

UNITED STATES PATENT OFFICE

2,668,864

PROCESS OF MAKING PERFLUORO OLEFINS

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No Drawing. Application November 26, 1951,
Serial No. 258,306

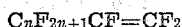
6 Claims. (Cl. 260—653)

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This application is a continuation-in-part of our copending application Ser. N. 138,264, filed January 12, 1950 (now abandoned).

This invention relates to our discovery of a new and useful process of making perfluoro olefins.

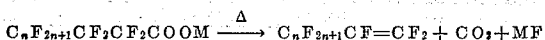
More particularly, the invention relates to the preparation of terminally-unsaturated aliphatic perfluoro mono-olefins having from two to nine carbon atoms in the molecule. These compounds are non-cyclic fluorocarbons, consisting solely of carbon and fluorine, wherein the molecule has one double bond, which unites a terminal carbon atom to the adjacent beta carbon atom. The generic formula is:



where n has a value from zero to seven.

We have discovered that these compounds can be prepared in very high yields by a simple dry-reaction procedure. This procedure involves the pyrolytic decarboxylation and defluorination of an anhydrous alkali-metal salt of a perfluoro-alkyl monocarboxylic acid having from three to ten carbon atoms in the molecule. It has been found that such a salt, if in an anhydrous state and free from hydroxyl compounds, can be heated at a temperature of the order of 200 to 350° C. so as to decompose at a controllable rate in a non-violent manner to yield the corresponding perfluoro olefin. The heating causes the carboxylate salt radical and a fluorine atom in beta position to be split off from the perfluoro salt molecule. This results in unsaturation between the alpha and beta carbon atoms of the resultant fluorocarbon molecule. The normal by-products formed are carbon dioxide and an alkali-metal fluoride salt. Under favorable conditions the yield of perfluoro olefin compound, having one less carbon atom in the molecule than the starting compound, is essentially quantitative (at least 90%).

This reaction can be represented as follows:



where M is an alkali-metal atom, and n has a value from zero to seven. When n is zero, the starting compounds are FCF_2CF_2COOM , that is, the alkali-metal salts of pentafluoropropionic acid. When n is unity, the starting compounds are $CF_3CF_2CF_2COOM$, that is, the alkali-metal salts of normal heptafluorobutyric acid. When n is a higher integer, the starting compounds are the alkali-metal salts of the higher perfluoro

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acids, in which case the perfluoro alkyl chain represented by the C_nF_{2n+1} formula can be either a straight chain or a branched chain.

It has been found that high yields can only be obtained when use is made of the alkali-metal salts (salts of lithium, sodium, potassium, rubidium and cesium). The other metal salts, the ammonium salts, and the acids, either do not yield the desired perfluoro olefins in significant amounts or do not form them in high yields. The potassium and sodium salts are of chief practical interest and the sodium salts are preferred. It should also be noted that the obtaining of high yields of fluorocarbon olefins is peculiar to the salts of monocarboxylic acids. The salts of polycarboxylic acids do not produce perfluoro olefins in good yields.

The effective use of the aforesaid alkali-metal salts is critically dependent upon freedom from the presence of water. Our process is a dry reaction process. Unless the salts are in an anhydrous state, and free from the presence of hydroxyl compounds, when heated at any temperature sufficiently high to cause decompositions, the formation of by-products due to the presence of water will reduce the yield of the desired perfluoro olefin. These undesired by-products are fluorocarbon hydrides, fluorocarbon acids, and fluorocarbon acid fluorides. They are produced when even a trace of water is present. When appreciable water is present the yield of the desired perfluoro olefin is reduced virtually to zero owing to the greater tendency of the salt to undergo reactions involving water as a reactant.

Thus it can be seen that experiments employing salts as a non-dehydrated or only partially dehydrated state would not reveal our discovery.

The desired result is not obtained if an alcohol is present, owing to the effect of the hydroxyl radicals.

Thus our process is a dry process wherein the anhydrous salt of the acid is heated at a decomposition temperature in the absence of hydroxyl compounds.

We have found that the salts which we employ can be effectively dehydrated by extended heating at temperatures which are sufficiently high for this purpose but which are not high enough to cause decomposition of the salt molecules. That is to say, and this is an important aspect, the alkali-metal salts of perfluoro-alkyl monocarboxylic acids are stable in aqueous solutions and are stable at temperatures which are sufficiently high to permit of dehydrating them

prior to being decomposed at still higher temperatures pursuant to our process.

The behavior of these salts is in marked contrast to that of the corresponding chlorinated salts. The latter decompose spontaneously and rapidly in aqueous solutions at room temperature. The eminent French chemist, J. Boeseken, reported in 1927 that the sodium salt of penta-chloropropionic acid ($\text{CCl}_3\text{CCl}_2\text{COONa}$) decomposes so rapidly in aqueous solution at 25°C . that he was unable to measure the conductivity (Rec. trav. chim., vol. 46, pp. 341-3). He stated that the salts of this acid can be prepared by neutralizing the acid with a cold saturated solution of a base and evaporating the neutral solution at a low temperature. The resultant salts would necessarily be in a hydrated form and Boeseken did not describe dehydrating the salts to an anhydrous state. He said that they are very unstable and decompose rapidly with the formation of salts of hydrochloric acid, carbon dioxide and tetrachloroethylene. The salts of higher perchloro acids would be even more unstable, and so far as we are aware neither they nor the higher perchloro acids have even been reported.

