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THE THERMAL CLEAVAGE OF BORON TRIS-TRIFLUOROMETHANESULFONATE(TRIFLATE) AND BORON TRIS-PENTAFLUOROETHANESULFONATE(PENTFLATE) TO TRIFLIC (PENTFLIC) ANHYDRIDE AND TRIFLUOROMETHYL TRIFLATE (PENTAFLUOROETHYL PENTFLATE)

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SUMMARY

Cleavage of boron tris-trifluoromethanesulfonate(triflate) and boron tris-pentafluoroethanesulfonate(pentflate) was studied at 200°C. Complete cleavage giving boron trifluoride, sulfur dioxide, carbonyl fluoride (trifluoroacetyl fluoride), triflic (pentflic) anhydride, triflic (pentflic) triflate (pentflate) and boric acid was observed. A mechanism for the cleavage based on formation of the identified compounds is suggested.

INTRODUCTION

Anhydrous perfluoroalkanesulfonic acids are stable to high temperatures up to 400°C in the absence of air and moisture, but decompose at this temperature in the presence of moisture [1]. Pyrolysis of perfluoropropanesulfonic acid at 500°C gives C_6F_{14}, C_2F_5COF and products of complete degradation [1] (SO_2, COF_2, SOF_2, HF etc). Thermal stability of perfluoroalkanesulfonic acids R_FSO_3H ($R_F = CF_3, C_2F_5, C_4F_9$) and their anhydrides under different conditions of varying severity has been studied by Germain et al. [2]. Under vacuum these acids or anhydrides in their pure state are stable for a few hours up to a temperature of at least 180°C. Triflic acid is cleaved by fluorosulfonic acid to give trifluoromethyl triflate [3a]. The anhydrides [3b] ($(R_FCF_2SO_2)_2O$, $R_F = CF_3, C_2F_5, C_4F_9$) in solution of their corresponding acids similarly yield quantitatively $CF_3SO_2OCF_3$, $C_2F_5SO_2OC_2F_5$, and $C_4F_9SO_2OC_4F_9$

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esters with release of sulfur dioxide. The procedure is used as a convenient method for the preparation of perfluoroalkyl perfluoroalkanesulfonates.

$$(R_FSO_2)_2O \xrightarrow[\Delta]{R_FSO_3H} R_FSO_2OR_F + SO_2$$

The latter, however, when allowed to react further with perfluoroalkanesulfonic acids cleave upon heating giving products resulting from a nucleophilic attack of a perfluoroalkanesulfonate anion of the acid on the sulfur atom of the sulfonate group of the ester, with heterolysis of the S-O bond [4].

Trifluoromethanesulfonic acid was found to induce cleavage of concentrated solutions of boron tris-trifluoromethanesulfonate(triflate) $B(OSO_2CF_3)_3$ [5] in the acid. We also prepared boron tris-pentafluoroethanesulfonate(pentflate) in the absence of protic impurities or moisture, as a stable compound [6]. We have recently reported the preparation of boron tris(triflate) and indicated its thermal cleavage [6]. In continuation of our study of the preparation and application of boron perfluoroalkanesulfonates, we now wish to report our detailed study on the cleavage of $B(OSO_2CF_3)_3$ as well as $B(OSO_2CF_2CF_3)_3$.

RESULTS AND DISCUSSION

When a carefully prepared sample of boron tris(triflate) ($B(OSO_2CF_3)_3$) [6,7] in a Schlenk-flask is gradually heated under a positive pressure of dry argon or nitrogen slow cleavage starts as observed by gaseous product formation around 90 - 100°C and continues if heated to higher temperatures. The cleavage products were collected in cold traps (-78°C). At a temperature of around 200°C the cleavage of $B(OSO_2CF_3)_3$ is continued for about one hour to be completed. A glassy residual remains in the flask. The volatile cleavage products were analyzed (experimental part) and found to consist of the compounds compiled in the Table.

