

Methods for hexafluoroacetone production (1,1,1,3,3,3-hexafluoropropanone-2)

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Introduction

For the first time hexafluoroacetone (HFA) was produced in 1941 by N.Fukuhara and L.A.Bigelow by direct fluorination of acetone. HFA is an extremely toxic reactive compound with the following main physical characteristics:

- Molecular mass 166.03 (1)
- Boiling point (760 mm of mercury column) 27.5°C
- Melting point -125.45 -129°C (1)

Nonflammable HFA is an active electrophile and reacts with alkenes, ketenes, aromatic compounds, compounds containing active hydrogen atom etc. HFA does not form homopolymers but is readily copolymerized with various monomers to form chemically and heat resistant polymers. A field of HFA application is wide enough: production of solvents (hexafluoroiso-propanol, for example), pharmaceuticals and agrochemicals, anticorrosive coatings, emulsifiers, dyes etc.

1.HFA production from acetone and its derivatives

1.1. HFA production by direct fluorination of acetone

In 1941 N. Fukuhara and L.A.Bigelow reported about a process of gas-phase fluorination of acetone by fluorine-nitrogen mixture at different ratios of $F_2:CH_3COCH_3:N_2$.

According to the authors, it was easy to fluorinate acetone in a reactor packed with copper gauze. The reaction products were separated and identified. The main reaction products were: HFA, monofluoroacetone, trifluoroacetyl fluoride, oxalyl fluoride, carbonyl fluoride and tetrafluoromethane. The fraction (b.p. -35- -16°C) containing HFA was separated in amount of 5-10% of the whole liquid volume (4).

The reaction of direct fluorination is dangerous and difficult to control, therefore this method was not spread widely but it is still of interest.

An attempt to use AgF (64) as a fluorinating agent for acetone fluorination should be mentioned, but it also did not find further development.

In the late 70-s, gas phase fluorination of acetone was carried out in a fused alumina reactor, a steel tube with inside alumina porous member fused as a tube. The fluorine-nitrogen mixture was fed into the tube of alumina and the compound to be fluorinated was fed into the intertubular space. The maximum temperature was 148°C, the HFA yield was 38-43%. Fluorinated acetones (from mono- to pentafluoroacetone) and a number of other products were produced as by-products (5).

The use of the low temperature gradient method in the presence of NaF at -100°C resulted in 39% HFA yield. According to the authors, sodium fluoride provided more gentle fluorination conditions and adsorbed the evolved hydrogen fluoride to form sodium bifluoride. Trifluoroacetyl fluoride and octafluoropropane were formed together with HFA. In the authors opinion, the process parameters are subject to optimization and the process can be brought to industrial implementation.

1.2. HFA production from perhalogenacetones.

1.2.1.Catalytic methods

Fluorination with anhydrous hydrogen fluoride

The halogen exchange reaction between hexafluoroacetone or chloroacetones and anhydrous hydrogen fluoride in the presence of a catalyst containing chromium (III) salts is the basis of the industrial method to produce HFA (1,6).

In the early 60-s, Farbwerke, Du Pont and Allied Chem. Companies developed catalytic methods for gas phase fluorination of a number of compounds, including perhalogenacetones, in the presence of a catalyst based on Cr(III) (7,8,9). The approach described in a Hoechst AG patent used chromium oxyfluorides produced by interaction of $\text{Cr}(\text{OH})_3$ (or "Guignet Green" commercial pigment) with hydrogen fluoride diluted with inert gas (nitrogen, argon) at a ratio of 1:10 at a temperature of 350-400°C. The atomic ratio of the elements in the catalyst produced was Cr:F:O=1: (1.5-2): (1-1.5).

Hexachloroacetone was fluorinated on the catalyst produced at 250°C to yield HFA in 81% as per hexachloroacetone (0.55M) and 4.02M HCl.

In works (8,9) CrO_3 was used as a catalyst. It can be produced by $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ dehydration (8) or CrO_3 reduction in an aqueous solution to form a gel-like product with following drying (10).

