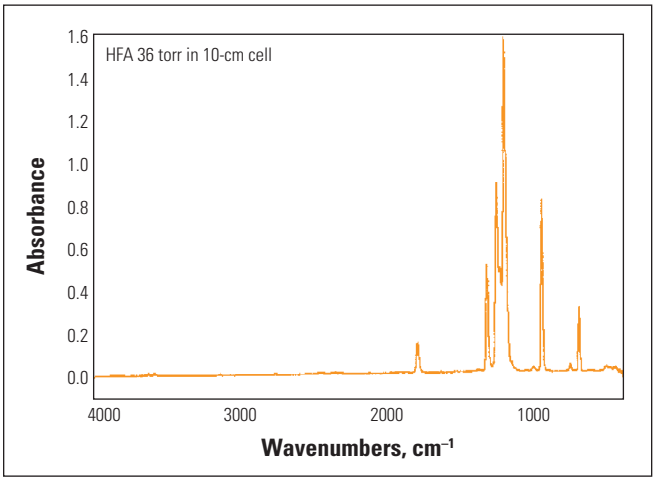


Figure 3. Infrared Spectrum of Hexafluoroacetone Vapor at 4.6 kPa in a 10-cm cell

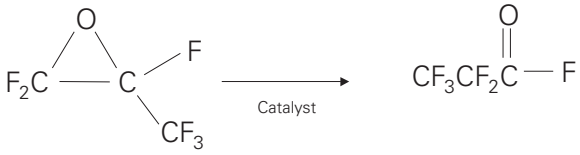


Uses

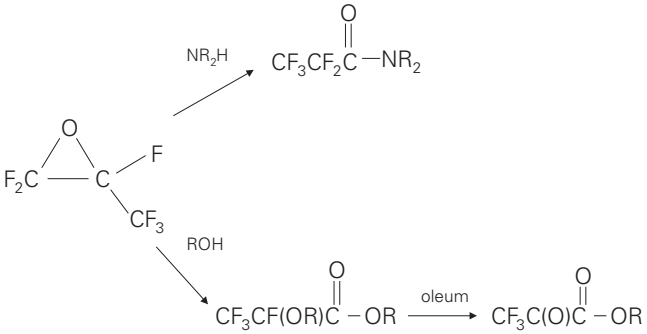
HFPO is a key intermediate in the synthesis of organofluorine compounds. Many commercial fluoropolymers use HFPO, either as a monomer or a monomer precursor. The epoxide ring is opened by nucleophiles to give a variety of derivatives. HFPO may be isomerized to either pentafluoropropionyl fluoride (PPF) or HFA. The thermolysis of HFPO can also serve as a source of difluorocarbene. A few examples of HFPO chemistry are given below; the chemistry of HFPO has been reviewed.[1,2]

Reactions of HFPO

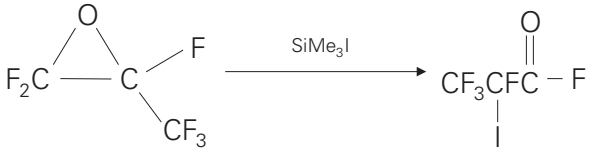
HFPO is easily isomerized to PPF by nucleophilic catalysts, such as halides or amines.



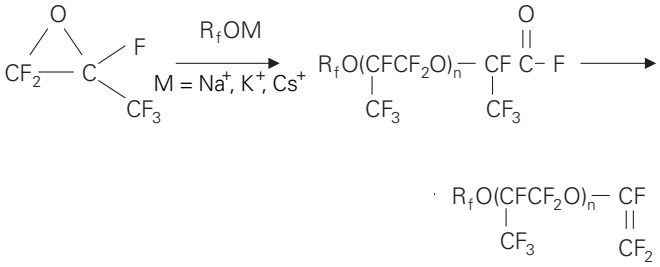
In the presence of alcohols or secondary amines, derivatives of PPF are formed. Methyl 2,3,3,3-tetrafluoro-2-methoxy propionate, prepared from methanol and HFPO, may be converted to methyl 3,3,3-trifluoropyruvate, a useful building block in organofluorine chemistry.



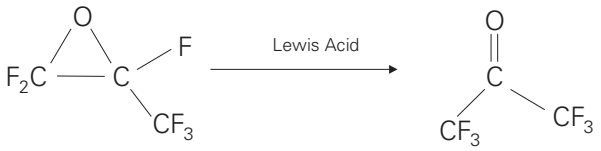
Ring-opening the HFPO with halogenating reagents, such as Me_3SiI, gives halogenated perfluoroalkyl-propionic acid derivatives, such as $CF_3CFIC(O)F$.



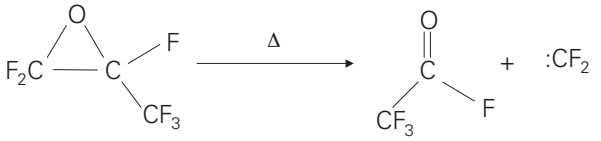
HFPO can serve as a source of the heptafluoro-propoxide ion owing to the equilibrium between PPF and fluoride ion in solution. The heptafluoro-propoxide ion, as well as other polyfluorinated alkoxides, open the HFPO ring to generate oligomers that can be isolated as the acid fluorides.The acid fluorides in turn may be converted to vinyl ethers that are themselves useful chemical intermediates.



