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Relative Acidities of the Trifluorovinylchloroboranes

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A relative acidity scale based on the proton shifts of the diethyl etherates of the Lewis acids BCl_3 and BF_3 has been developed by Deters, *et al.*² Since the trifluorovinylboranes $(\text{C}_2\text{F}_3)_3\text{B}$, $(\text{C}_2\text{F}_3)_2\text{BCl}$, and $\text{C}_2\text{F}_3\text{BCl}_2$ are among the few stable fluorocarbon boranes,³ it is of interest qualitatively to compare their acidities with those of the boron halides.

Experimental Section

The fluorocarbon boranes were handled exclusively in a glass vacuum system while all other materials were handled to exclude moisture.

Materials. Diethyl ether was distilled from calcium hydride under a nitrogen atmosphere. Boron trichloride was purified by fractional condensation in the vacuum system with the material used that stopped in a -111° trap. The vapor pressure was 477 Torr, lit. value 477 Torr at 0° . Boron trifluoride etherate was distilled under nitrogen and the fraction boiling at 126° was collected. The $(\text{C}_2\text{F}_3)_2\text{BCl}_2$ and $(\text{C}_2\text{F}_3)_2\text{BCl}$ were prepared as described in the literature.² The procedure for $(\text{C}_2\text{F}_3)_3\text{B}^2$ was modified by the addition of Du Pont E-5 fluorinated ether to the reaction mixture in order to moderate the vigor of the reaction. In the absence of the ether we obtained only polymers.

Nmr Measurements. The samples were prepared either on the vacuum system or in a drybox. Weighed amounts of ether and acid were allowed to react with the latter in excess and tetramethylsilane was added as an internal reference. The sample tubes were sealed off and kept in liquid nitrogen until being warmed immediately before measurement on a Varian A-60 spectrometer. The methylene proton shifts for the 1:1 ether-acid complexes were measured relative to those of the pure ether⁴ and are as follows (Hz): BCl_3 , 79.8; $(\text{C}_2\text{F}_3)_2\text{BCl}_2$, 73.5; $(\text{C}_2\text{F}_3)_2\text{BCl}$, 64.5; $(\text{C}_2\text{F}_3)_3\text{B}$, 59.0; BF_3 , 50.5.

Discussion

On the basis of the relative shifts of the complexes the Lewis acidities fall in the order $\text{BCl}_3 > \text{C}_2\text{F}_3\text{BCl}_2 > (\text{C}_2\text{F}_3)_2\text{BCl} > (\text{C}_2\text{F}_3)_3\text{B} > \text{BF}_3$. A more quantitative set of values may be assigned by plotting the chemical shifts in hertz against the relative acidities for a series of Lewis acids as assigned by Deters, *et al.* When this is done, the relative values are 100, 92, 82, 74, and 63 Hz in the order given above. The relatively linear decrease in acid strengths as trifluorovinyl groups are substituted for chloride suggests that the effects are solely electronic and steric factors do not play any role. Although it is well known that fluorine is more electronegative than chlorine, this is more than offset by the back-donation of electron density by the former, making BCl_3 a stronger acid than BF_3 . Based on the relative acid strengths the trifluorovinyl group falls between fluorine and chlorine in its composite inductive-back-donation effect. It is interesting that the trifluorovinyl group shows so little interaction between its π electrons and the boron p_z orbital despite its well-known ability to react with transition elements.⁵

(1) Abstracted from a portion of the Ph.D. thesis of N. W.

(2) J. F. Deters, P. A. McCusker, and R. C. Pilger, Jr., *J. Amer. Chem. Soc.*, **90**, 4583 (1968).

(3) S. L. Stafford and F. G. A. Stone, *ibid.*, **82**, 6238 (1960).

(4) A referee has raised the objection that the chemical shifts may be affected by intermolecular effects. However, both Deters and ourselves have observed that a plot of the chemical shifts as a function of acid:base ratio gives a straight line up to the 1:1 pure adduct ratio. Thus intermolecular effects must be small.

(5) M. Green, R. L. Osborne, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc. A*, 2525 (1968).

