

The chemistry of fluorocarbon sulfonic acids

2. Thermal reactions of perfluorosulfonic anhydrides. Infinite-dilution NMR evidence for oriented association of perfluoroiodides¹

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Abstract

Perfluorocycloalkanesulfonic anhydrides decompose thermally to give bicyclohexyls, presumably by a homolytic mechanism. Reaction with iodine, sulfur, and benzene gives, respectively, the cyclohexyl iodide, disulfide, or benzene, the latter in poor yield. Upon extrapolation of NMR shifts to infinite dilution, only the CFI group gives an anomalous slope, attributable to reversal of $R_F I$ -to- IR_F association. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Perfluorosulfonic anhydrides, notably $(CF_3SO_2)_2O$, are known to decompose to give esters, e.g., $CF_3SO_2OCF_3$ [1], with elimination of SO_2 ; this has been shown to go by an acid-catalyzed ionic mechanism. In preparing and studying certain perfluorocycloalkanesulfonic anhydrides [2] it was observed that attempted high-temperature distillation at atmospheric pressure resulted in substantial decomposition, with loss of SO_2 and SO_3 .

2. Results and discussion

From the 300°C thermolysis product of perfluoro(4-ethylcyclohexanesulfonic) anhydride the dimerized fluorocarbon, perfluoro-4,4'-diethylbicyclohexyl, was recovered in high yield, formed presumably by free-radical combination. As this suggested possible broader synthetic utility, several tests were run. Reaction of the anhydride at 300°C with iodine and with sulfur gave the corresponding iodide and disulfide in good yield, as expected for a homolytic decomposition. The

attempted direct perfluoroalkylation of benzene proceeded, but in low yield, very likely as a result of oxidation or sulfonation by SO_3 ; for synthetic purposes a two-step reaction via the iodide would be preferable. By similar means, but allowing escape of SO_2 and SO_3 , polysubstitution on thermally-stable dyes was achieved, as evidenced by rendering them soluble in perfluorinated solvents [3]. Polyperfluoroalkylation results from homogeneous attack on initially-monosubstituted dye molecules made soluble by the high temperature.

The structures of several products were later verified by NMR spectroscopy. A particular feature of the NMR measurements was the linear extrapolation of δ -values to the standard state, zero concentration in CCl_3F (at 25°C) [4]. These extrapolated values, δ° , are free from uncontrolled shifts due to self-association, and thus become truly comparable for purposes of analytical identification, or for researches to indicate molecular sites of association-via-polarizability.

Such latter studies would require knowledge of the sign and magnitude of the slope of the extrapolation; this information should always be furnished along with δ° . The slope, S , does require further designation to enable future interpretation, as at least four practical dilution techniques exist. It has been shown that, in the absence of strong complex formation, extrapolation by volume fraction is linear [4]. The corresponding slope, S_v , is expressed as $\Delta(\delta)/\Delta$ (volume

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fraction). It follows that other dilutions, for example by weight, may give only approximately linear extrapolations, with 'slope' S_w differing numerically from S_v , though not greatly, and not in sign. The resulting δ° , while imprecise, will be close to the 'true' value. Of course, given information on densities, S_v and 'true' δ° are calculable.

The foregoing clarifies the interpretation of the present NMR data. The δ° -values for the $\text{CF}_3\text{CF}_2\text{CF}$ segments of $(4\text{-C}_2\text{F}_5\text{C}_6\text{F}_{10}^-)_2$, $4\text{-C}_2\text{F}_5\text{C}_6\text{F}_{10}\text{I}$, and $(4\text{-C}_2\text{F}_5\text{C}_6\text{F}_{10}\text{S}^-)_2$ are virtually identical. The slopes are all small and positive, as are those for the CFX fluorines except for $\text{X}=\text{I}$. The large negative slope in the latter case signifies that these molecules tend to associate at their highly-polarizable iodine atoms. Thus the slope S_v may be termed a 'self-association parameter'. At finite concentrations this geminal fluorine experiences an iodine-rich, highly-polarizable environment, analogous to the case of CBr_3F [4]. It is significant that no such effect is seen for the distant $\text{CF}_3\text{CF}_2\text{CF}$ grouping, confirming that the self-association is oriented.

When a mixture containing a compound is diluted, the magnitude(s) of the slope(s) will differ from that for the unmixed material, but the δ° -value(s) will not change. One could rightfully conclude that much has been lost by failure of workers to prepare a second NMR tube in the almost 40 years since publication of the infinite-dilution technique.