When boron tris(pentflate) ($B(OSO_2CF_2CF_3)_3$) [8] was thermally cleaved under identical conditions, products shown in the Table were formed. The residual glassy material, obtained in the cleavage of both boron tris(triflate) and boron tris-(pentflate) was found to consist of boric oxide together with some boric acid as was confirmed by IR analysis. All volatile cleavage products were collected in a cold trap at -78°C as an ethereal solution.

$$B(OSO_2CF_2R_F)_3 \xrightarrow{200^\circ C} \text{Products (Table)}$$

$RF = F,\ CF_3$

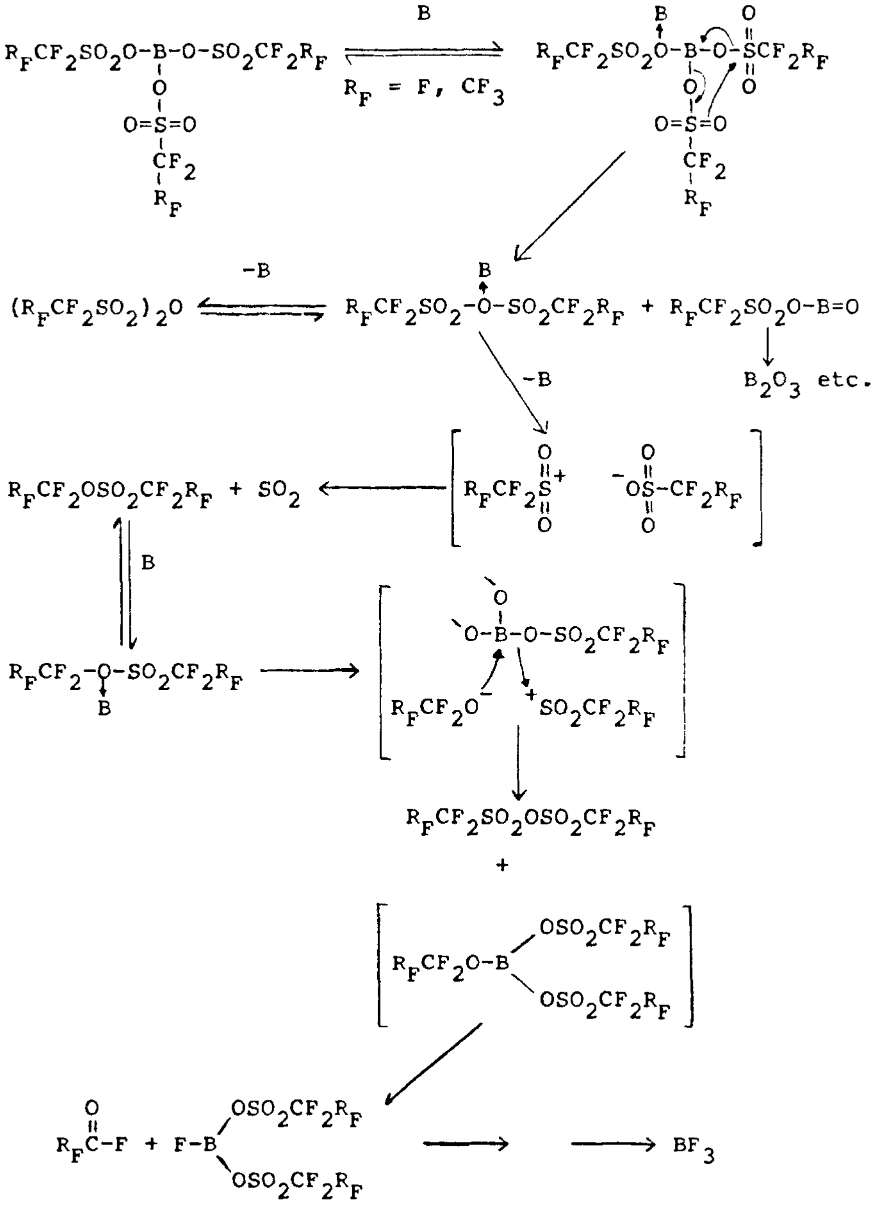
TABLE

Cleavage products obtained from boron tris(triflate) and boron tris(pentflate)