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Registry No. $\text{BCl}_3 \cdot \text{Et}_2\text{O}$, 2102-03-6; $(\text{C}_2\text{F}_3)_2\text{BCl}_2 \cdot \text{Et}_2\text{O}$, 42886-05-5; $(\text{C}_2\text{F}_3)_2\text{BCl} \cdot \text{Et}_2\text{O}$, 42886-06-6; $(\text{C}_2\text{F}_3)_3\text{B} \cdot \text{Et}_2\text{O}$, 42886-07-7; $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 109-63-7.

Contribution from the Department of Chemistry,
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Oxidations of Partially Fluorinated Alkyl Sulfides. Preparation of Methyl Trifluoromethyl Sulfoxide and Methyl(trifluoromethyl)sulfur Tetrafluoride

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Traditionally, sulfoxides are formed by the oxidation of sulfides. Although there are many oxidations of this nature reported in the literature,²⁻⁶ these occur with sulfides containing nonfluorinated alkyl or aryl groups. An exception was the reported oxidation of methyl trifluoromethyl sulfide with hydrogen peroxide or HNO_3 in glacial acetic acid.⁷ In attempts to repeat this oxidation, the reaction product was invariably methyl trifluoromethyl sulfone. While our work was in progress, a study of the oxidation of various methyl polyfluoroalkyl sulfides was reported.⁸

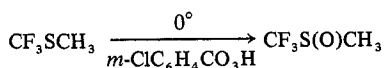
Completely fluorinated alkyl sulfides have been shown to be totally inert to the normal oxidative methods.⁹ However, oxidation with chlorine monofluoride has yielded bis(perfluoroalkyl)sulfur difluorides or bis(perfluoroalkyl)sulfur tetrafluorides.¹⁰⁻¹³ The difluorides, when treated with anhydrous HCl in Pyrex glass, resulted in sulfoxide formation. In contrast to bis(perfluoroalkyl) sulfides, when CH_3SCF_3 was treated with ClF , no methyl(trifluoromethyl)sulfur difluoride was formed. However, good yields of methyl(trifluoromethyl)sulfur tetrafluoride were obtained. Oxidation of CF_3SCH_3 with *m*-chloroperoxybenzoic acid at 0° gave high yields of methyl trifluoromethyl sulfoxide. At 25° or above, the sulfide was oxidized to sulfone. In similar fashion, $(\text{CF}_3)_2\text{CH}_2$ was slowly oxidized by *m*-chloroperoxybenzoic acid to $\text{CF}_3\text{SCH}_2\text{S}(\text{O})\text{CF}_3$ and other unidentified oxidation products.

Results and Discussion

The controlled reaction of methyl trifluoromethyl sulfide

- (1) Alfred P. Sloan Foundation Fellow, 1970-1972.
- (2) R. Giovini, S. Colonna, and M. Cinquini, *Chem. Ind. (London)*, 1737 (1969).
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- (4) C. R. Johnson and N. J. Leonard, *J. Org. Chem.*, **27**, 282 (1962), and references therein.
- (5) J. Stating, B. Zwanenburg, and L. Thys, *Tetrahedron Lett.*, **36**, 3453 (1967).
- (6) J. S. Grossert and R. F. Langler, *J. Chem. Soc., Chem. Commun.*, 49 (1973).
- (7) L. M. Yagupol'skii and A. G. Panteleimonov, *Zh. Obshch. Khim.*, **35**, 1120 (1965); *Chem. Abstr.*, **63**, 98006 (1965).
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- (10) D. T. Sauer and J. M. Shreeve, *Chem. Commun.*, 1679 (1970).
- (11) D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, **1**, 1 (1971).
- (12) T. Abe and J. M. Shreeve, *J. Fluorine Chem.*, **3**, 17 (1973).
- (13) T. Abe and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, **9**, 495 (1973).

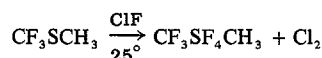
with *m*-chloroperoxybenzoic acid provided a direct route to the synthesis of methyl trifluoromethyl sulfoxide. If the



reaction temperature was greater than 0° the monosulfide was oxidized to the sulfone, $\text{CF}_3\text{SO}_2\text{CH}_3$.