In striking contrast to such behavior, the sodium salt of pentafluoropropionic acid



for instance, is highly stable in aqueous solutions and it can be fully dehydrated, even at elevated temperatures, without decomposing. Hence it is evident that our discovery that this salt can be thermally dehydrated without decomposition and can then be further heated in an anhydrous state at a still higher temperature (e. g., $200\text{--}350^\circ\text{C}$.) to cause decomposition and obtain a quantitative yield of tetrafluoroethylene (C_2F_4), does not involve any analogy to the behavior reported by Boeseken, but is entirely disparate and peculiar to the perfluoro salt. The formation of C_2F_4 is also contra-indicated if analogy is relied on, since this salt when moist does not yield C_2F_4 on decomposition, contrary to the behavior of moist $\text{CCl}_3\text{CCl}_2\text{COONa}$ in yielding C_2Cl_4 when decomposed.

We have found that the sodium salts of the perfluoro acids are more easily dehydrated than the potassium salts, which is one reason for preferring them. It has been found that heating the sodium salts (at say 100°C .) to cause dehydration need not be fully carried to completion prior to beginning the heating of the salts up to the decomposition temperature (e. g., $200\text{--}350^\circ\text{C}$.), since reliance can be placed on appreciable further dehydration occurring during such heating up so as to complete the dehydration prior to decomposition and thus obtain a quantitative yield of the desired perfluoro olefin. However, even a sodium salt requires more than mere evaporation to apparent "dryness" of an aqueous solution thereof in order to be properly conditioned, since the water of hydration will not be adequately removed merely upon direct heating of the hydrated salt up to a decomposition temperature unless a very gradual elevation of temperature over a long time is employed.

The anhydrous salts can be prepared by neutralizing an aqueous solution of the selected perfluoro acid with sodium hydroxide (or other alkali-metal hydroxide), evaporating to dryness, and heating the salt at 100°C . for a sufficient period to dehydrate it. Heating the sodium salt solutions in air at 100°C . for eight hours results in a properly dehydrated salt mass, which can

then be pulverized before being charged to the reaction vessel. The anhydrous salt must be stored in an hermetically sealed container to exclude moisture, as it is very hygroscopic.

The present process can be carried out in a simple reaction vessel which is direct-fired, or is heated in a furnace, or, preferably, is indirectly heated by means of a heat-exchange fluid (e. g., a fused salt type, or molten lead, or a high-boiling fluorocarbon compound) to permit of more uniform heating and better temperature control. Either batch or continuous procedures can be used. As hydrogen fluoride is not evolved, laboratory experiments can be conveniently performed with "Pyrex" glass vessels. Vessels of stainless steel are suitable.

A suitable laboratory apparatus is a distilling flask located in an electrically-heated furnace and connected to a trap cooled by Dry Ice-acetone. A further trap, cooled by liquid air, can be used for condensing the by-product carbon dioxide, if desired. The reaction can be carried out at atmospheric pressure, and at reduced and elevated pressures.

The particular temperature in any given case is chosen and regulated to cause a smooth controlled reaction and non-violent evolution of the gaseous products. The temperature will depend upon the particular salt employed and its purity, and upon the processing conditions. The reaction appears to be slightly exothermic, the continued application of heat serving to overcome heat losses from the reaction zone which otherwise would cause the temperature to fall. When a batch procedure is used, the salt mass should be slowly heated up to the reaction temperature to avoid over-shooting and the onset of a violent reaction, and the further application of heat should be carefully regulated. The best control is effected not by a control of temperature as indicated by a temperature measuring device (such as a thermometer) but by using the evolution of gas as the indicator of the heating condition. When incipient decomposition commences, as indicated by the onset of gas evolution, the further application of heat should be carefully regulated.

Higher temperatures can be employed when a continuous process is used. In this case the reaction can be regulated by introducing the salt into the reaction zone at a rate that is slow enough to prevent a violent reaction condition. Thus a temperature of 350°C . might be used even though in the case of a particular batch procedure a temperature of 300°C . might be found to be the highest safe temperature.

The temperatures to which reference is being made are those measured just outside the wall of the reaction vessel.

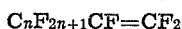
Decomposition generally occurs most effectively at a temperature somewhat above the melting point of the fluorocarbon salt, so that pyrolysis occurs with the salt in a fused or molten condition. Thus sodium n-heptafluorobutyrate ($\text{CF}_3\text{CF}_2\text{CF}_2\text{COONa}$) has a melting point of about 240°C . and will be in a molten state when decomposing at 300°C . The sodium fluoride reaction product has a melting point of about 1000°C . and hence is present in a solid state, so that the reaction residue is a solid porous mass. However, decomposition of the fluorocarbon starting salt can occur when it is in a solid state (below the melting point), in which case the reaction will be of the solid phase type.

