United States Patent [19]

Thom

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[54] **PREPARATION OF PERFLUOROACYL FLUORIDES AND PERFLUOROCARBOXYLIC ACIDS**

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[*] Notice: The portion of the term of this patent subsequent to Oct. 26, 1988, has been disclaimed.

[22] Filed: **Feb. 20, 1970**

[21] Appl. No.: **13,159**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 872,726, Oct. 30, 1969, Pat. No. 3,615,169.

[52] **U.S. Cl.** .....**260/408,** 260/514 R, 260/539 R, 260/539 A, 260/544 F

[51] **Int. Cl.** **C07c 61/18,** C19c 3/00

[58] **Field of Search** .....260/539 R, 539 A, 260/544 F, 541 R, 408

[56] **References Cited**

UNITED STATES PATENTS

3,254,107	5/1966	Houplschien et al.	260/539 R
2,765,326	10/1956	Severson et al.	260/544 F

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[57] **ABSTRACT**

Pyrolysis of perfluoroalkanesulfonate salts of yttrium, scandium and rare earth metals in an inert atmosphere provides acyl fluorides when anhydrous salts are employed and carboxylic acids when the hydrated salts are employed. The acyl fluorides and carboxylic acids are useful intermediates known and used in the art.

4 Claims, No Drawings

PREPARATION OF PERFLUOROACYL FLUORIDES AND PERFLUOROCARBOXYLIC ACIDS

This application is a continuation-in-part of my copending U.S. Pat. application Ser. No. 872,726, filed Oct. 30, 1969, now U.S. Pat. No. 3,615,169.

This invention relates to a new process for the production of perfluoroacyl fluorides and carboxylic acids from sulfonic acids having the same total carbon atoms. In particular it relates to a pyrolytic decomposition of the rare earth, yttrium and scandium salts of perfluoroalkanesulfonic acids.

Perfluoroacyl fluorides which could be converted to the corresponding perfluorinated carboxylic acids have heretofore been obtained largely by the fluorination of the common aliphatic carboxylic acids. The early history of fluorine chemistry including descriptions of the electrochemical fluorination processes of the alkanoic acids are described in the book "Fluorine Chemistry," edited by Dr. J. H. Simons, Academic Press, Inc. Publishers 1950. It is more convenient to fluorinate the sulfonic acids and the yields are generally considered to be better. The conversion of the sulfonic acids to the perfluorinated carboxylic acids is now possible by the present process. There are, of course, other possible routes to these carboxylic acids but, sofar as is known, the present reaction is one which has neither been observed nor would it have been expected.

It is an object of this invention to provide a process for the production of perfluoroacyl fluorides and perfluorocarboxylic acids. Other objects will become apparent hereinafter.

It has been discovered quite unexpectedly that the pyrolysis of the perfluoroalkanesulfonates of scandium, yttrium and the rare earth metals proceed by loss of sulfur dioxide, the formation of the metallic fluoride and at the same time there is formed a perfluoroacyl fluoride including the carbon atoms of the original perfluoroalkane group. The acid has one less fluorinated carbon atom.

This is quite an interesting and unexpected reaction inasmuch as it involves the removal of a fluorine attached to carbon and replacement by oxygen. It also involves a cleavage of the sulfonic acid linkage which in itself is not to be expected.

The preparation of perfluoroacyl fluorides and perfluorocarboxylic acids according to this invention is by heating from about 400° to 1,000° C in argon as approximated by the following respective equations:

(I)

$$(R_f\text{—}CF_2SO_2O)_3M \xrightarrow[\Delta]{Ar} 3R_fC(=O)F + MF_3 + 3SO_2$$

(II)

$$(R_f\text{—}CF_2SO_2O)_3M + H_2O \xrightarrow[\Delta]{Ar} 3R_fC(=O)\text{—}OH + MF_3 + 3SO_2 + 3HF$$

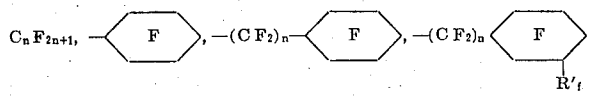
where M is a trivalent ion of rare earth metal, Y^{+3} or Sc^{+3}. Nitrogen or other inert gases may be used or alternatively pyrolysis may be carried out under reduced pressure.

