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ADDITION OF FLUOROPEROXIDES TO PERFLUOROVINYLSULFUR PENTAFLUORIDE

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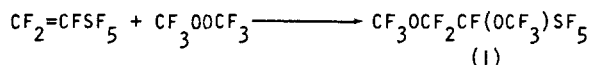
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SUMMARY

The addition of CF_3OOCF_3 and SF_5OOSF_5 across the double bond in $\text{CF}=\text{CFSF}_5$ was studied with 1:1 addition products being observed in both cases. For CF_3OOCF_3 , the product was $\text{CF}_3\text{OCF}_2\text{CF}(\text{OCF}_3)\text{SF}_5$, whereas for SF_5OOSF_5 it was $\text{SF}_5\text{CF}_2\text{CF}_2\text{OSF}_5$. The different reaction paths are attributed to steric reasons.

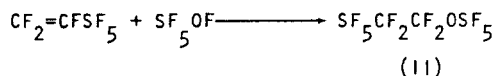
The telomerization of fluoroolefins with fluoroperoxides has been reported [1,2]. Hexafluoropropene, when telomerized with bis(trifluoromethyl) peroxide, $(\text{CF}_3\text{O})_2$, [1] yielded a series of oils having the composition $\text{CF}_3\text{O}(\text{C}_3\text{F}_6)_n\text{OCF}_3$ where $n \geq 2$. Similarly, hexafluoropropene reacted with bis(pentafluorosulfur) peroxide, $(\text{SF}_5\text{O})_2$, [2] to yield a series of oils of the composition $\text{SF}_5\text{O}(\text{C}_3\text{F}_6)_n\text{OSF}_5$ where n was also equal to or larger than two. Surprisingly, in neither case was the 1:1 addition product found.

During our investigation of new thermally stable high density fluoroils, the thermal and photochemical reactions of perfluorovinylsulfur pentafluoride, $\text{CF}_2=\text{CFSF}_5$, with the fluoroperoxides $(\text{CF}_3\text{O})_2$ and $(\text{SF}_5\text{O})_2$ were studied. By analogy with the previous work on C_3F_6 [1,2], the main products were higher telomers, however in the case of $(\text{CF}_3\text{O})_2$ and $\text{CF}_2=\text{CFSF}_5$ we were able to isolate also the 1:1 addition product according to:

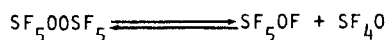


The necessary $\text{CF}_3\text{O}\cdot$ radicals were generated either thermally at 185°C or by uv-photolysis at ambient temperature. The yields of (1) were 4% in the thermal and 8% in the photolytic reaction. Compound (1) is a clear liquid and was characterized by elemental analysis, molecular weight, and infrared and mass spectroscopy.

When in the above reaction CF_3OOCF_3 was replaced by SF_5OOSF_5 , again a 1:1 addition product was obtained in low yields. However in this case, the compound actually added across the olefin double bond was not SF_5OOSF_5 but SF_5OF .



As in the case of CF_3OOCF_3 , both thermal and photolytic activation were used to initiate the addition, resulting in yields of (11) of 10 and 5%, respectively. The fact that the $-\text{OSF}_5$ group added exclusively to the CF_2 group is not surprising in view of the well known steric hindrance by the bulky $-\text{SF}_5$ group [3]. The inability of an $-\text{OSF}_5$ group to add to a carbon atom already containing a bulky $-\text{SF}_5$ ligand also explains why in the above experiments no evidence for the formation of $\text{SF}_5\text{OCF}_2\text{CF}(\text{OSF}_5)\text{SF}_5$ was observed. Therefore, we believe that the observation of compound (11) as the sole 1:1 addition adduct is due to this steric hindrance by the $-\text{SF}_5$ group and not due to the equilibrium [4]



being shifted all the way to the right. Compound (11) was a clear liquid and was characterized by elemental analysis, molecular weight, infrared, mass and qualitative ^{19}F NMR spectra which showed only two resonances of equal areas in the region expected for CF_2 groups.

The observed difference in the addition products of CF_3OOCF_3 and SF_5OOSF_5 to the double bond in $\text{CF}_2=\text{CFSF}_5$ is very interesting. It demonstrates that two reactions which, from a chemical point of view, are expected to proceed in the same manner can result in totally different products due to steric reasons. The pseudo-tetrahedral and therefore less bulky $-\text{OCF}_3$ group can still be added to an SF_5 substituted carbon, whereas the more bulky pseudo-octahedral $-\text{OSF}_5$ group cannot.

EXPERIMENTAL

Materials

Bis(trifluoromethyl) peroxide was obtained commercially from Peninsular Chem Research Inc. Bis(pentafluorosulfur) peroxide was prepared according to the method of Witucki [5]. Perfluorovinylsulfur pentafluoride was prepared by the method of Case, et al [6].

Thermal reactions were carried out in a 30 cc stainless steel bomb. Liquid reagents were added at room temperature while gaseous materials were condensed at -196°C into the vessel from a passivated metal-Teflon FEP vacuum line. After the reaction was completed, the bomb was cooled to room temperature and the volatile material was pumped off and examined on the vacuum line. Non-volatile materials were handled in the dry N_2 atmosphere of a glove box.

