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Isolation and Characterization of Methyl Hypofluorite (CH_3OF)

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Abstract: Methyl hypofluorite (CH_3OF) has been prepared by the reaction of elemental fluorine with methanol in acetonitrile or propionitrile at low temperature. It was removed from the reaction mixture in a stream of nitrogen and purified by fractional distillation. The compound is moderately long-lived, although the liquid has exploded upon rapid warming. The liquid compound has a freezing point of about −142 °C, and vapor pressure measurements indicate a normal boiling point of −32.6 ± 0.9 °C and an enthalpy of vaporization of 23.37 ± 0.26 kJ/mol. The infrared spectrum of the vapor is consistent with the molecule being isostructural with CH_3OH and CF_3OF. The compound has also been characterized by mass spectrometry and by ^1H, ^{19}F, and ^{13}C NMR spectrometries. This novel reagent adds across various double bonds to form the corresponding fluoro methoxy adducts, which are not easily accessible by other methods.

The fluoroxy or hypofluorite group (OF) is relatively weakly bonded and possesses strong oxidizing and fluorinating capabilities. No hypofluorite is thermodynamically stable with respect to all possible decomposition modes, and the only molecules of this type that persist indefinitely at ambient temperature are ones in which the OF unit is bonded either directly to another fluorine atom (OF_2) or indirectly to a perfluorinated moiety (CF_3OF, SF_5OF).[1] Unstable gaseous hypofluorites derived from inorganic and organic oxyacids (NO_3F, ClO_4F, $CF_3C(O)OF$) have nevertheless been known for many decades,[2] and the unstable hydrogen-containing compound HCF_2CF_2OF was identified by NMR spectroscopy in the 1960s.[3] In more recent times, two hydrogen-containing hypofluorites, the archetypal hypofluorous acid (HOF)[4] and acetyl hypofluorite ($CH_3C(O)OF$),[5,6] have been synthesized and found to be sufficiently long-lived to be characterized and even to be used as reagents, while during the past year several higher acyl hypofluorites have been reported to result from fluorination of the corresponding carboxylates at low temperatures.[7] These latest compounds, however, have yet to be isolated or fully characterized.

Despite all of these developments, however, no alkyl hypofluorites have heretofore been prepared, and most chemists have tended to discount the possibility of binding an OF group directly to a hydrogen-bearing carbon atom, assuming that it would be too easy for such a molecule to evolve HF with concomitant formation of a C=O double bond:[8]

$$CH_3OF \rightarrow H_2C{=}O + HF$$

In recent studies, we have found that it is possible to synthesize HOF by passage of elemental fluorine through water-containing acetonitrile,[9] and these results have encouraged us to attempt an analogous synthesis of CH_3OF:

$$CH_3OH(CH_3CN) + F_2 \rightarrow CH_3OF + HF$$

The attempt has proven successful, and in this paper we report the isolation of this new fluoroxy compound and its physical and chemical characterization.

Experimental Section

Reagents. Elemental fluorine was obtained from Air Products and Chemicals either as the 98% material or as a 20% v/v mixture with argon. The cylinder was equipped with a special purgeable pressure regulator, and gas flows were monitored with a 0–100 cm^3/min mass flow meter. Both the regulator and the flow meter were made of Monel and were obtained from Matheson Co. The fluorine was sometimes further diluted with nitrogen to give concentrations of 7–15%. Commercial organic compounds and solvents were used without additional purification.

Fluorination Procedures and Analyses. Reactions with elemental fluorine were carried out in Teflon or glass reaction vessels, and connections were usually made with Teflon or Kel-F valves, tubing, and fittings. In some cases, however, a stainless steel gas disperser was used (vide infra). Routine assays of CH_3OF oxidizing power were effected by adding samples to an acidified solution of KI and titrating the resulting iodine with thiosulfate.

Vapor Pressure and Melting Point Measurements. The vapor pressure of CH_3OF was measured in a small vacuum line equipped with an MKS Baratron capacitance manometer. During these measurements, the liquid was contained in a Kel-F tube while the vapor came in contact with stainless steel, Monel, and Kel-F. The melting point of CH_3OF was measured on a sample contained in a Kel-F tube immersed in an isopentane bath in an unsilvered Dewar flask. Temperatures for vapor pressure and melting point measurements were determined to ±0.5 °C with a propane thermometer calibrated against a platinum resistance thermometer.

