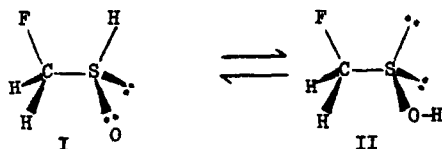


FLUORINATION OF DIMETHYLSULFOXIDE

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We wish to report the formation of novel products in the controlled fluorination of dimethyl sulfoxide (DMSO) with iodine pentafluoride. The major product is a compound which appears to be  $\text{CH}_2\text{FS}(\text{O})\text{H}$ , I, the tautomer of the sulfenic acid, II, an almost unknown class of compounds (1).



A further novel characteristic of this reaction is the formation of numerous compounds in which the oxygen atom has transferred from sulfur to carbon. These compounds include  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{CF}_2\text{O}$ ,  $\text{HCFO}$ ,  $\text{CH}_2\text{O}$ , the recently discovered (2)  $\text{CH}_3\text{SCFO}$ , apparently its isomer  $\text{CH}_2\text{FSCHO}$ , and four unidentified minor products with infrared bands in the carbonyl region. Other products included the expected  $\text{HF}$ , small amounts of other degradation products ( $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_2\text{O}$ ,  $\text{SF}_2\text{O}_2$ ,  $\text{SF}_6$ ,  $\text{SO}_2$ ,  $\text{CS}_2$ ),  $\text{CH}_3\text{SO}_2\text{F}$ , and several minor liquid products which are incompletely characterized. (The degree of degradation increases rapidly with the strength of the reaction conditions and especially with temperature.) In addition, polymer-like solids are formed by further reaction of some of the primary products.

Three methods have been used with some success in moderating\* the reaction: A. one reactant was added at  $18^\circ$  to a paste of the second in sodium fluoride; B.  $\text{IF}_5$  was added dropwise to a stirred 10% solution of DMSO in tetramethylene sulfone at  $15^\circ$ ; C. gaseous  $\text{IF}_5$  was bubbled into DMSO (either neat or in tetramethylene sulfone solution). In methods A and B volatile

\* Caution. The uncontrolled reaction is explosive. The melting points of  $\text{IF}_5$  ( $10^\circ$ ) and DMSO ( $18^\circ$ ) and their insolubilities in  $\text{CFCl}_3$  or similar materials precluded simple reaction at low temperatures. Reactions of DMSO with  $\text{AgF}_2$  is also violent.

materials were pumped off through a vacuum line fractionation system periodically as the pressure rose, while in method C pumping was continuous. Procedures A and B produced more solids in the reactor, lower yields of volatiles and higher yields of more highly fluorinated products, e.g. containing  $-\text{CF}_2\text{H}$  and  $-\text{CF}_3$  groups. The volatile fractions were examined by infrared, nmr and mass spectroscopy. The complexity and variation of the mixtures and the instability or low yields of several products has made purifications and identifications difficult.

A major product from all three procedures is a colorless, volatile liquid compound of moderate stability. A sizable sample of this compound has not been obtained in high purity, but it has been tentatively identified as  $\text{CH}_2\text{FS}(\text{O})\text{H}$  on the basis of the following information. A molecular weight of 83 (calc.: 82) was obtained by the gas density method and mass spectral analysis (3) shows the principal major peak at mass number 81 with a small parent peak at 82. The remainder of the mass spectrum shows several peaks attributable to the expected fragments of  $\text{CH}_2\text{FS}(\text{O})\text{H}$ , but is complicated by intramolecular rearrangement fragments (4) and small impurity peaks. The most intense peak at 33 is attributed to  $\text{SH}^+$  with a contribution by  $\text{CH}_2\text{F}^+$ . The  $\text{OH}^+$  peak was insignificant. The  $^{19}\text{F}$  nmr spectrum (5) consists of a triplet at 155.6 ppm and the  $^1\text{H}$  spectrum shows a doublet centered at 5.24 ppm, which confirm the presence of the  $\text{CH}_2\text{F}$  group ( $J = 55$  cps), and a singlet at 1.99 ppm, which can be reasonably attributed (6) to the  $\text{S}(\text{O})\text{H}$  group.\* Finally, the infrared spectrum of this compound (Fig. 1) shows some unusual features, which, however, appear to be consistent with the proposed structure, i.e., 3015 and 2940  $\text{cm}^{-1}$ , C-H stretch; 2810  $\text{cm}^{-1}$ , S-H stretch (normal  $\text{RSH}$ , 2600-2550  $\text{cm}^{-1}$ ); 1410  $\text{cm}^{-1}$ ,  $\text{CH}_2$  bend; 1265  $\text{cm}^{-1}$  H-C-F-bend, 1185  $\text{cm}^{-1}$ ,  $\text{S} \rightarrow \text{O}$  stretch; 1050 to 1100  $\text{cm}^{-1}$ ; S-H bend (impurity bands possible); 1005  $\text{cm}^{-1}$  C-F stretch; 680  $\text{cm}^{-1}$  C-S stretch, 590  $\text{cm}^{-1}$  F-C-S bend. No absorptions due to S-OH were identified in the 750-900  $\text{cm}^{-1}$  region. In contrast the recently described (1) t-butyl sulfenic acid apparently exists primarily in the S-OH form.