Boron tris(perfluoroalkanesulfonate)	Cleavage Products
$B(OSO_2CF_3)_3$	SO_2 BF_3 COF_2 $CF_3SO_2OSO_2CF_3$ $CF_3SO_2OCF_3$ B_2O_3, boric acid
$B(OSO_2CF_2CF_3)_3$	SO_2 BF_3 CF_3COF $CF_3CF_2SO_2OSO_2CF_2CF_3$ $F_3CF_2SO_2OCF_2CF_3$ B_2O_3, boric acid

On warming, the collected product mixture was degassed at 0°C, gaseous products being transferred to a gas-container. These products were found to consist of sulfur dioxide as the major product (identified by IR, gas chromatography and GC-MS) and COF_2 as the minor product. ^{11}B NMR spectral analysis of the ethereal solution showed boron trifluoride (as its ether complex) as the only boron containing product. ^{13}C and ^{19}F NMR spectral analysis of the ethereal solution of the product mixture identified $CF_3SO_2OSO_2CF_3$ and $CF_3SO_2OCF_3$ with COF_2 as the minor product. ^{19}F NMR spectra also confirmed BF_3:Et_2O in the products. The product mixture obtained in ethereal solution from the thermal cleavage of boron tris-(pentflate) was similarly analyzed.

The mechanism of formation of the products from the thermal cleavage of boron tris(triflate) and boron tris(pentflate) is suggested in Scheme. The formation of boric acid, besides boric oxides in the residual product indicates that despite precautions taken the presence of traces of moisture could not be excluded. Consequently besides indicated predominant cleavage pathway of boron tris(triflate) and boron tris(pentflate) moisture impurity can also cause protolytic hydrolysis of boron perfluoroalkanesulfonates. There is, however, no ready hydrolysis observed in solution at lower temperatures. Formed triflic and pentflic anhydrides further cleave to sulfur dioxide and perfluoroalkyl perfluoroalkanesulfonates [3b]. Reaction of the latter with boron tris(triflate) and boron tris(pentflate) respectively leads to the formation of the final cleavage products [4].



$B = B(OSO_2CF_2R_F)_3$

Scheme

EXPERIMENTAL

Boron tris(triflate) [6,7] and boron tris(pentflate) [8] were prepared as reported previously. Trifluoromethanesulfonic acid anhydride was obtained from Aldrich and was used as authentic sample. ^{13}C NMR and ^{19}F NMR spectra were obtained on a Varian (VXR-200) superconducting NMR spectrometer using Me_4Si and $CFCl_3$ respectively as external references. ^{11}B NMR spectra were recorded on a Varian FT 80 NMR spectrometer at -60°C using $BF_3{:}Et_2O$ as external reference. Infrared spectra were recorded on a Perkin-Elmer (model 7500) FTIR Spectrometer. GC-MS were recorded on a Varian (model 3400) Gas Chromatograph interfaced with a Finnigan Mat (model INCOS 50) Mass Spectrometer.

Cleavage of boron tris(triflate) and boron tris(pentflate)

5 g of the boron tris(perfluoroalkanesulfonate) was placed into a flame-dried 100 ml Schlenk-flask. The gas-inlet tube was connected to a argon or nitrogen cylinder, the gas-outlet was connected to a trap (-78°C) which itself was connected to a trap containing dry ether (-78°C). The system was closed by means of a drying tube. A slow flow of carrier gas was passed through the apparatus and the boron tris-(perfluoroalkanesulfonate) was slowly heated to 180 - 200°C. Heating was continued for an additional hour. Boron trifluoride and sulfur dioxide were formed as the major gaseous products, identified by both ^{11}B NMR and ^{19}F NMR spectroscopy and IR. The glassy residue consisted of boric oxides together with boric acid (identified by IR [9]). Trapped and identified products were triflic (pentflic) anhydride and trifluoromethyl triflate (pentafluoroethyl pentflate) (identified by GC-MS, ^{19}F NMR or ^{13}C NMR).

a) Cleavage of boron tris(triflate)