Mass, Infrared, and NMR Spectrometries. The 70-eV electron-impact mass spectra of CH_3OF and its decomposition products were determined with a Finnigan 400 quadrupole mass spectrometer equipped with a Kel-F inlet tube and with use of a data system provided by Shrader Analytical Labs. The infrared spectrum of CH_3OF vapor at ambient temperature was measured at 1-cm^{-1} resolution with a Bruker 113-V spectrometer. Samples were contained in a Kel-F cell of 10-cm path length, fitted with AgCl windows. NMR spectra of CH_3OF dissolved in CD_3CN were measured in glass tubes (10-mm o.d. for ^{13}C, 5-mm o.d. for ^1H and ^{19}F) on a Bruker AM300 spectrometer. The sample probe was cooled to −43 °C. The proton-decoupled ^{13}C spectra were measured with the DEPT pulse sequence. The ^1H and ^{19}F spectra were referenced, respectively, to solutions of $(CH_3)_4Si$ and $CFCl_3$ in CD_3CN that were measured separately at the same temperature. The ^{13}C spectra were measured with respect to the methyl carbon of the CD_3CN solvent, which was taken to have a shift of 1.3 ppm vs $(CH_3)_4Si$.

For the identification of organic reaction products, mass spectra were measured with a Du Pont 21-491B spectrometer and infrared spectra were measured in KBr pellets with a Perkin-Elmer 177 spectrometer. The ^1H and ^{19}F NMR spectra were measured in $CDCl_3$ with a Bruker

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[1] The hypofluorites $O_2NCF_2CF_2OF$, $ClCF_2CF_2OF$, and Cl_2CFCF_2OF are also reported to be extremely stable kinetically: Prager, J. H.; Thompson, P. G. *J. Am. Chem. Soc.* **1965**, *87*, 230–238.

[2] Lustig, M.; Shreeve, J. M. In *Advances in Fluorine Chemistry*; Tatlow, J. C., Peacock, R. D., Hyman, H. H., Eds.; Butterworths: London, 1973; Vol. 7, pp 175–198.

[3] Lustig, M.; Pitochelli, A. R.; Ruff, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 2841–2843.

[4] Studier, M. H.; Appelman, E. H. *J. Am. Chem. Soc.* **1971**, *93*, 2349–2351.

[5] Rozen, S.; Lerman, O.; Kol, M. *J. Chem. Soc., Chem. Commun.* **1981**, 443–444.

[6] Appelman, E. H.; Mendelsohn, M. H.; Kim, H. *J. Am. Chem. Soc.* **1985**, *107*, 6515–6518.

[7] Rozen, S.; Hebel, D. *J. Org. Chem.* **1990**, *55*, 2621–2623.

[8] A similar argument may be used to explain the instability of α-fluoro alcohols. The argument becomes less compelling, however, when we note that trifluoromethanol (CF_3OH), though unstable, has in fact been synthesized: Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 322–323. Its persistence has been rationalized in terms of a large intramolecular H–F distance, a factor that may also play a role in explaining the relatively high kinetic stability of CH_3OF.

[9] Rozen, S.; Kol, M. *J. Org. Chem.* **1990**, *55*, 5155–5159.

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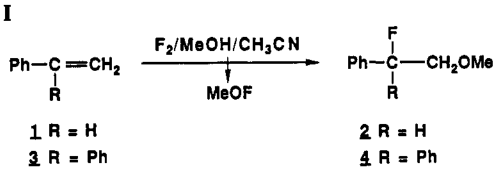
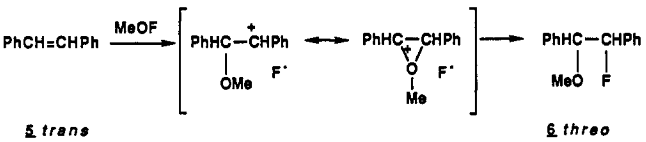
Scheme I



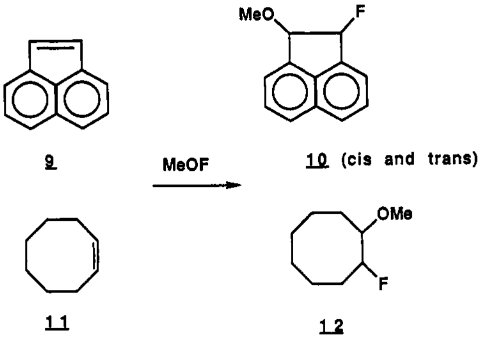
1 R = H
3 R = Ph
2 R = H
4 R = Ph

Scheme II



5 trans
8 cis
6 threo
7 erythro

Scheme III



WH-360 spectrometer, with use of $(CH_3)_4Si$ and $CFCl_3$, respectively, as internal standards.