In the presence of Lewis acids, such as SbF_5, HF, or ACl_xF_{3-x} (x = 0.05–0.3), HFPO isomerizes to HFA. This can even happen in storage containers if precautions are not taken to prevent the rearrangement reaction from occurring.



Thermolysis of HFPO gives difluorocarbene and trifluoroacetyl fluoride. The difluorocarbene may be generated *in situ* to prepare useful intermediates, such as CF_2I_2 or cyclopropanes.



Storage and Handling

Shipping Containers in the U.S.

HFPO is a liquefied, nonflammable compressed gas. According to the U.S. Department of Transportation (DOT), a nonflammable compressed gas is defined as a nonflammable material having an absolute pressure greater than 40 psia at 21 °C (70°F) and/or an absolute pressure greater than 104 psi at 54 °C (130 °F).

The appropriate DOT designation is as follows:

Proper Shipping Name	Liquefied Gas, N.O.S. Hexafluoropropylene Oxide
Hazard Class	2.2
UN Number	3163
DOT Labels	Nonflammable Gas
DOT Placards	Nonflammable Gas

Containers

Water Capacity	Dimensions	DOT Specification	Neight Weight HFPO	Liquid Dip Tube	Phase Available
17,000 L ISO	2.4 m x 2.6 m x 6.1 mL (frame) 6.1 mL x 2.4 m OD	51	15,000 kg	Yes	Liquid or Vapor

Smaller sizes are available upon request for developmental purposes.

HFPO Rearrangement Concerns

HFPO can rearrange to toxic HFA in the presence of Lewis acids. This can occur in shipping containers, storage vessels, or other process equipment. Because higher temperatures cause faster rearrangement, it is highly recommended to maintain HFPO below 25 °C (77 °F), unless required for process purposes (i.e., purification or chemistry).

Corrosion by-products in carbon steel containers can catalyze the HFPO rearrangement to HFA. Stainless steel is recommended for HFPO containers. In order to inhibit the rearrangement reaction, toluene is commonly added to carbon steel containers. Low levels of toluene have been shown to be effective as an inhibitor in this rearrangement reaction. If the end user requires even lower levels of toluene, it is strongly recommended that shipping containers be constructed of stainless steel when toluene is not intentionally added as an inhibitor.

Because the potential for rearrangement of HFPO to HFA is always present, it is recommended that HFPO be treated as though it always contains HFA, unless a recent analysis suggests otherwise.

Material Compatibility Concerns

Most metal components are suitable for use with HFPO; however, corrosion-resistant materials, such as stainless steel, are recommended. If less corrosion-resistant materials, such as carbon steel, are used in process equipment, toluene-inhibited HFPO is the preferred product.

Handling Precautions

The following rules for handling HFPO containers are strongly recommended:

- Use proper personal protective equipment, such as side shield safety glasses, gloves, and safety shoes, when handling containers.
- Exposure to HFPO should be prevented or minimized using proper ventilation and chemical hygiene practices.
- Always treat HFPO containers as though they contain HFA, unless a recent analysis indicates otherwise.
- Use proper backflow prevention methods when connecting and disconnecting HFPO cylinders. Introduction of water into an HFPO cylinder can lead to HFA formation by slowly generating HF, leading to corrosion and ultimately HFA.
- To reduce the rearrangement of HFPO to HFA, carbon steel cylinders should be maintained below 25 °C (77 °F).

- To reduce rearrangement of HFPO to HFA, it is recommended that product shipped in carbon steel containers be used within 90 days of shipping.
- Skin contact with HFPO liquid or escaping vapor can lead to frostbite.
- Never heat a container to temperatures higher than 45 °C (113 °F).
- Maintain filled containers with the correct orientation as indicated on cylinders to ensure relief protection is located in the vapor phase.
- Never apply direct flame or live steam to a container or valve.
- Never refill disposable cylinders with anything. The shipment of refilled disposable cylinders is prohibited by DOT regulations.

  NOTE: Disposable cylinders are often used when supplying lab-scale samples.
- Never refill returnable cylinders without Chemours consent. DOT regulations forbid the transportation of returnable cylinders refilled without Chemours authorization.
- Never use a lifting magnet or sling (rope or chain) when handling containers. A crane may be used when a safe cradle or platform is used to hold the container.
- Never use containers as rollers, supports, or for any other purpose other than originally intended.
- Protect containers from any object that will result in a cut or other abrasion in the surface of the metal.
- Never tamper with the safety devices in valves or containers.
- Never attempt to repair either containers or valves.
- Never force connectors that do not fit properly. Make sure threads on the regulators or auxiliary equipment are the same as those on the container valve outlets.
- Keep valves tightly closed and valve caps and hoods in place when containers are not in use.

NOTE: Storage and Handling: Store and handle in accordance with all current regulations and standards subject to storage regulations: U.S. OSHA 29 CFR 1910.101.

References

1. Tarrant, P.; Allison, C. G.; Barthold, K. P. *Fluorine Chem. Rev.* **1971**, 5, 77-113.
2. Millauer, H.; Schwertfeger, W.; Siegemund, G. *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 161-179.

For more information, visit www.chemours.com/fluorointermediates

Replaces: K-05132-2
C-11707 (10/18)