According to (8), HFA was produced in a tubular reactor of 3.5 m length and 5.1 cm diameter filled with 5 kg of Cr_2O_3 gel. As a result of the reaction, HFA, chloropentafluoroacetone and dichlorotetrafluoroacetone were produced at hexafluoroacetone conversion of 98%.

Paper (9) describes fluorination of perhalogenacetones over Cr_2O_3 catalyst produced by precipitation of *chromoxide* hydrate from a water-soluble chromium salt (nitrate, for example) with an alkali reagent followed by filtration, washing, drying and pressing into tablets. The tablets produced were preheated in a reactor at a temperature of 370 - 400°C. HFA was produced by fluorination of dichlorotetrafluoroacetone at a temperature of 330-380°C. The yield attained 21%, the rest was unreacted dichlorotetrafluoroacetone.

In the early 70-s, a continuous process to fluorinate perchloroacetone was developed using three-zone catalytic bed of chromium (III) hydroxide treated with hydrogen fluoride(11). The temperatures of every bed were different: 234-236°C, 260-271°C, 280-340°C respectively. The contact time in every bed was different also: 6-10.9 s, 3.8-4.8 s and 3.5-6.2 s. Every catalyst bed was separated with a bed of aluminum oxide. As a result, a reaction mixture containing HFA, CF_3COF , CF_3CHO and $\text{CF}_3\text{CF}_2\text{COCF}_3$ was produced in 95.3-97.4% yield at the total fluorination degree of 97.2-98.9%.

Work (12) proposed a mixture of oxalates of Cr (III) and Ni(II) as their hydrates , $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ and $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, as fluorination catalyst.

A catalyst with the specific surface of 360m²/g was treated with hydrogen fluoride in a mixture with nitrogen at a ratio of 1:4.

In the 70-80s., some works were carried out with the purpose to increase the process selectivity and the catalyst life time without reduction in its activity.

It was found that chromium oxide catalysts produced by reduction of CrO_3 of the " Guignet Green" pigment , precipitation of trihydroxide from aqueous solutions of Cr (III) salts possess orthorhombic crystallinity effect. Treatment of such a gel-like catalyst with water at 250°C for 20h leads to its structure transition to Cr (III) oxide hydroxide (CrOOH) hexagonal structure. CrOOH was applied on calcium difluoride. The life time of this catalyst in the hexachloroacetone fluorination was 700h, the life time of the catalyst with orthorhombic structure was 400h (13).

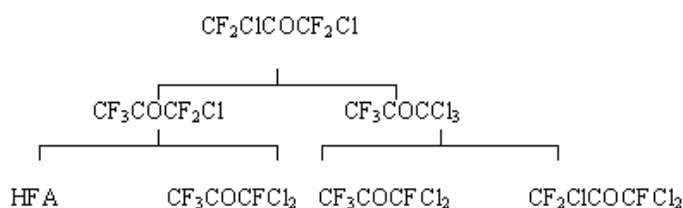
Work (14) proposed Cr_2O_3 catalyst as microspheres of 0.1-0.3mm diameter according to *sol-sel* technology. The use of this catalyst in the hexachloroacetone fluorination resulted in the following reaction products: HFA (75%), chloropentafluoroacetone, small amounts of dichlorotetrafluoro-acetone and trichlorotrifluoroacetone at 76% hydrogen fluoride conversion.

Another method to produce a long-lived catalyst is described in (15). $\text{Cr}(\text{OH})_3$ without ionic admixtures was dried and calcined at 450-550°C.

Paper (16) considers a procedure to produce Cr₂O₃ by CrO₃ reduction with methanol followed by activation of the Cr₂O₃ produced with hydrogen fluoride and trifluorotrichloroethane at 400°C.

Disproportionation of perhalogenacetones.