The products of this oxidation were easily identified by their characteristic spectra. Although the close proximity of the C-F asymmetric and sulfoxide stretching frequencies caused difficulties in the assignment of either, the strong band at 1210 cm^{-1} was attributed to the S=O stretch.¹⁴⁻¹⁶

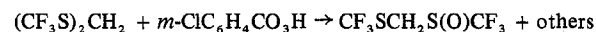
Methyl trifluoromethyl sulfide was also oxidized by reaction with chlorine monofluoride. In contrast to the reaction with totally fluorinated alkyl sulfides, even at -98° , none of the methyl(trifluoromethyl)sulfur difluoride was formed. At that temperature, a 30% yield of methyl(trifluoromethyl)sulfur tetrafluoride was obtained and this yield was increased to 70% when the reaction mixture was warmed from -183 to $+25^\circ$ over a 10-15 min period. The relative amounts of CF_3SCH_3 and ClF seem to have no influence on the final product since the sulfur tetrafluoride was invariably formed. Unlike the bis(perfluoroalkyl)sulfur tetrafluorides



where both the *cis* and *trans* isomers were formed in fluorination of the sulfide with ClF ,¹³ only the *trans* isomer was formed here. Other substituted sulfides are now being studied.

The sulfides became increasingly more difficult to oxidize with standard reagents as the fluorine content of the alkyl groups (electron-withdrawing power) increased. *m*-Chloroperoxybenzoic acid did not oxidize $\text{CF}_3\text{SCF}_2\text{H}$ under the conditions studied. More vigorous oxidizing agents did not provide a useful route to the formation of sulfoxides.

Bis(trifluoromethylthio)methane, $(\text{CF}_3\text{S})_2\text{CH}_2$, was slowly oxidized by *m*-chloroperoxybenzoic acid to yield a mixture containing $\text{CF}_3\text{SCH}_2\text{S(O)CF}_3$ as the predominant product.



Although this molecule was not completely characterized, the spectral assignments of the nmr, ir, and mass spectra indicated the assigned structure. The presence of a very strong band near 1210 cm^{-1} corresponded to the S=O band previously assigned for $\text{CF}_3\text{S(O)CH}_3$. Since the band was not present in $(\text{CF}_3\text{S})_2\text{CH}_2$, an intense absorption in this region indicated a sulfoxide group. The mass spectrum contained a $\text{M} - \text{CF}_3^+$ ion as well as other ions supporting the assigned structure. The ^{19}F nmr spectrum contained two resonances in a 1:1 ratio. A quartet at 42.3 ppm ($J_{\text{CF}_3\text{S}-\text{CF}_3} = 0.6\text{ Hz}$) is in the region expected for a CF_3S -function. Likewise, the resonance at 73.9 ppm is in the expected range for a $\text{CF}_3\text{S(O)}$ resonance. The proton resonance is a singlet at $\delta\ 4.93$. The absence of an SO_2 asymmetric stretch in the infrared spectrum indicated that a sulfone moiety was not present.

Experimental Section

Trifluoromethylsulfonyl chloride was prepared by the reaction of CCl_3SCl (Eastman Organic Chemicals) and NaF (J. T. Baker and Co.).¹⁷ Methyl iodide, methylene iodide, and *N*-chlorosuccinimide

were purchased from Eastman Organic Chemicals, silver acetate was from J. T. Baker and Co., and sodium metaperiodate was from J. T. Baker and Co. Chlorine monofluoride was obtained from Ozark Mahoning and silver difluoroacetate and *m*-chloroperoxybenzoic acid were from Aldrich Chemical Co., Inc. All chemicals were used as purchased without further purification.

General Procedures. The gases and volatile liquids were handled in a conventional glass vacuum apparatus. Gaseous starting materials and purified products were measured quantitatively by standard PVT techniques. Purification of products was carried out by fractional condensation and gas chromatography. The chromatograph columns were constructed of 0.25-in. copper tubing packed with 20% Kel-F polymer oil (3M Co.) on Chromosorb P.

