THERMAL STABILITY OF PERFLUOROALKANESULFONIC ACIDS AND THEIR ANHYDRIDES.
## NEW AND EASY APPROACH TO $R_FSO_2OR_F$ ESTERS.

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SUMMARY : Perfluoroalkanesulfonic anhydrides $(R_FSO_2)_2O$ when mixed with acids decompose into perfluoroalkanesulfonic esters $R_FSO_2OR_F$, thereby providing a new facile synthesis of these esters from perfluoroalkanesulfonic acids and phosphorus pentoxide.

An interest in the use of perfluoroalkanesulfonic acids R_FSO_3H in reaction conditions of varying severity has led us to undertake a study of their stabilities under various conditions. This paper reports the effect of heat on the acids CF_3SO_3H, $C_2F_5SO_3H$ and $C_4F_9SO_3H$ and their corresponding anhydrides.

In sealed tubes under vacuum these acids or anhydrides in the pure state are stable for a few hours up to a temperature of at least 180°C. However, under the same conditions solutions of the anhydrides in their corresponding acids yield quantitatively $CF_3SO_2OCF_3$, $C_2F_5SO_2OC_2F_5$ and $C_4F_9SO_2OC_4F_9$ esters, and release SO_2 according to the following reaction

$$(R_FSO_2)_2O \xrightarrow[\Delta]{R_FSO_3H} R_FSO_2OR_F + SO_2$$
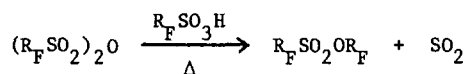
These perfluorinated esters are separated from the reaction mixture by water washing and distillation ($CF_3SO_2OCF_3$ b.p = 21°C[1,2], $C_2F_5SO_2OC_2F_5$ b.p = 65°C [3], $C_4F_9SO_2OC_4F_9$ b.p = 141°C [3]).

They are identified by means of their ^{19}F NMR[1,2,3], IR [1,2] and mass spectra [3] and by elemental analyses.

Sulfur dioxide, trapped during the reaction is characterized by means of its U.V.[4] IR [5] and mass spectra ($\frac{m}{e} = SO_2^+$ and SO^+).

The observed reaction times for $R_F = CF_3$ and C_2F_5 under various conditions, are given in table I. Even at room temperature, anhydrides in contact with their corresponding acids slowly decompose and the more dilute the solution, the faster the reaction. The progress of the reaction was followed by means of ^{19}F NMR spectroscopy . These results explain the previously observed instability of trifluoromethanesulfonic anhydride which has never been studied in detail.[6]

| R_F	$\dfrac{(R_FSO_2)_2O}{R_FSO_3H}$	$\theta°$ (C)	t i m e (hours)
C_2F_5	0.1	180	5
C_2F_5	0.1	25	$3,6 \quad 10^3$
C_2F_5	0.5	180	15
CF_3	0.1	180	1

TABLE I : Time for the complete decomposition of anhydrides in various conditions.

From these results we have developed a straight forward synthetic method for symmetrical perfluoroalkanesulfonic esters from the acids and phosphoric pentoxide.

$$6R_FSO_3H + P_2O_5 \xrightarrow{\Delta} 3R_FSO_2OR_F + 3SO_2 + 2H_3PO_4 \quad (R_F=CF_3, C_2F_5, C_4F_9)$$
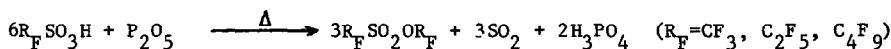
In order to obtain the esters rather than the anhydrides, it is necessary to keep the latter in contact with the acids. Thus, a smaller amount of P_2O_5 (R_FSO_3H/P_2O_5 = 6) and a slower distillation than for the synthesis of the anhydride [6,7] are required. This method is easier than those already known [1,2,8]. The pure ester is obtained in 70% yield and the unreacted acid can be recovered by distillation.

Similarly sulfur trioxide dehydrates the acids into anhydrides [9]. Thus, the esters $R_FSO_2OR_F$ can be obtained from the acids R_FSO_3H and the oleums.

$$2R_FSO_3H + SO_3 \xrightarrow{\Delta} R_FSO_2OR_F + SO_2 + H_2SO_4$$
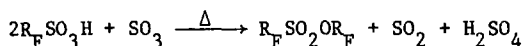
From such a reaction we can explain the formation of trifluoromethyl trifluoromethane sulfonate by the reaction of trifluoromethanesulfonic acid with fluorosulfuric acid,[2] because it is known that this acid always contains sulfur trioxide.[10]

On mixing an anhydride with a non corresponding acid, i.e. $(CF_3SO_2)_2O-C_2F_5SO_3H$ or $(C_2F_5SO_2)_2O-CF_3SO_3H$, a preequilibrium between acids and anhydrides was noted, even at room temperature.

$$(R_FSO_2)_2O + 2R'_FSO_3H \rightleftharpoons 2R_FSO_3H + (R'_FSO_2)_2O$$
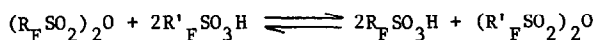
When such a solution is heated, it produces a mixture of esters : $CF_3SO_2OCF_3$, $C_2F_5SO_2OC_2F_5$ and $C_2F_5SO_2OCF_3$.

Their relative proportions depend on initial conditions but it is noteworthy that $CF_3SO_2OC_2F_5$ was never obtained (cf. table II).

$\dfrac{(R_FSO_2)_2O}{R'_FSO_3H}$	$\theta(°C)/t(H)$	$CF_3SO_2OCF_3$	$C_2F_5SO_2OC_2F_5$	$C_2F_5SO_2OCF_3$
$R_F = CF_3$ 0.11	80/15	25	–	75
$R'_F = C_2F_5$ 5.00	150/30	83	–	17
$R_F = C_2F_5$ 0.08	60/4	100	–	–
0.40	80/6	67	–	33
$R'_F = CF_3$ 5.00	180/48	–	82	18

TABLE II : Relative composition of esters formed by thermal decomposition of perfluorosulfonic anhydride in non related acids.

The new compound trifluoromethyl pentafluoroethanesulfonate is identified in the mixture by means of its ^{19}F N.M.R. spectrum. (external reference : $CFCl_3$) Φ_1 = 55, 3ppm (t, OCF_3, J_{FF} = 5,4 Hz), Φ_2 = 80,9 ppm (t, $\underline{CF}_3-CF_2$, J'_{FF} = 0,9 Hz) and Φ_3 = 110,6 ppm (qq, $CF_3-\underline{CF}_2$, J_{FF} = 5,4 Hz, J'_{FF} = 0,9 Hz).

Alkaline hydrolysis of the esters leads to sulfonic and carboxylic acids [3] (carbonic acid from $CF_3SO_2OCF_3$ [1]).

$$R_FSO_2OCF_2R'_F \xrightarrow[-2HF]{2H_2O} R_FSO_3H + R'_FCO_2H \quad (R_F = R'_FCF_2)$$
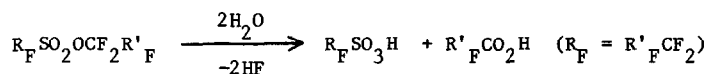
It follows from the reactions studied above that to be stable the anhydrides must be free from acids. The mechanism of the thermal decomposition of the anhydrides will be discussed in a full paper.

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