HFA and chloropentafluoroacetone are produced by catalytic disproportionation of perhalogenacetones in the presence of Cr₂O₃ in gas phase at 225-400°C according to the scheme:



The yield of HFA from dichlorotetrafluoroacetone is 12.2% and 40.7% from chloropentafluoroacetone. The authors believe that the advantage of this route is that the mixture of HCl and HF difficult to separate is absent, while it is formed in the fluorination with hydrogen fluoride.

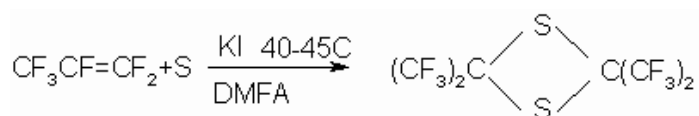
1.2.2. Non-catalytic methods

According to the authors, a simple and controlled method to produce HFA by fluorination of perhalogenketones is their interaction with KF taken in a stoichiometric amount and suspended in tetrahydrothiophene-1,2-dioxide, an inert polar solvent. HFA is produced from dichlorotetrafluoroacetone in 67% yield at a temperature of 180-190°C at the starting perhalogenacetone conversion of 56%. It is possible to use other fluorides: CsF, LiF, AgF but potassium fluoride is the most preferable (18).

The study of the properties of polyfluoroacetylfluorosulfates has found that their interaction with SbF₅ at a temperature of 35 °C results in the formation of HFA in yield of 77.5% yield (19).

2. Hexafluoroacetone production by oxidation of hexafluorothioacetone (HFTA) dimer

In the 80-s a method to produce HFA from 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithioethane, being hexafluorothioacetone (HFTA) dimer, and also to produce the dimer itself was developed (2,20-24). HFA was produced by treatment of the dimer with oxidizer in a medium of aprotic solvent in the presence of alkali metal fluoride as a catalyst at a temperature of 140-149 °C in 80-89% yield. The process takes place according to the scheme:



The following substances were used as oxidizers: HgO, Ag₂O, Cu₂O, CuO, MeI₃, MeI₄ where Me is alkali or alkali-earth metal (21), also air, O₂, O₃, NO₂, NO (22). Dimethylformamide, dimethylsulfoxide and N-methylpyrrolidone were used as aprotic solvents.

The dimer can be converted to HFA for 24 h without oxidizer fed in 25% yield. The dimer was also used, beside HFA production, to produce perfluoroisobutene by its treatment in an aprotic solvent with formaldehyde or with a compound forming formaldehyde (paraformaldehyde for example) in the presence of alkali metal fluoride at 110-150 °C (24).

The authors considered the following as the advantage:

- the proposed method to produce the dimer is easier than that used for the dimer production earlier according to the reaction of bis(perfluoroisopropyl)mercury with sulfur vapors at 445°C and the yield of HFTA of 60% followed by its dimerization in the presence of excess triphenylphosphine (25).
- In comparison with the known methods to produce HFA (hexafluoro-propylene epoxidation followed by isomerization to HFA, high-temperature halogen exchange with hydrogen fluoride/Cr(III), perfluoroisobutene oxidation), this method is

3. Hexafluoroacetone production by oxidation of olefins

3.1. Hexafluoropropylene oxidation

A study of the hexafluoropropylene oxidation reaction in a flow-type reactor has found that fluorides such as CsF, RbF, LiF, KF and NaF catalyze this reaction. A multi-component mixture containing CF_3COF , COF_2 , $\text{CF}_3\text{CF}_2\text{COF}$, HFA, $\text{CF}_3\text{OCF}_2\text{COF}$ etc. has been produced. In addition to oxygen, CrO_3 and KMnO_4 may be used as an oxidizer. Works carried out in Russia have shown that chromium (VI) oxide reacts with HFP to form carbonyl compounds. The reaction was carried out in an autoclave at stirring for 3 days. The starting components were HFP, HF, CrO_3 . The synthesis products were run through water, the water solution was then extracted with ether. There were produced 24% HFA and 23% of ethyl ether of trifluoroacetic acid (27).