Carbonyl fluoride, COF_2
^{13}C NMR: $\delta = 133.6$ ppm, $^1J = 308$ Hz (Lit.[10] : 134.2 ppm, $^1J = 309$ Hz)
^{19}F NMR: $\delta = -22.8$ ppm (Lit. [10] : -23.0 ppm)
MS : 66 (55) 47 (100) 28 (16) , (identical with Lit. [11]) trifluoromethyl trifluoromethanesulfonate, $CF_3SO_2OCF_3$:
^{19}F NMR: $\delta = -52.9$ ppm (OCF_3) , -73.6 ppm (SCF_3)
(Lit. [12] : -53.3 ppm (OCF_3) , -74.0 ppm (SCF_3))
^{13}C NMR: $\delta = 115.93$ ppm, q, $^2J = 310$ Hz, (CF_3S), 117.28 ppm , q,
$^2J = 286$ Hz, (OCF_3)
trifluoromethanesulfonic acid anhydride, $CF_3SO_2OSO_2CF_3$:
^{19}F NMR: $\delta = -72.6$ ppm (identical with authentic sample)

^{13}C NMR: δ = 116 ppm, q, ^2J = 310 Hz (CF_3S) (identical with authentic sample)
MS : 149 (0.4) , 133 (1.4) , 117 (0.3) , 69 (100) , 64 (24) , 48 (33) (identical with authentic sample)

b) Cleavage of boron tris(pentflate)

trifluoroacetyl fluoride, CF_3COF:
MS : 116 (0.4), 97 (2), 69 (27), 28 (100)
^{19}F NMR: δ = -76.2 ppm (CF_3) , -13.5 ppm (CF).
(Lit. [13] : -76.7 ppm (CF_3) , -13.7 ppm (CF))
pentafluoroethyl pentafluoroethanesulfonate [4],
$CF_3CF_2SO_2OCF_2CF_3$:
^{19}F NMR: δ = -79.6 ppm (CF_3CF_2S), -84.6 ppm (OCF_2CF_3), -86.5 ppm (OCF_2CF_3), -113 ppm (CF_3CF_2S)
(Lit. [14]: -80.0 ppm (CF_3CF_2S), -84.8 ppm (OCF_2CF_3), -87.0 ppm (OCF_2CF_3), -113.3 ppm (CF_3CF_2S))
MS : 199 (10) , 135 (3.5) , 119 (100) , 69 (92) , 48 (34) [2] pentafluoroethanesulfonic acid anhydride, $CF_3CF_2SO_2OSO_2CF_2CF_3$:
MS: 199 (0.1), 183 (2.4), 119 (39), 64 (97), 48 (100)

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REFERENCES

1 T. Gramstad and R.N. Haszeldine, J. Chem. Soc. (1957) 2640.

2 M. Oudrhiri-Hassani, A. Germain, D. Brunel and A. Commeyras Tetrahedron Letters, 22 (1981) 65.

3 a) G.A. Olah and T. Ohyama, Synthesis (1976) 319; b) M. Oudrhiri-Hassani, D. Brunel A. Germain and A. Commeyras, J. Fluorine Chem., 25 (1984) 219.

4 M. Oudrhiri-Hassani, D. Brunel and A. Germain, J. Fluorine Chem., 32 (1986) 163.

5 V.A. Engelbrecht and E.Z. Tschager, Z. A. Inorg. Allg. Chem., 433 (1977) 19.

6 G.A. Olah, O. Farooq, S.M.F Farnia and J.A. Olah, J. Am. Chem. Soc., 110 (1988) 2560.

7 G.A. Olah, K. Laali and O. Farooq, J. Org. Chem., 49 (1984) 4591.

8 G.A. Olah, T. Weber and O. Farooq, Synthesis, in press.
9 R.A. Nyquist and R.O Kagel in : 'Infrared Spectra of Inorganic Compounds', Academic Press, New York and London, 1971.
10 W. Gombler, Spectrochim. Acta, Part A, 37 (1981) 57.
11 S.R. Heller and G.W.A. Milne in: 'EPA/NIH Mass Spectral Data Base', Vol. 1 U.S. Government Printing Office, Washington (1978).
12 S.L. Taylor and J.C. Martin, J. Org. Chem.,52 (1987) 4147.
13 G.A. Olah, A. Germain and H.C.Lin, J. Am. Chem. Soc.,97 (1975) 5481.
14 A. Germain and A. Commeyras, Tetrahedron, 37 (1981) 487.