3. Experimental details

Pressure reactions were carried out in heavy-walled 30 ml Pyrex ampoules placed inside a double-strength iron pipe closed at the bottom by a 1.5 cm long brazed-in (to avoid embrittlement at low temperatures) iron plug and at the top by a threaded pipe cap having four pressure-relief holes (in case of breakage) and a central hole through which the sealed-off ampoule neck protruded. (This provision allows the liquid- N_2 -chilled ampoule to be opened in safety; additionally, the course of the reaction may sometimes be observed.) A sturdy rocking heater, controlled by a sensitive and adjustable thermal switch contained therein, was used for the ampoule reactions.

Fractional distillations utilized a 10×1 cm Helipak-filled column.² Melting points were metal-calibrated [5] to ITS-90, the International Temperature Scale of 1990.

^{19}F NMR spectra were run at 470 MHz on a Varian UNITY 500 spectrometer. In each case two measurements were made, the second being at a known dilution, usually 50% by volume, with pure CCl_3F ; the original solvent was (by volume) usually 94% CCl_3F , 5% acetone- d_6 (NMR lock), and 1% TMS. The shielding values δ ($= -\phi^*$ [4]) thus measured at $24 \pm 1^\circ\text{C}$ were linearly extrapolated to give δ° .

From a single dilution nonlinearity cannot be demonstrated; however if volume fractions give linearity, with a

slope S_v , then in general weight fractions cannot, and the 'slope' S_w is at best approximate. Likewise, the 'slope' S_D , for weights of solute combined with known volumes of CCl_3F , will be inexact unless densities are equal. But when weights of solute are diluted to known volumes (e.g., molarity) a true slope, S_C , results. While of similar magnitude, these slopes all differ; yet, given sufficient information, they are interconvertible. For these reasons the subscript designations are significant and necessary when reporting slopes, whether true or approximate.

3.1. Perfluoro-4,4'-diethylbicyclohexyl

$(4\text{-C}_2\text{F}_5\text{C}_6\text{F}_{10}\text{SO}_2)_2\text{O}$ [2], 56.0 g (0.124 mol), was heated in a distilling flask to ca. 300°C . The distillate, b.p. $246^\circ\text{--}254^\circ\text{C}$, 43.2 g, was a 92% yield of mostly solid crude dimer. Reactive impurities were removed by treatment with piperidine, followed by washing with acetone, ethanol, and water. Upon recrystallization from hot isooctane it had m.p. $107.5\text{--}108.5^\circ\text{C}$, b.p. 252°C . By suspension in bromoform/ethanol its density at 25°C was found to be 2.104. Analysis: calculated for $\text{C}_{16}\text{F}_{30}$: C, 25.2%; F, 74.8%; found: C, 25.0%; F, 74.3%. Its 470 MHz ^{19}F NMR spectrum was complex but showed strong characteristic peaks at $\delta^\circ = -81.646$ ($S_v = +.07$), -117.174 ($S_v = +.62$), and -187.335 ($S_v = +1.64$) for the $4\text{-CF}_3\text{CF}_2\text{CF}$ unit, and -181.113 ($S_v = +1.15$) for the CF–CF fluorines (well-resolved and presumed axial) at the ring juncture. (At 9.0 vol.% in CCl_3F the δ were, respectively, -81.640 , -117.118 , -187.187 , and -181.009 .) Additional broadened minor peaks were present, perhaps for a/e isomers. The principal powder X-ray lines were, in Å (relative intensities) 14.7 (100), 7.37 (10), and 5.82 (8); from this the calculated density for hexagonal packing is 2.20, which agrees reasonably well with the measured value.

3.2. Perfluoro-4,4'-dimethylbicyclohexyl

In similar fashion there was obtained from $(4\text{-CF}_3\text{C}_6\text{F}_{10}\text{SO}_2)_2\text{O}$ [2] the liquid dimer $(4\text{-CF}_3\text{C}_6\text{F}_{10})_2$, b.p. 218°C , n_D^{25} 1.3207 supercooled, which, upon standing, partially crystallized. Analysis showed that both the crystals, m.p. 62°C , d^{25} 2.169, and the residual liquid were dimers. Analysis: calculated for $\text{C}_{14}\text{F}_{26}$: C, 25.4%; F, 74.6%; found (crystals): C, 25.3%; F, 74.5%; found (residual liquid): C, 25.1%; F, 74.9%. It is evident that isomers, presumably axial/equatorial, are present. Principal powder X-ray lines for the crystals were 11.3 (100), 8.6(b) (31), 5.50 (45), 5.40 (61), 3.9 (40), and 3.5 (30), suggestive of tetragonal packing; a calculated density of 2.13 based on the three independent italicized lines lends some support.