An investigation of the HFP oxidation in HFA in details has been performed by Daikin, Japan company. A high yield of HFA was attained by oxidation with oxygen over Al_2O_3 treated with SF_4 at 350°C or with HF at 450°C (28). In addition to HF and SF_4 , in paper (29) other promoters are mentioned: SiF_4 , SF_6 , NH_4F , organic fluorides including freons. HFA was produced in a yield of 4 to 21.2% (mol) at a temperature of 170°C and pressure of $5\text{kg}/\text{cm}^2$. Further a blend catalyst, fluorinated Al_2O_3 - SiO_2 , was used. The oxidation was carried out both in the presence of water and without it. The process over fluorinated aluminum oxide (without SiO_2) was conducted in the presence of water. A mixture of hexafluoropropylene with oxygen containing water in amount of 0.008 - $0.0016\text{mol}/\text{HFP mol}$ was passed over the fluorinated Al_2O_3 at 175°C . The conversion was 15.4%, selectivity 70.4% after 450 h. If the process was carried out in the absence of water, the conversion of HFP was reduced to 34.4% but the selectivity was reduced to 29.8% after 160 h (30).

Besides the catalyst based on aluminum, other ones were studied also. Paper (31) has considered the HFP oxidation process over oxides of Sn (IV), Fe (III), In (III) at a temperature of 150 - 300°C . Using SnO_2 catalyst and at 250°C , the conversion of HFP was 70.6% the selectivity to HFA 53.9%. Under the same conditions and Fe_2O_3 catalyst, the figures were 49.3% and 52.4% respectively, in case of using In_2O_3 : 54.1% and 52.2%. CF_4 and COF_2 were formed together with HFA. Comparative experiments with V_2O_5 and PbO_2 showed their low activity. Also, commercially produced metals of the platinum group, applied on activated carbon, have been investigated. The HFP oxidation was carried out in a circulation reactor at 110 - 190°C . At the same time the process was carried out using oxides of vanadium, molybdenum and silver at 250 °C. The highest HFP conversion of 63.2(mol)% was reached with a 5% Ru/C catalyst at HFA selectivity of 87.4% and 120 °C. The use of a 0.5% Pd/C catalyst brought to 54.7% conversion and 87.4% (mol) selectivity at 150°C . The authors of these investigations considered the HFP oxidation the most simple and convenient method to produce HFA.

3.2. Oxidation of perhalogenisobutenes

Oxidation of perhalogenisobutenes is one of the first directions in the development of HFA production methods. A.L.Henne, J.W.Shepard, J.Evan proposed their method as an alternative to the direct fluorination. Potassium permanganate directly oxidized $(\text{CF}_3)_2\text{C}=\text{CCl}_2$ which was produced in its turn by a multi-stage method from $\text{CF}_3\text{C}(\text{CH}_3)\text{ClCH}_2\text{Cl}$. In spite of the multi-stage mode, the authors considered the use of commercial compounds and common operations as the advantage. The yield in every stage attained 90-95% taken into account recycle. HFA yielded in 60% (33). First, perfluoroisobutene oxidation with an aqueous solution of potassium permanganate at 100°C resulted in the formation of HFA hydrate which was then converted to HFA according to the Henne procedure by the hydrate addition to phosphorus (V) oxide dropwise and heating to 30°C . The yield of HFA attained 27%, perfluoroisobutene conversion was 67% (34).

The yield of HFA has been found low (~16%) in case of oxidation of fluorine-hydrogen containing isobutenes with potassium permanganate because this compound does not contain the halogen atom joined directly to the olefin carbon. Replacement of one hydrogen with bromine followed by oxidation with permanganate increased HFA yield to 55% (35).

Later, oxygen was proposed as an oxidizer(36). The process was carried out in a nickel tube at a temperature of 500°C . HFA yield was 96% of the theoretical one. The technical product contained admixtures of perfluorocyclobutane and butenes. Oxidation of another derivative of perfluoroisobutene, $(\text{CF}_3)_2\text{C}=\text{CFOR}$ (where R=alkyl) at photoinitiation with a mercury lamp led to 19.2% yield of HFA (37).