The product compound tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$, has previously been produced com-

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mercially by another process on a substantial scale. It is used in manufacturing the polymer thereof, polytetrafluoroethylene (commercially available from Du Pont under the trade-mark "Teflon"). Our process provides an alternative procedure for making $\text{CF}_2=\text{CF}_2$ that has commercial utility.

The present process has particular importance for making the higher perfluoro olefins containing from three to nine carbon atoms in the molecule, represented by the formula:



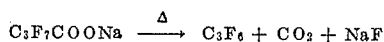
where n has an integer value of one to seven. These are made from the corresponding alkali-metal salts represented by the formula:



where n likewise has an integer value of one to seven. These higher perfluoro olefins have not previously been made by any process known to us which is at all comparable in cost to our process.

Example

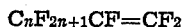
A batch of 17 lbs. of anhydrous sodium normal heptafluorobutyrate was charged to a closed 9 gallon stainless steel kettle, which was then heated by means of external electrical heaters to a temperature at which a controlled evolution of gas took place (about 10 cubic feet per hour). Heating was regulated to maintain this rate of gas formation. The gas mixture was scrubbed with an aqueous KOH solution to remove the carbon dioxide, and was then condensed in a receiver. The reaction was completed in 4 hours. The product collected in the receiver weighed 10.4 lbs. and was identified as substantially pure hexafluoropropylene, $\text{CF}_3\text{CF}=\text{CF}_2$. The yield was 96%. In other experiments, a 99% yield was obtained. This reaction can be written as follows:



The following table shows illustrative perfluoro olefins, having two to nine carbon atoms in the molecule, which we have obtained by our process. The boiling points were measured at 730-745 mm.

Compound	B. P. (° C.)	Mol. Weight		Percent Fluorine	
		Found	Calc.	Calc.	Found
$\text{CF}_2=\text{CF}_2$	-76 to -75	99	100		
$\text{CF}_3\text{CF}=\text{CF}_2$	-29	150	150		
$\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$	-2 to -1	201	200	76.0	75.9
$\text{CF}_3(\text{CF}_2)_2\text{CF}=\text{CF}_2$	29 to 30	250	250	76.0	75.9
$\text{CF}_3(\text{CF}_2)_3\text{CF}=\text{CF}_2$	123 to 124		450	76.0	75.5

These perfluoro olefins have in common an infrared absorption peak at 1795 cm^{-1} which is characteristic of the double bond in



We have published a brief account of our process in the August 1951 issue of the Journal of the American Chemical Society, vol. 73, page 4054.

We claim:

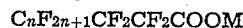
1. A dry-reaction process of making terminally unsaturated perfluoro olefins having from two to nine carbon atoms in the molecule and having the formula:



by pyrolytic decarboxylation and defluorination

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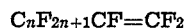
of alkali-metal salts of perfluoro-alkyl monocarboxylic acids having the formula:



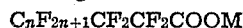
where n has a value from zero to seven and M is an alkali-metal atom, which comprises heating the salt, in an anhydrous state and in the absence of hydroxyl compounds, at a decomposition temperature of the order of 200 to 350°C ., regulating the heating conditions to obtain a smooth controlled reaction of sufficient duration to produce a high-yield conversion of the salt to the corresponding perfluoro olefin, and recovering the latter.

2. A process according to claim 1, wherein a sodium salt is used.

3. A dry-reaction process of making terminally unsaturated perfluoro olefins having from three to nine carbon atoms in the molecule and having the formula:



by pyrolytic decarboxylation and defluorination of alkali-metal salts of perfluoro-alkyl monocarboxylic acids having the formula:



where n has an integer value from one to seven and M is an alkali-metal atom, which comprises heating the salt, in an anhydrous state and in the absence of hydroxyl compounds, at a decomposition temperature of the order of 200 to 350°C ., regulating the heating conditions to obtain a smooth controlled reaction of sufficient duration to produce a high-yield conversion of the salt to the corresponding perfluoro olefin, and recovering the latter.

4. A process according to claim 3, wherein a sodium salt is used.

5. A dry-reaction process of making hexafluoropropylene ($\text{CF}_3\text{CF}=\text{CF}_2$) which comprises heating anhydrous sodium normal heptafluorobutyrate ($\text{CF}_3\text{CF}_2\text{CF}_2\text{COONa}$) in the absence of hydroxyl compounds and at a temperature of the order of 200 to 350°C . at which controlled decomposition occurs, until there has been at least a 90% conversion to hexafluoropropylene, and recovering the latter.

6. A dry-reaction process of making perfluoro monoolefins from alkali-metal salts of perfluoro-

alkyl monocarboxylic acids having from three to ten carbon atoms in the molecule, which comprises heating the salt, in an anhydrous state and in the absence of hydroxyl compounds, at a decomposition temperature of the order of 200 to 350°C . at which controlled decomposition occurs and until a high yield of perfluoro olefin product is obtained, and recovering the latter.

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GEORGE H. SMITH.

References Cited in the file of this patent

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Number	Name	Date
2,601,536	La Zerte	June 24, 1952