3.3. Perfluoro-4-iodo(ethyl)cyclohexane

In a 30 ml ampoule 9.0 g $(4\text{-C}_2\text{F}_5\text{C}_6\text{F}_{10}\text{SO}_2)_2\text{O}$ (0.010 mol) and 3.5 g I_2 were heated for 20 h at 275°C . The crude

² Size A: available from Reliance Glass Works, P.O. Box 825, Bensenville, IL 60106, USA.

liquid product, 9.8 g, had n_D^{25} 1.3504. Upon distillation the best fractions of 4-C₂F₅C₆F₁₀I, 5.7 g (56%), had b.p. 158.5°C and n_D^{25} 1.3541. Analysis: calculated for C₈F₁₅I: C, 18.9%; F, 56.1%; found: C, 18.7%; F, 56.9%. The complex ¹⁹F NMR spectrum had strong characteristic peaks for the 4-CF₃CF₂CF segment at $\delta^\circ = -81.637$ ($S_V = +.11$), -117.072 ($S_V = +.29$), and -186.159 ($S_V = +.65$), and for the CFI unit at -144.636 ($S_V = -10.7$).

3.4. Perfluoro-4,4'-bis(ethylcyclohexyl) disulfide

In a tall test tube (300 × 12 mm) were heated (4-C₂F₅C₆F₁₀SO₂)₂O, 13.5 g (0.015 mol) and sulfur, 1.3 g (0.040 g at.) at ca. 300°C in a Wood's metal bath. After about 8 h the sulfur phase had been consumed, but the heating was continued for 50 h. Upon fractionation at atmospheric pressure there was obtained 5.3 g (43%) of (4-C₂F₅C₆F₁₀S)₂, b.p. 283°C, n_D^{25} 1.3552. Analysis: calculated for C₁₆F₃₀S₂: C, 23.3%; F, 69.0%; found: C, 23.5%; F, 68.4%. The ¹⁹F NMR spectrum had strong peaks at $\delta^\circ = -81.664$ ($S_V = +.20$), -117.007 ($S_V = +.67$), and -187.052 ($S_V = +.96$) for the 4-CF₃CF₂CF segment, and at -161.270 ($S_V = +.71$) for the CFS unit.

3.5. (Perfluoro-4-ethylcyclohexyl)benzene

In a 30 ml ampoule 9.0 g (4-C₂F₅C₆F₁₀SO₂)₂O (0.010 mol) and 2.0 g benzene (0.025 mol) were heated at 310°C for 2 h. From the black, charred reaction mix the fluorine-containing products were extracted by dissolution in 20 g perfluoro(2-ethyltetrahydrofuran), b.p. 56°C. Upon distillation the best fraction, 0.15 g out of 0.5 g (6%) total, was acceptably pure 4-C₂F₅C₆F₁₀C₆H₅, b.p. 215°C, n_D^{25}

1.3826. Analysis: calculated for C₁₄H₅F₁₅: C, 36.7%; F, 62.2%; found: C, 36.7%; F, 62.6%. It had a strong infrared band for a monosubstituted benzene at 14.41 μ , with weaker ones at 13.59 and 13.75 μ .

3.6. Perfluoroalkylation of dyes

By the open-tube technique 1.5 (4-C₂F₅C₆F₁₀SO₂)₂O (0.0016 mol) and 0.5 g pyranthrone (0.0012 mol) were heated together for 1 h at ca. 300°C. The product was mostly soluble in perfluoro(2-ethyltetrahydrofuran). Upon dilution of the brown solution the characteristic yellowish-green pyranthrone fluorescence appeared [3]. Similarly, 1.5 g of the anhydride and 0.5 g (0.0008 mol) of copper phthalocyanine gave a deep blue solution which, when dried on PTFE and heated to the PTFE transition temperature, 325°C, stained it a permanent strong blue color [3]. In the absence of substantial polyperfluoroalkylation, to give a fluorine content of ca. 50%, such solubility is not achieved.

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