Hydrogen peroxide in the presence of carbonates or hydroxides of alkali or alkali-earth metals may be used as an oxidizer. Perfluoroisobutene was added to 30% hydrogen peroxide and methanol, the mixture was then treated with aqueous potassium carbonate. The both stages were carried out at room temperature. HFA yield as hydrate was 40.8% (38).

4. HFA production by isomerization of hexafluoropropylene oxide (HFPO)

4.1. Isomerization in the presence of fluorides

Antimony pentafluoride was used for HFPO isomerization to HFA (39) in the early 60-s, in the 80-s the process used HFPO contact with antimony pentafluoride at a temperature of 31°C and a pressure of 0.3-13.76 MPa. HFPO conversion was 99% (40).

The following other fluorides were used:

- hydrogen fluoride in equal mass parts with HFPO. In this case HF was both the catalyst and the solvent. By this method HFA was produced in over 90% yield at 100°C. At HFPO conversion of 95.7% HFA was produced in 98.3% selectivity, at 99.1% HFPO conversion Selectivity of HFA was 94.3% (41).
- Cobalt trifluoride at a temperature of 40-90°C, the yield was 99.2% at complete HFPO conversion (42).

4.2. Isomerization in the presence of the Lewis acids

In the early 60-s a gas phase process to produce HFA by HFPO isomerization on Al₂O₃ catalyst as spheres of 3 mm diameter on a support, 6 mm glass rings, was developed. The process temperature was 100°C, nitrogen was used as a gas-carrier. The reaction was carried out to 49% yield of HFA. At the same time a liquid-phase method at room temperature in liquid SO₂ in the presence of AlCl₃ as a catalyst was developed. HFA was produced in 79% yield (43).

But a low yield of HFA required further investigations on search of more effective catalyst.

Work (44) describes a process with the use of fluorinated alumina or silica-alumina at 170°C. The use of alumina containing 10% of fluorine resulted in HFPO conversion close to the calculated one. Catalyst regeneration was performed with oxygen.

To avoid a reduction in catalyst activity, it was proposed to carry out the isomerization in the oxygen presence (45).

Al₂O₃ promotion with fluorine-oxygen-containing compounds such as perfluoroethylisopropylketone, perfluoroethylhexylketone, HFPO trimer increases the yield to 93.5-97.4% at 100% HFPO conversion and at a process temperature of 80-120°C. Tetrafluoroethylene and carbonyl fluoride were by-products (46).

At 100% conversion, HFA yield increases to 99.5% if Al₂O₃ is promoted with antimony pentafluoride in amount of 0.03-0.3 equiv. blowing dry nitrogen together with antimony pentafluoride vapors through calcined aluminium oxide at a temperature of 5-100°C. The isomerization process had a temperature of 25 to 220°C (3).

97% of HFA was attained at 100% HFPO conversion using fluorinated Al₂O₃ containing 31% fluorine (47).

In work (40) Al₂O₃ was promoted with 0.01-0.04 mol/g of hexafluoro-propylene at 400-650°C. According to the authors, more cheap and simple in preparation is a catalyst promoted with hexafluoropropylene oxide. The yield of HFA reached 99% at HFPO conversion of 100% (49).

94% HFA yield at 98% HFPO conversion was attained using Cr₂O₃ treated with hydrogen fluoride in a nitrogen flow at 150-250°C. The fluorine content in the catalyst reached 13% (50).

5. Other methods to produce HFA.

5.1. HFA production from carbonyl compounds and ethers.

HFA has been produced by electrochemical fluorination of CF₃CO₂CHCH₃ to produce CF₃CO₂CF(CF₃)₂ followed by its treatment with sodium fluoride to form HFA and CF₃COF (51).

Investigation of reactions of perfluoroalkylbromides or iodides with derivatives of carbonic acids in the presence of Zn powder has found that interaction of trifluoroethylacetate with bromotrifluoromethane at 20°C in pyridine led to the formation of HFA in 54% yield (52).

