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Fluorine-19 Chemical Shifts in Nuclear Magnetic Resonance Spectra of Fluorosulfate-Containing Compounds

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Since the synthesis of peroxydisulfuryl difluoride ($S_2O_6F_2$) by Dudley and Cady,[1] the number of compounds containing the fluorosulfate group, OSO_2F, has increased rapidly inasmuch as reactions of the former or its derivatives provide a facile route to the introduction of this group into fluoroolefins and simple inorganic molecules. In characterizing some of these fluorosulfates, the chemical shift of the fluorine bonded to sulfur was reported with respect to an internal or an external standard. The literature reports no attempts to compare the magnitudes of the chemical shifts as a function of chemical or molecular environment. However, it has been stated that resonances in the −50-ppm region are diagnostic of the fluorine in fluorosulfate since the frequency in organic molecules seems to be relatively constant.[2] In order to study this relationship, several of these compounds have been synthesized and their nuclear magnetic resonance spectra have been measured with trichlorofluoromethane as the internal reference.

Experimental Section

The compounds examined were prepared through the use of conventional methods. A Varian Model 4311B high-resolution spectrometer equipped with a 40-Mc oscillator was used to determine the nuclear magnetic resonance spectra. Reproducibility of chemical shift values was about ±0.1 ppm for consecutive measurements on the same or different preparations of a compound or for measurements separated by 24 hr. The samples were contained in sealed 5-mm o.d. Pyrex tubes heated to 35° prior to use to check pressure stability. Roughly 50% solutions (by volume) were prepared with CCl_3F, which had been dried over P_2O_5, as the reference compound. In the case of $HOSO_2F$, because of immiscibility with CCl_3F, an external reference was used. CCl_3F was sealed into a 2-mm o.d. tube, and this was placed in the liquid $HOSO_2F$. External references were also used with $ClOSO_2F$ and $BrOSO_2F$.

In Table I, the fluorosulfate compounds are listed with the respective chemical shifts given in ppm.

TABLE I

F^{19} CHEMICAL SHIFTS OF OSO_2F IN FLUOROSULFATE-CONTAINING COMPOUNDS RELATIVE TO CCl_3F

Compound	Shift, ppm	Compound	Shift, ppm
$ClOSO_2F^a$	-33.9^h	$FO_2SOSO_2F^b$	−48.8
$FOSO_2F^b$	−36.3	$CF_2(OSO_2F)_2{}^e$	−48.7
CF_3OOSO_2F	−37.9	$C_2F_5OSO_2F^a$	−49.6
$FO_2SOOSO_2F^b$	−40.4	$O_2S(OSO_2F)_2$	−49.6
$BrOSO_2F$	-41.3^h	$NF_2CF_2CF_2OSO_2F^f$	−50.4
$FOOSO_2F^b$	−42.6	$C_2F_4(OSO_2F)_2$	−50.7
NF_2OSO_2F	−44.1	$CF_3CBrFCF(OSO_2F)CF_3{}^g$	−51.0
CF_3OSO_2F	−46.8	$CF_3CF_2CF(OSO_2F)CF_3{}^c$	−51.2
$CF_3C(O)OSO_2F^{c,d}$	−47.4	$HOSO_2F$	-65.6^h
$CClF_2OSO_2F^d$	−48.0		

[a–g] For comparison with previously reported shifts, consult the following: (a) W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2,** 496 (1963); (b) G. Franz and F. Neumayr, *ibid.*, **3,** 921 (1964); (c) J. J. Delfino and J. M. Shreeve, *ibid.*, **5,** 308 (1966); (d) D. D. DesMarteau and G. H. Cady, *ibid.*, **5,** 169 (1966); (e) see ref 2; (f) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4,** 1441 (1965); (g) B. L. Earl, B. K. Hill, and J. M. Shreeve, *ibid.*, in press. [h] External reference.

Although the observed shifts as a function of the substituent group cannot be simply related to any single factor, the data, in general, appear to be internally consistent, which makes some interesting comparisons possible. (1) Introduction of CF_2 group(s) shifts resonances to lower field: $FOSO_2F > CF_3OSO_2F > C_2F_5OSO_2F$; $ClOSO_2F > ClCF_2OSO_2F$; $FO_2SOOSO_2F > FO_2SOCF_2OSO_2F > FO_2SOC_2F_4OSO_2F$; $NF_2OSO_2F > NF_2C_2F_4OSO_2F$. (2) Substitution of SO_3F for fluorine shifts to lower field: $FO_2SOSO_2F > FO_2SOSO_2OSO_2F$; $CF_3OSO_2F > FO_2SOCF_2OSO_2F$; $FOSO_2F > FO_2SOOSO_2F$. (3) Substitution of a halogen or pseudo-halogen for a fluorine may shift to lower field: $CF_3OSO_2F > ClCF_2OSO_2F$; $FOSO_2F > NF_2OSO_2F$; $FOSO_2F > BrOSO_2F$; or to higher field: $FOSO_2F < ClOSO_2F$. (4) Introduction of an oxygen atom varies: $FOSO_2F > FOOSO_2F$, while $CF_3OSO_2F < CF_3OOSO_2F$.

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[2] M. Lustig, *Inorg. Chem.*, **4,** 1828 (1965).

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Trimethylsiloxydimethylgold

BY HUBERT SCHMIDBAUR AND MANFRED BERGFELD

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We wish to report the synthesis of trimethylsiloxydimethylgold, a heterosiloxane species[1] containing the Si–O–Au linkage.

Trimethylgold, prepared according to a method described by Gilman and Woods,[2] was converted to

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[2] H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, **70,** 550 (1948).