The photochemical apparatus consisted of a standard Nester Faust NF UV-300 source contained in a quartz center tube of the Pyrex glass reaction vessel.

Reaction of Perfluorovinylsulfur Pentafluoride with Bis(trifluoromethyl) Peroxide.

Perfluorovinylsulfur pentafluoride (7.9 mmol) and bis(trifluoromethyl) peroxide (7.6 mmol) were heated at 185°C for 15 hr. The bomb was cooled to room temperature and the volatile material removed on the vacuum line. There remained 150 mg of non-volatile colorless oil. The volatile material was separated by fractional condensation at -46 , -80 , -112 , and -196°C yielding trace amounts of SOF_2 , SO_2F_2 and SF_6 , unreacted starting materials ($\sim 80\%$), the 1:1 addition product $\text{CF}_3\text{OCF}(\text{SF}_5)\text{CF}_2\text{OCF}_3$, 1,2-bis(trifluoromethoxy) perfluoroethylsulfur pentafluoride (0.62 mmol; 4% yield) and trace amounts of the volatile lower members of the series $\text{CF}_3\text{O}[\text{CF}(\text{SF}_5)\text{CF}_2]_n\text{OCF}_3$ where $n \geq 2$.

Photochemical Reaction

The photochemical reaction involved a 1:1 stoichiometry of perfluorovinylsulfur pentafluoride and bis(trifluoromethyl) peroxide. The reactants were irradiated for one day at room temperature. The products obtained were essentially the same as those found in the thermal reaction. The yield of the 1:1 addition product, $\text{CF}_3\text{OCF}(\text{SF}_5)\text{CF}_2\text{OCF}_3$, was 8%. $\text{CF}_3\text{OCF}(\text{SF}_5)\text{CF}_2\text{OCF}_3$ was identified by molecular weight, elemental analysis, infrared and mass spectroscopy. Analyses: Found: C, 12.9; F, 71.2. Calculated for $\text{C}_4\text{F}_{14}\text{O}_2\text{S}$: C, 12.7; F, 70.3%. Molecular Weight: Found 376. Calculated for $\text{C}_4\text{F}_{14}\text{O}_2\text{S}$: 378.

The infrared spectrum had major absorptions at 1310, 1240(vs) 1160-1140 (doublet), 1005, 895-885 (doublet) (s), 815, 765, 725 and 605 cm^{-1} . Mass spectrum (m/e, ion, relative intensity): 31, CF, 8.20; 32, S, 1.44; 47, CF₀, 2.42; 50, CF₂, 1.48; 51, SF₂, 8.20; 66, CF₂O, 1.08; 67, FSO, 4.10; 69, CF₃, 100; 70, SF₂, 1.48; 82, CSF₂, 4.10; 85, CF₃O, 3.77; 89, SF₃, 35.25; 101, CF₃S, 9.83; 109, C₃F₃O, 1.60; 117, CF₃SO, 6.56; 127, SF₅, 10.16; 135, C₂F₅O, 7.38; 155, CSF₅O, 6.56; 158, CF₆S, 0.41; 166, C₃F₆O, 0.74; 224, C₂F₈SO, 0.57; 243, C₂F₉SO, 4.92; 293, C₃F₁₁SO, 0.87.

Reaction of Perfluorovinylsulfur Pentafluoride with Bis(pentafluorosulfur) Peroxide

Perfluorovinylsulfur pentafluoride (10 mmol) and bis (pentafluorosulfur)-peroxide (5 mmol) were heated at 165°C for 16 hr. The reactor was cooled to room temperature and the volatile material removed on the vacuum line. There remained 200 mg of non-volatile colorless oil. Fractional condensation at -46, -80, and -196°C yielded trace amounts of SO₂F₂, SF₆ and SiF₄, unreacted starting materials (~80%), the 1:1 addition product SF₅OCF₂CF₂SF₅, 1-pentafluorosulfuroxy 2-pentafluorosulfur perfluoroethane (0.5 mmol; 10% yield) and trace amounts of the lower members of the series SF₅O([CF₂CF(SF₅)]_n)_nF.

Photochemical Reaction

The photochemical reaction also involved a 2:1 stoichiometry of perfluorovinylsulfur pentafluoride and bis(pentafluorosulfur) peroxide. The reactants were irradiated for five days at ambient temperature. The products obtained were essentially the same as those found in the thermal reaction. The yield of the 1:1 addition product SF₅OCF₂CF₂SF₅ was 5%.

SF₅OCF₂CF₂SF₅ was identified by molecular weight, elemental analysis, infrared and ¹⁹F NMR spectroscopy and mass spectroscopy. Analyses: Found: C, 6.3; F, 70.2. Calculated for C₂F₁₄O₂S₂: C, 6.5; F, 71.9%. Molecular Weight: Found 367. Calculated for C₂F₁₄O₂S₂: 370. The infrared spectrum had major absorptions at 1120, 1180, 1150, 1010, 935-945 (s) doublet, 895-885 (s) doublet, 860, 805 (s) and 790 cm^{-1} .

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