\* A more complex spectrum appeared upon higher resolution, but the presence of impurities has prevented analysis. The postulated structure has an asymmetric sulfur atom which could make the two H atoms in the  $\text{CH}_2\text{F}$ -group dissimilar, and lead to an ABX pattern or even an ABMX pattern in event of coupling with the H atom on S.

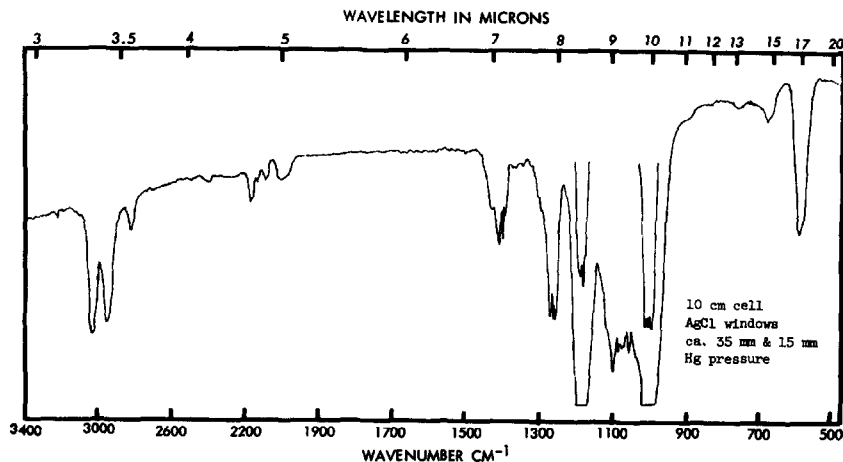


Fig. 1  
Infrared Spectrum of Compound Tentatively Identified as  $\text{CH}_2\text{FS}(\text{O})\text{H}$

The purified samples of  $\text{CH}_2\text{FS}(\text{O})\text{H}$  used in the preceding characterization were obtained by vacuum distillation past a  $-55^\circ$  trap and collection at  $-63.5^\circ$ . The vapor pressure of this compound is ca. 170 mm at  $25^\circ$ . The major impurity was  $\text{CH}_3\text{SCFO}$  with smaller amounts of other impurities as described later. The liquid  $\text{CH}_2\text{FS}(\text{O})\text{H}$  is quite stable at  $-78^\circ$ , but yields a white or yellowish solid over several days at  $25^\circ$  in a sealed glass or Kel-F tube. The vapor, on the other hand, decomposes to white solids (7) in a glass bulb in just a few hours, but is much more stable in Kel-F or metal. Decomposition of the vapor in glass generated  $\text{SiF}_4$  while that of the liquid did not. The decomposition then likely proceeds via loss of  $\text{HF}$  on a fresh glass surface to give the sulfine,  $\text{CH}_2=\text{S}=\text{O}$ , the simplest of a little known class of compounds (8). Further, the mass spectrum of the  $\text{CH}_2\text{FS}(\text{O})\text{H}$  sample at 13 v (where  $\text{CH}_2\text{FS}(\text{O})\text{H}$  peaks are negligible) revealed parent peaks at 62 and 80 attributable respectively to  $\text{CH}_2=\text{S}=\text{O}$  and to  $\text{CHF}=\text{S}=\text{O}$  (we also observed a very small peak at 98 which could be  $\text{CF}_2=\text{S}=\text{O}$ , but may be a trace of  $\text{CH}_3\text{SO}_2\text{F}$ ). Preliminary tests indicate that  $\text{CH}_2\text{FS}(\text{O})\text{H}$  is soluble in water without rapid decomposition.