HFA and its hydrates have been produced from hepta- or octafluoroiso-butenyl ethers or their derivatives by ozonation or thermal oxidation with oxygen on an activated carbon catalyst. The produced compounds were decomposed with water. Ozonation of heptafluoroisobutenylmethyl ether led to 69.7% yield of HFA (53).

Decomposition of branched perfluoroalkyl ether fluid with anhydrous aluminum chloride in an oxygen-free medium leads to the formation of volatile products, mainly HFA and fluorine-chlorine-containing compounds and oligomers as well (54).

5.2. HFA production from olefins and its derivatives.

HFA together with perfluoropropylsulfide was produced from HFP and SOF₂ in a close system in a tubular reactor containing CsF at 120°C for 40 hours (55).

HFA in 77% yield was produced by heating a mixture of HFPO and perfluoroisobutene for 10h at 170°C (56).

Nucleophilic oxidation of 3-chloropentafluoro-1-propene led to the formation of 3-chloropentafluoropropene-1,2,-oxide which subjected to antimony pentafluoride formed a mixture of fluorinated acetones in total yield of 81.1% at the ratio of chloropentafluoroacetone:HFA=72:28 (57).

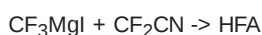
5.3. HFA production from HFCs.

One of the possible ways to produce HFA and other perfluoroketones is electrochemical oxidation of aliphatic secondary and tertiary hydrofluorocarbons in a medium of fluorosulfonic acid followed by pyrolysis of perfluoroalkylsulfates obtained over cesium fluoride to the appropriate ketones (58).

In the middle 90-s a catalytic process of oxidation of hydrofluorocarbons including 1,1,1,3,3,3-hexafluoropropane with oxygen and fluorine in the presence of Al₂O₃ catalyst at 50-300°C and the contact time of 2-60s was developed (59).

5.4. Other methods to produce HFA.

The Grignard reagents can be converted to ketones including HFA as well according to the reaction:



to form HFA in 33% as per CF₃MgI (60).

Diazomethane oxidation with molecular oxygen under exposure to radiation of 305nm wave length brings to the formation of HFA-O-oxide which is converted to HFA under exposure of 590nm wave length (61).

Work (62) has considered a way to produce HFA from its oximes by their heating with concentrated mineral acid (H₂SO₄). Oximes were produced from heptafluoroisobutyryl carbanion alkylammonium salts. HFA yield was 78%. More over, HFA is possible to produce from 1-methoxy-1-perfluoroisobutene by its interaction with sodium nitrite in 59%yield and from methoxy-2H-octafluoro-isobutane and N₂O₄ in 51% yield. Also, HFA is formed in bis(trifluoromethyl)-sulfine photolysis (63).

Conclusions

Commercially important routes to produce HFA are

- fluorination of acetone halides with hydrogen fluoride
- hexafluoropropylene oxidation
- hexafluoropropylene isomerization

All three methods are catalytic and the main problem in their development was to establish an effective catalytic system, technology of separation of the multi-component reaction mixture, purification and separation of the goal products. The method of fluorination of acetone halides was implemented in industrial production by American companies. Du Pont and

Allied Chem Corp. (Allied Signal at present), as early as in the 60s. By the 80-s no publications on further improvement of this process were found.

The method of hexafluoropropylene oxidation was developing in the 70-80s in Japan (Daikin Co Ltd) and considered as the most convenient and simple in the authors opinion. Publications on the method came to the end by the late 80-s.

Development of the process of hexafluoropropylene oxide isomerization was conducted in the USA (Du Pont and AlliedSignal), the USSR (Russia) and Japan (Asachi Glass Co, Daikin Co Ltd) since the middle 60-s to the middle 80-s. The publication of (42) is not an exception because the patent application was filed in 1980.

The publications of the last years are rather of a scientific interest but patent (59) of Allied Signal possessing great experience in development of the technology and production of HFA.

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