Apparatus. Infrared spectra were recorded with a Perkin-Elmer Model 457 infrared spectrometer using a 10-cm gas cell fitted with KBr windows and were calibrated against known absorption bands in polystyrene film. Fluorine nmr spectra were determined with a Varian HA-100 nmr spectrometer using CFCl_3 as an internal standard while ^1H nmr spectra were recorded with a Varian A-60 nmr spectrometer with tetramethylsilane as reference. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer. A 140-W Hanovia uv lamp was utilized in all photolysis reactions.

Preparations of CF_3SCH_3 . (a) CF_3SCH_3 was prepared quantitatively by the reaction of bis(trifluoromethylthio)mercury and methyl iodide. Typically, 2.5 mmol of CH_3I was condensed into a Pyrex vessel which contained excess mercurial and was allowed to react at 25° for 7 days. Methyl trifluoromethyl sulfide was isolated (~ 2.4 mmol) by fractional condensation.

(b) Alternatively, CF_3SCH_3 was prepared by the photolysis of $\text{CF}_3\text{SOC(O)CH}_3$ which resulted from the reaction of trifluoromethylsulfonyl chloride and silver acetate. In a typical reaction, 10 mmol of CF_3SCl was treated with an excess of AgOC(O)CH_3 to yield $\text{CF}_3\text{SOC(O)CH}_3$ quantitatively. This product was photolyzed in a 1-l. Pyrex bulb for 4 hr. The resulting mixture was fractionally condensed through a trap at -50° (which retained acetic acid anhydride), a trap at -98° which stopped CF_3SCH_3 and CF_3SSCF_3 , and a trap at -183° which trapped the CO_2 evolved. CF_3SCH_3 (40%) and CF_3SSCF_3 were separated by gas chromatography.

Spectra of CF_3SCH_3 . Infrared bands were as follows: 3020 (w), 2956 (w), 1445 (w), 1328 (w), 1222 (w), 1279 (vs), 1240 (vs), 980 (m), 761 (m) cm^{-1} . The ^1H and ^{19}F nmr spectra consisted of singlets at $\delta\ 2.33$ and $\phi\ 45.0$, respectively. The molecule ion had a relative abundance of 91% in the mass spectrum. Other mass spectral species included $\text{M} - \text{F}^+$, CF_2S^+ , FCSCH_2^+ , CF_3^+ , CFS^+ , CH_3S^+ , CH_3S^+ , and CHS^+ .

Reactions of CF_3SCH_3 . (a) With *N*-Chlorosuccinimide. CF_3SCH_3 was condensed into a vessel containing 5 ml of absolute methanol. The vessel was warmed to 25 or 100° and 0.5 mmol of *N*-chlorosuccinimide was added in small portions. No reaction was observed after 3 days.

(b) With Sodium Metaperiodate. After 4 days at 25° , CF_3SCH_3 (1 mmol) in contact with excess sodium metaperiodate in a 50-ml Pyrex vessel showed no change.

(c) With Chlorine Monofluoride. Chlorine monofluoride (8.5 mmol) and CF_3SCH_3 (2 mmol) were condensed into a 75-ml SS Hoke vessel at -183° . The vessel was warmed to 25° over a 15-min period. The resulting mixture was fractionally condensed through a trap cooled at -63° , the contents of which were further separated by gas chromatography. $\text{CF}_3\text{SF}_4\text{CH}_3$ (1.4 mmol) was isolated and found to have the following absorption bands in the infrared spectrum: 1252 (vs), 1160 (s), 1070 (sh), 1030 (m), 1000 (sh), 839 (s), 809 (vs), 750 (ms) (pqr), 570 (ms) cm^{-1} . The ^1H nmr spectrum consisted of a pentet at $\delta\ 3.3$ ($J_{\text{CH-SF}} = 10\text{ Hz}$). The ^{19}F nmr spectrum contained a pentet centered at $\phi\ 64.5$ assigned to CF_3 ($J_{\text{CF-SF}} = 26\text{ Hz}$) and a quartet of quartets centered at $\phi\ -51.4$ for SF_4 . No $\text{CH}_3\text{-CF}_3$ coupling was observed. The mass spectrum contained ions CF_3SF_2^+ , CH_3SF_4^+ , $\text{CF}_3\text{SCH}_2^+$, CH_3SF_3^+ , CF_3^+ , SFCH_2^+ , and CH_3^+ . Fluorine analysis gave 67.4% (calcd 68.8%). The experimental molecular weight for $\text{CF}_3\text{SF}_4\text{CH}_3$ was 189 (calcd 193).