Preparation and Purification of CH_3OF. *Caution: Although methyl hypofluorite is more stable than we might have expected, several samples have exploded violently upon warming to dry ice temperature. In the absence of further information, neat CH_3OF should be treated as an unpredictably explosive substance.* It was found possible to produce CH_3OF by reaction of elemental fluorine with solutions of methanol in acetonitrile at -45 °C, with solutions of methanol in propionitrile at temperatures between -78 and -45 °C, and even with neat methanol at -78 °C. For the synthesis and isolation of the compound, our method of choice consisted of passing fluorine (diluted to ca. 10% with argon and nitrogen) at a rate of 90–100 cm^3/min through 5 cm^3 of a 50% v/v solution of methanol in propionitrile at -78 °C. A limiting oxidant concentration of ca. 2 N (5 mmol of CH_3OF) was reached after about 50 min. The solution was then warmed to about -45 °C while a stream of nitrogen was passed at 100 cm^3/min through it and then through a Kel-F U-tube cooled with liquid nitrogen. After 15 min, two-thirds of the oxidant had been transferred to the U-tube.

The U-tube containing the crude product was then connected to a Kel-F vacuum manifold, and the nitrogen was pumped away. The U-tube was warmed to about -115 °C (ethanol slush) and pumped on briefly to remove such relatively volatile impurities as CO_2. The sample was then distilled from the ethanol bath until mass spectrometric monitoring indicated that less volatile impurities such as methanol were becoming noticeable, at which point ca. 80–90% of the CH_3OF had been distilled.

To prepare a sample for NMR measurements, a nitrogen stream was passed through the original reaction mixture at -45 °C and then into a tube containing CD_3CN cooled to the same temperature. In this way, a rather pure sample was obtained that contained a few percent of the CH_3OF originally produced.

A slightly different preparative procedure was used to synthesize CH_3OF for reaction with organic substrates. In a typical experiment, 3.5 cm^3 (100 mmol) of CH_3OH was dissolved in 70 cm^3 of CH_3CN in a glass vessel and the solution cooled to -40 °C. Fluorine diluted in nitrogen (about 15% v/v F_2) was passed through this solution at ca. 120 cm^3/min with use of a vibrating stainless steel gas disperser (VibroMixer, Chemap AG, Männedorf, Switzerland) for efficient gas dispersion. After about 2 h, a solution was obtained that was 0.06–0.17 M in CH_3OF.

General Procedure for Reaction of CH_3OF with Organic Substrates. The substrate was dissolved in 5–10 cm^3 of CH_2Cl_2 (or $CHCl_3$ in the case of acenaphthylene), and the solution was cooled to -40 °C and added to a solution of CH_3OF in 70 cm^3 of CH_3CN at the same temperature. The reaction mixture was warmed to room temperature, and after 40 min it was poured into water, extracted with CH_2Cl_2, washed with water until neutral, and dried on $MgSO_4$. The pure products were isolated by vacuum flash column chromatography on Merck silica gel 60H by eluting with increasing concentrations of ethyl acetate in petroleum ether. Styrene and 1,1-diphenylethene gave hitherto unreported products that were characterized by mass, IR, and NMR spectroscopies. The products of other reactions were identified by mass, IR, and NMR spectroscopic properties that were in agreement with literature values.

Styrene (1; Scheme I). Reaction of 570 mg (5.1 mmol) of **1** with 7 mmol of CH_3OF produces 1-fluoro-1-phenyl-2-methoxyethane (**2**; oil) in 75% yield. IR: 2820 cm^{-1}. ^1H NMR (ppm): 7.32 (5 H, s), 5.58 (1 H, ddd, J_1 = 49 Hz, J_2 = 8 Hz, J_3 = 4 Hz), 3.65 (2 H, m), 3.39 (3 H, s). ^{19}F NMR (ppm): -183.76 (ddd, J_1 = 49 Hz, J_2 = 30 Hz, J_3 = 19 Hz). MS, *m/e*: 154 (M^+). Anal. Calcd for $C_9H_{11}FO$: C, 70.13; H, 7.14. Found: C. 69.83; H, 7.17.

1,1-Diphenylethene (3; Scheme I). Reaction of 250 mg (1.4 mmol) of **3** with 4.5 mmol of CH_3OF forms 1,1-diphenyl-1-fluoro-2-methoxyethane (**4**; oil) in 71% yield. IR: 2815 cm^{-1}. ^1H NMR (ppm): 7.30 (10 H, m), 4.05 (2 H, d, J = 22.4 Hz), 3.41 (3 H, s). ^{19}F NMR (ppm): -151.8 (t, J = 22.4 Hz). MS, *m/e*: 210 ($[M - HF]^+$). Anal. Calcd for $C_{15}H_{15}FO$: C, 78.26; H, 6.52. Found: C, 77.83; H, 6.50.