Reaction procedure C gave considerable amounts of  $\text{HCFO}$  and the little known (2)  $\text{CH}_3\text{SCFO}$  which was characterized as follows: mass spectrum: parent peak, 94, and an extremely intense peak at 47 from the equal fragments  $\text{CH}_3\text{S}^+$  and  $\text{CFO}^+$ ; nmr:  $-43.4 \delta$ ,  $\text{CFO}$ ;  $2.18 \delta$

(doublet:  $J = 2.6$ )  $\text{CH}_3$ ; and infrared: 2940 (m), C-H; 1815 db, (vs), C=O; 1080 (vs), C-F; 760 (m) S-CFO; 650 (mw)  $\text{CH}_3$ -S; It distilled very slowly at  $-45^\circ$  under vacuo. The several remaining products could not be completely separated and identified. One material appears to be  $\text{CH}_2\text{FSCHO}$ : the mass spectrum shows a strong parent peak at 94 and a moderate peak at 61 ( $\text{SCHO}^+$ ), but without the strong peak at 47 observed with  $\text{CH}_3\text{SCFO}$ . It is slightly less volatile than  $\text{CH}_3\text{SCFO}$ . This compound may be the source of a weak  $^{19}\text{F}$  peak observed at 157 ppm (or possibly another at 124.8 ppm). Another significant product which gave a mass spectral parent peak at 108 was tentatively assigned as  $\text{CH}_2\text{FS(O)CHCH}_2$  on the basis of the fragment peaks at 27 ( $\text{C}_2\text{H}_3^+$ ) and 59 ( $\text{C}_2\text{H}_3\text{S}^+$  after oxygen transfer), and incomplete nmr data ( $^{19}\text{F}$  triplet at 187.2  $\delta$  and doublet 5.30  $\delta$  ( $J = 52.4$ ) arising from a  $\text{CH}_2\text{F}$  group). Identification of other compounds including  $\text{CHF}_2$  and  $\text{CF}_3$  derivatives is incomplete. Mass spectral peaks have been observed in some samples at 186 and 167 which could arise from traces of  $(\text{CF}_3)_2\text{SO}$ . Although electrochemical fluorination of dimethyl sulfone gave moderate yields of  $(\text{CF}_3)_2\text{SO}_2$ , (9), no perfluorosulfoxides were obtained in the few studies reported (10-12).

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3. Mass spectral analysis by Morgan-Schaeffer Corporation, Montreal, Canada.
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5. Nuclear magnetic resonance and A-60 Varian Associates Model HA-100 Spectrometers. Shifts in ppm relative to internal  $\text{CFCl}_3$  and  $(\text{CH}_3)_4\text{Si}$  at 0.
6. Resonances for RSH usually occur at 1.2 to 1.7 ppm, E. Mohaesi, J. Chem. Educ., **41**, 38 (1964).
7. Solids show C to H ratios of 1:2.1 to 1:2.2 with low and variable Fluorine and Sulfur. Their infrared spectra also vary, but all show some similarities to that of  $(\text{CH}_2\text{O})_x$ . Their insoluble natures also resemble  $(\text{CH}_2\text{O})_x$ , but their decomposition temperature, 115-120°, is 60-80° lower.
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11. F. W. Hoffman, T. C. Simmons, et al., J. Am. Chem. Soc., **79**, 3424 (1957).
12. Thus  $(n\text{-C}_4\text{H}_9)_2\text{SO}$  gave (11)  $\text{C}_4\text{F}_{10}$  and  $\text{SF}_6$  plus 1-2%  $n\text{-C}_4\text{F}_9\text{SF}_5$  and  $(n\text{-C}_4\text{F}_9)_2\text{SF}_4$ .