(d) With *m*-Chloroperoxybenzoic Acid. Methyl trifluoromethyl sulfide (1.0 mmol) was condensed into a 50-ml Pyrex vessel containing 1.2 mmol of *m*-chloroperoxybenzoic acid. The mixture was allowed to remain at 25° for 7 days. Separation of the volatile components showed that only $\text{CF}_3\text{SO}_2\text{CH}_3$ ($\sim 18\%$) and unreacted CF_3SCH_3 were present.

At 0° , 2 mmol of CF_3SCH_3 was treated with 2.5 mmol of *m*-

(14) H. Szmant and W. Emerson, *J. Amer. Chem. Soc.*, **78**, 454 (1956).

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(16) D. T. Sauer and J. M. Shreeve, *An. Asoc. Quim. Argent.*, **59**, 157 (1971).

(17) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2061 (1960).

chloroperoxybenzoic acid to produce methyl trifluoromethyl sulfoxide in 78% yield. Traces of $\text{CF}_3\text{SO}_2\text{CH}_3$ and unreacted CF_3SCH_3 were removed by trap-to-trap distillation. $\text{CF}_3\text{SO}_2\text{CH}_3$ was retained at -20° while $\text{CF}_3\text{S(O)CH}_3$ was stopped in a trap cooled to -30° . The infrared spectrum of $\text{CF}_3\text{SO}_2\text{CH}_3$ at 4 Torr showed the following bands: 1397 (vs), 1330 (w), 1246 (vs), 1210 (vs), 1146 (vs), 960 (m) (pqr), 780 (w-m), 742 (w-m), 540 (m) (pqr), and 484 (w-m) cm^{-1} . Mass spectral fragments included $\text{M} - \text{CH}_3^+$, $\text{M} - \text{CF}_3^+$, and CF_3^+ . A quartet at ϕ 79.5 ($J_{\text{H-F}} = 1$ Hz) occurred in the ^{19}F nmr spectrum and a quartet at δ 3.1 occurred in the ^1H nmr spectrum.

Properties of Methyl Trifluoromethyl Sulfoxide. $\text{CF}_3\text{S(O)CH}_3$ existed as a colorless liquid at room temperature. Its infrared spectrum contained the following bands: 2899 (w), 1425 (w), 1245 (w), 1210 (vs), 1170, 1164 (m) (doublet), 1125 (s), 960 (w-m), 740 (w) cm^{-1} . The ^{19}F nmr spectrum showed a quartet at ϕ 76.6 ($J_{\text{H-F}} = 1.1$ Hz) and the ^1H nmr spectrum showed a quartet at δ 2.75. A mass spectrum showed ions attributed to M^+ , CF_3SO^+ , CF_3^+ , and CH_3SO^+ . Fluorine analysis gave 47.0% (calcd 47.8%).

Preparation of $\text{CF}_3\text{SCF}_3\text{H}$. Reaction of $\text{CF}_3\text{HCO}_2\text{Ag}$ (7 mmol) with CF_3SCl (5 mmol) at 25° for 10 min produced the colorless compound $\text{CF}_3\text{HC(O)OSCF}_3$, which was retained in a trap at -78° during trap-to-trap distillation. $\text{CF}_3\text{HC(O)OSCF}_3$ was photolyzed in a 1-l. Pyrex bulb for 1 hr to produce CF_3HSCF_3 (75%). Large amounts of CF_3SSCF_3 (25%) which formed during the photolysis were removed by gas chromatography.