The perfluoroalkanesulfonate salts used in these reactions are described in the parent hereof, Ser. No. 872,726, now U.S. Pat. No. 3,615,169, and have the general formula:

$$(R_fCF_2SO_2O)_3M.XH_2O$$

where M = Sc, Y, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; X is an indefinite number up to about nine, and R_f is a monovalent fluoroaliphatic radical of one to 20 carbon atoms. The fluoroaliphatic radical may contain not more than one hydrogen or chlorine for two carbons in the chain, such as omega-hydroperfluoroalkyl and omega-chloroperfluoroalkyl. It may be an acyclic straight or branched chain structure or a combination thereof or it may be cyclic or heterocyclic including one or more oxygen atoms each linking two carbon atoms or nitrogen atoms linking together three carbon atoms in either an acyclic or cyclic structure. The preferred fluoroaliphatic radical is perfluoroalkyl. Sofar as is known this provides a convenient process for converting any fluoroaliphatic sulfonic acid to a fluoroaliphatic carboxylic acid as shown in the above equations.

Examples of R_f radicals include



where R'_f is CF_3 to C_3F_7 and n is an integer.

The salts, as produced, contain various amounts of water of crystallization which must be removed carefully by vacuum and/or moderate heating if the perfluoroacyl fluoride is the desired product. Alternatively, the water liberated in pyrolysis must be carefully separated from the perfluoroacyl fluoride by trapping in a cold trap. If the perfluorocarboxylic acid is the desired product, the water of crystallization merely hydrolyzes the acyl fluoride and need not be removed.

The novel reaction is apparently restricted to salts of the trivalent rare earth metals, yttrium and scandium. Mixed cation salts may also be utilized and no deleterious effects are observed. That is, mixtures of rare earth metal cations as present in mischmetall can be employed as obtained directly from ores. The divalent transition metal fluoroaliphatic sulfonate salts do not yield detectable quantities of perfluoroacyl fluorides or carboxylic acids. Thus copper, cobalt and chromium are ineffective. The coordinated rare earth compounds (Werner complexes) described in the parent application do not yield the desired acids or acid fluorides because the liberated ligands react with the acyl fluoride and complex mixtures are obtained.

In the most general practice of this invention, the perfluoroalkanesulfonic acid is selected as required for the desired carboxylic acid or acyl fluoride. This acid is reacted with rare earth oxide (or yttrium or scandium oxide) and the resulting salt recovered. Reaction may be carried out using an ore as described in my copending application Ser. No. 872,726 now U.S. Pat. No. 3,615,169. Mixed rare earth oxide from decomposition of oxalates may be used or individual rare earths may be used as the oxides. The salt is dried and pyrolyzed and the perfluoroacyl fluoride recovered. If the perfluorocarboxylic acid is desired, the salt need not be dried and a small amount of water may even be added to hydrolyze the perfluoroacyl fluoride as formed.

Having described the invention in general terms it is now more specifically described in examples.

EXAMPLE 1

Neodymium salts are prepared by the above procedure using perfluorobutanesulfonic acid, perfluorohexanesulfonic acid, perfluoroethylcyclohexanesulfonic acid, perfluoroethanesulfonic acid, β-hydroperfluoropentanesulfonic acid ($C_3F_7CHFCF_2SO_3H$), and β-hydroperfluoroethanesufonic acid ($CHF_2CF_2SO_3H$). These neodymium salts are dried and portions decomposed in argon at 800° C. to give pure neodymium fluoride. The perfluorobutane and perfluorohexane groups are recovered in part as perfluoropropionic and perfluorovaleric acids respectively.