***trans*- and *cis*-Stilbene (5 and 8; Scheme II).** Reaction of 260 mg (1.4_5 mmol) of either compound with 7 mmol of CH_3OF gives a mixture of *threo*- and *erythro*-1-fluoro-2-methoxy-1,2-diphenylethane (**6** and **7**)[10] in 60% yield. The ratio of threo to erythro is 1.8 for *trans*-stilbene and 1.3 for *cis*-stilbene.

Acenaphthylene (9; Scheme III). Reaction of 205 mg (1.3_5 mmol) of **9** with 9.6 mmol of CH_3OF gives 1-fluoro-2-methoxyacenaphthene (**10**)[11] in 60% yield. *trans/cis* = 2.3.

Cyclooctene (11; Scheme III). Reaction of 650 mg (5.9 mmol) of **11** with 12 mmol of CH_3OF gives 1-fluoro-2-methoxycyclooctane (**12**)[12] in 65% yield.

Table I. Vapor Pressure of Methyl Hypofluorite

temp, °C	vapor pressure, Torr obsd	calcd[a]
-117	1.38	1.37
-109.4	3.1	3.16
-103.6	5.5	5.69
-97.4	10.5	10.2
-91.9	17.0	16.6
-87	24.9	25.0
-82	37.6	37.1
-74.1	69.8	66.4
-63.7	127	134
-55.9	213	217
-48	345	342

[a] From the equation $\ln p \text{ (Torr)} = 18.314 - 2810/T \text{ (K)}$.

Results

At low temperature, methyl hypofluorite is a white solid, melting at -142 ± 1 °C to a pale yellow liquid. The liquid and solid are quite stable at temperatures below -110 °C. (*But see cautionary note in Experimental Section.*) The stability of the compound in the reaction mixture from which it is prepared (50% v/v methanol in propionitrile) appears to be significantly less than that of the neat material and to be somewhat irreproducible. More stable solutions of CH_3OF can be prepared in acetonitrile or propionitrile containing less methanol (ca. 5% v/v), but in such solutions the maximum attainable concentration of the hypofluorite is considerably reduced. Methyl hypofluorite vapor decomposes gradually at ambient temperature, although a 50-Torr sample of the vapor in an infrared cell showed only partial decomposition after storage over a weekend in the dark. Both mass spectra and infrared spectra indicated HF and formaldehyde to be principal decomposition products. In some cases, decomposition produced a white solid, identified by pyrolysis mass spectrometry as paraformaldehyde.

Because of the compound's volatility, the characteristic mass spectrum of CH_3OF can even be observed from crude reaction mixtures. The cleanest spectra, however, were obtained from

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(10) Barton, D. H. R.; Hesse, R. H.; Jackman, G. P.; Ogunkoya, L.; Pechet, M. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 739–742.

(11) Stavber, S.; Zupan, M. *J. Org. Chem.* **1987**, *52*, 919–921.

(12) Hebel, D.; Rozen, S. *J. Org. Chem.* **1987**, *52*, 2588–2590.