Properties of CF_3HSCF_3 . CF_3HSCF_3 existed as a gas at room temperature which condensed to a colorless liquid. The ^1H nmr spectrum showed a triplet at δ 7.06 ($J_{\text{H-F}} = 55.6$ Hz) while the ^{19}F nmr spectrum showed a triplet for the CF_3 resonance ($J_{\text{F-F}} = 7.0$ Hz) at ϕ 38.4 and a doublet of quartets for the CF_2H resonance at ϕ 93.2. The infrared spectrum showed the following absorbance bands: 3005 (w), 1321 (m), 1192 (vs), 1168 (vs), 1142 (vs), 1095 (vs), 794 (m), 761 (m), 482 (vw) cm^{-1} . The major ions observed in the mass spectrum were attributed to M^+ , $\text{C}_2\text{F}_4\text{SH}^+$, CF_2S^+ , CF_3^+ , CFS^+ , and CF_2H^+ . Fluorine analysis gave 61.0% (calcd 62.5%).

Reaction of CF_3HSCF_3 with $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$. $\text{CF}_3\text{SCF}_3\text{H}$ (2.5 mmol) was condensed into a vessel containing excess m -chloroperoxybenzoic acid. After 7 days at 25° , no reaction had occurred.

Preparation of $(\text{CF}_3\text{S})_2\text{CH}_2$. The reaction of 6 g of $\text{Hg}(\text{SCF}_3)_2$ in a 10-ml thick-walled Pyrex tube with 1.5 g of CH_2I_2 at 80° gave approximately quantitative conversion to $(\text{CF}_3\text{S})_2\text{CH}_2$.

Properties of $(\text{CF}_3\text{S})_2\text{CH}_2$. Bis(trifluoromethylthio)methane existed as a colorless liquid at 25° and froze to a colorless solid. The gas-phase infrared spectrum had the following absorption bands: 1305 (w), 1238 (m), 1185 (vs), 1154 (vs), 1113 (vs), 821 (w), 763 (m), 738 (w, sh), 450 (w) cm^{-1} . Mass spectral species included M^+ , $\text{CF}_3\text{SCH}_2^+$, CF_3S^+ , CH_2S_2^+ , CF_3^+ , CH_2S^+ , and CHS^+ . The ^1H nmr spectrum contained a singlet at δ 4.35 and likewise the ^{19}F nmr spectrum had a singlet at ϕ 42.8. Anal. Calcd: F, 52.9; S, 29.70; C, 16.65; H, 0.92. Found: F, 52.9; S, 29.73; C, 16.50; H, 0.91.

Reaction of $(\text{CF}_3\text{S})_2\text{CH}_2$ with $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$. Oxidation of 2 mmol of $(\text{CF}_3\text{S})_2\text{CH}_2$ with 4.4 mmol of $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$ at 25° for 4 days resulted in a mixture of involatile compounds. Isolation of two major components was effected by gas chromatography; they were tentatively identified as $\text{CF}_3\text{SCH}_2\text{S(O)CF}_3$ (~65%) and $\text{CF}_3\text{-SCH}_2\text{SO}_2\text{CF}_3$ (~10%).

The product believed to be $\text{CF}_3\text{SCH}_2\text{S(O)CF}_3$ was a colorless liquid at 25° and had the following infrared spectrum: 3010 (w), 1412 (w), 1390 (w), 1215-1200 (vs, br), 1163 (s-vs), 1123 (s), 830 (w), 765 (w), 748 (w) cm^{-1} . Ions present in the mass spectrum confirming the proposed structure were $\text{CF}_3\text{SCH}_2\text{S(O)}^+$, $\text{CF}_3\text{S(O)}^+$, $\text{CF}_3\text{SCH}_2^+$, CF_3S^+ , CF_3^+ , SO^+ , and SCH_2^+ . The ^1H nmr spectrum showed a single resonance at δ 4.93 while the ^{19}F nmr displayed quartets ($J_{\text{CF}_3-\text{CF}_3} = 0.6$ Hz) at ϕ 42.3 (CF_3S) and 73.9 ($\text{CF}_3\text{S(O)}$).