Other lanthanide metals and group 3b metals are also converted to trifluoromethane sulfonates, the salts pyrolyzed and the fluorides recovered. Suitable metals (in trivalent form) are cerium, praeseodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, yttrium, scandium.

These various fluoroaliphatic sulfonate salts form hydrates.

EXAMPLE 2

Neodymium perfluoromethanesulfonate is prepared from the oxide and sulfonic acid. 10 grams of this salt are placed in an alumina boat and the boat and salt are then placed in a Pyrex tubular furnace. Nitrogen gas is used to sweep out the volatile products during thermal decomposition of the salt (800° C 4 hours). The volatilized products are collected in traps immersed in liquid nitrogen. Infrared analysis of the gases identifies COF_2 and SO_2.

EXAMPLE 3

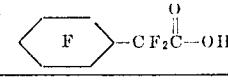
Neodymium perfluoroethanesulfonate is decomposed similarly at 600° C for 1 hour in nitrogen to give perfluoroacetyl fluoride.

EXAMPLE 4

Neodymium perfluorooctanesulfonate (10 gm.) is prepared as described above. The salt is pyrolyzed in an inverted U-shaped apparatus having a detachable leg provided with a glass wool plug inserted above it. The apparatus is evacuated to one micron. A Dewar flask containing liquid nitrogen is placed on the other leg of the apparatus and the leg containing the salt is heated at 600° C for one hour. After pyrolysis and cooling the apparatus, moist air is admitted. The product is identified by boiling point and IR spectrum as $C_7F_{15}CO_2H$. An 80 percent yield of the acid is obtained.

The following Examples 5 to 9 are run in the same manner as Example 4 above. The results are summarized in Table 1.

TABLE 1

	Rare earth salt			Vacuum pyrolysis		Product		
Example	Formula	Amount, gm.	H_2O, percent	Temp., ° C.	Time, hour	Identification	B.P. ° C. at 740 mm.	Percent yield
5	$Nd(SO_3C_6F_{13})_3$	20	6	700	1	$C_5F_{11}C(=O)OH$	162	64
6	Mixed R.E. $(SO_3C_6F_{13})_3$	20	6.8	800	1	$C_5F_{11}C(=O)OH$	160	78
7	$Y(SO_3C_6F_{13})_3$	20	5.8	700	1	$C_5F_{11}C(=O)OH$	160	54
8	$Nd(SO_3C_8F_{17})_3$	20	2.7	700	1	$C_7F_{15}C(=O)OH$	189	73
9	$Nd(SO_3C_2F_4-C_6H_4F)_3$	20	4.5	700	1		190	80

What is claimed is:

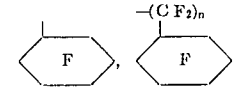
1. The process for the preparation of perfluoro-carboxylic acids or acid fluorides comprising

heating yttrium, scandium or rare earth trivalent metal salts, or combinations thereof, of fluor aliphatic sulfonic acid having the formula:

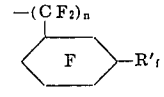
$$R_fCF_2SO_3H$$

wherein R_f is fluoroaliphatic radical of 1 20 carbon atoms of the group of:

C_nF_{2n+1},



and



wherein R'_f is CF_3 to

C_3F_7 and n is an integer for a time sufficient for gas evolution to come to a halt at a temperature of about 400° to 1,000° C. while condensing off-gases

whereby perfluoroacyl fluorides are recovered under anhydrous conditions and perfluoro-carboxylic acids are recovered when water vapor is present.

2. The process of claim 1 wherein the salts are hydrated and carboxylic acids are recovered from the condensate.

3. The process of claim 1 wherein the salts are essentially anhydrous and the carboxylic acid fluorides are recovered from the condensate.

4. The process according to claim 1 wherein R_f is a perfluoroalkane group C_nF_{2n+1}.

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