The structure of $\text{CF}_3\text{SCH}_2\text{SO}_2\text{CF}_3$ was proposed on the basis of ^{19}F nmr data with resonances at ϕ 44.0 and 79.6 and the presence of an SO_2 asymmetric stretch in the infrared spectrum.

Acknowledgment. Fluorine chemistry at Idaho is supported by the Office of Naval Research and the National Science Foundation. We thank Dr. R. A. De Marco and Mr. N. R. Zack for the mass spectra and Mr. C. Srivanavith for the nmr spectra.

Registry No. CF_3SCH_3 , 421-16-9; $(\text{CF}_3\text{S})_2\text{Hg}$, 21259-75-6; $\text{CH}_3\text{-I}$, 74-88-4; $\text{CF}_3\text{S(O)CH}_3$, 42530-92-7; CF_3H , 7790-89-8; *trans*- $\text{CF}_3\text{-SF}_4\text{CH}_3$, 42530-93-8; $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$, 937-14-4; $\text{CF}_3\text{SO}_2\text{CH}_3$, 421-82-9; $\text{CF}_3\text{S(O)CH}_3$, 2697-49-6; $\text{CF}_3\text{HCO}_2\text{Ag}$, 383-88-0; CF_3SCl , 421-

17-0; CF_3HSCF_3 , 371-72-2; $(\text{CF}_3\text{S})_2\text{CH}_2$, 819-67-0; $\text{CF}_3\text{SCH}_2\text{S(O)-CF}_3$, 42530-99-4.

Contribution from the Department of Chemistry,
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Assignment of the Photoelectron Spectra of $\text{Mn}(\text{CO})_5\text{CH}_3$ and $\text{Mn}(\text{CO})_5\text{CF}_3$

Dennis L. Lichtenberger and Richard F. Fenske*

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Study of the electronic structure of the series of compounds $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{H}, \text{Cl}, \text{Br}, \text{I}, \text{CH}_3, \text{CF}_3$) via photoelectron spectroscopy has provided considerable insight into the nature of the bonding in these systems.¹ Of particular interest have been the ionizations occurring at less than 12 eV, which have been found to be sensitive to the nature of the group X. Using the criterion that the area under an ionization band should reflect the orbital degeneracy for orbitals with closely similar localization properties, the original workers concluded that the metal e orbital is above the metal b_2 orbital for all complexes of the series except $\text{Mn}(\text{CO})_5\text{CH}_3$.² This assignment has recently been confirmed for the pentacarbonylmanganese halides with the aid of the pe spectrum of $\text{Mn}(\text{CO})_4(\text{CNCH}_3)\text{Br}$.³ The spectra of the perfluoromethyl and methyl complexes however exhibited significant deviations from the trends observed in the spectra of the halide complexes. Using the intensity assignment criterion for these spectra leads to some unusual conclusions regarding the bonding in these systems. In the perfluoromethyl complex the ratio of the first to second band has become 3:1, suggesting a considerable enhancement of the ionization cross section of the e orbital over the b_2 orbital in this molecule. This may indicate that these orbitals possess significantly different localization properties from the e and b_2 orbitals in the corresponding halides. Nevertheless the assignment was in accord with qualitative expectations concerning the orbital ordering. In the methyl complex the ratio of the first two bands is 1:2, suggesting a reversal in the order of the e and b_2 ionizations. To rationalize this unexpected inversion of the e and b_2 levels it has been proposed that the e orbital is stabilized below the b_2 orbital through back-bonding into the π^* levels of the methyl group. However, such an interpretation of the band assignment does not conform with the other properties of the methyl complex.^{4,5} In any event, the two spectra appeared to indicate a substantial change in the character of the e and b_2 levels from that observed in the pentacarbonylmanganese halides.

Approximate molecular orbital calculations on these two molecules using our method⁶ did not support these interpretations. Instead, the calculations show that another ioniza-

(1) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, **47**, 112 (1969).

(2) The metal levels of the CH_3 and CF_3 complexes may be quite closely described by the local C_{4v} symmetry of the $\text{Mn}(\text{CO})_5$ portion.

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