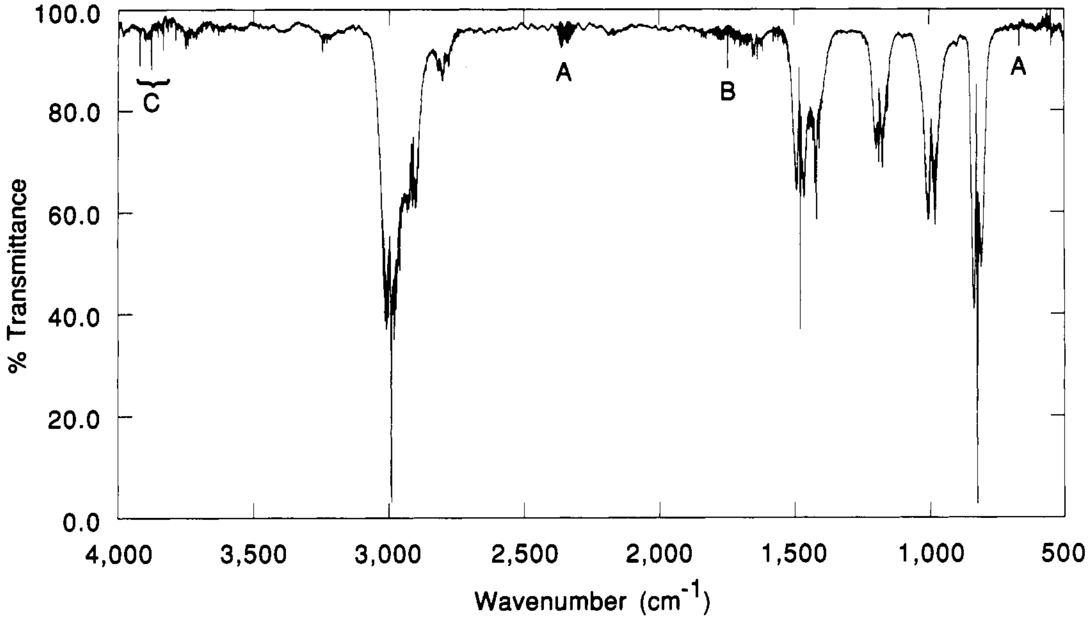

Figure 1. Midinfrared spectrum of methyl hypofluorite: sample pressure, ca. 50 Torr; optical path, 10 cm. Bands marked A are assigned to CO_2 impurity. Bands marked B and C are assigned, respectively, to H_2CO and HF decomposition products.

Table II. Principal Infrared Frequencies of Methyl Hypofluorite

frequency, cm^{-1} (intensity)	tentative assignment
2991 (s)	CH_3 stretch
2914 (m)	
2803[a] (w)	
1479 (m)	CH_3 deform
1476 (m)	
1418 (m)	
1188 (m)	CH_3 rock
994 (m)	C–O (or O–F) stretch
824.5 (s)	O–F (or C–O) stretch

[a] May instead be 2 × 1418.

purified liquid samples held at about −115 °C. The principal mass peaks are observed at *m/e* 50 (M^+, 70%), 29 (HCO^+, 100%), and 15 (CH_3^+, 80%).

The vapor pressure of methyl hypofluorite as a function of temperature is presented in Table I. The results indicate an enthalpy of vaporization of 23.37 ± 0.26 kJ/mol and yield an extrapolated normal boiling point of −32.6 ± 0.9 °C, where uncertainties are given at the 2σ level.

The midinfrared spectrum of CH_3OF vapor is shown in Figure 1, and the principal bands are listed and tentatively assigned in Table II. Assignments are based on analogy with CH_3OH and CF_3OF.[13,14] As in the case of CF_3OF, an ambiguity exists in distinguishing between the C–O and O–F stretching frequencies.[15]

The ^{19}F NMR spectrum of CH_3OF shows the low-field quartet expected for a relatively deshielded fluorine atom coupled to the three protons of a methyl group (+120.3 ppm, $^3J_{HF}$ = 45–46 Hz). The ^1H NMR spectrum exhibits a corresponding doublet (4.51 ppm, $^3J_{HF}$ = 45.2 Hz), and the proton-decoupled ^{13}C spectrum also shows a doublet (70.3 ppm, $^2J_{CF}$ = 11 Hz). The assignment of these resonances to CH_3OF was confirmed by observing their disappearance as the compound decomposed.

Methyl hypofluorite adds readily to several types of olefins to produce the corresponding α-fluoro methoxy compounds in yields ranging from 60 to 75%. Thus, styrene and 1,1-diphenylethene (**1** and **3**; Scheme I) yield, respectively, 1-fluoro-1-phenyl-2-methoxyethane and 1,1-diphenyl-1-fluoro-2-methoxyethane (**2** and **4**). Addition of the radical scavenger *m*-dinitrobenzene had no effect on the formation of **2** or its yield, nor did irradiation of a solution containing **1** and CH_3OF with a sun lamp at −40 °C result in a reaction. However, when the irradiation was carried out at room temperature, a fast radical destruction of both the substrate and the CH_3OF took place, and no single product could be isolated.

With nonterminal alkenes, stereochemical considerations become relevant. *trans*- and *cis*-stilbene (**5** and **8**; Scheme II) both react with CH_3OF to give a mixture of *threo*- and *erythro*-1-fluoro-2-methoxy-1,2-diphenylethane (**6** and **7**).[10] The results show that while there is some preference for syn addition, the reaction is mainly thermodynamically controlled.

Acenaphthylene (**9**; Scheme III) reacts with CH_3OF to produce a 2.3/1 mixture of *trans*- and *cis*-1-fluoro-2-methoxyacenaphthene (**10**).[11] Nonbenzylic olefins also react successfully, as is demonstrated by cyclooctene (**11**), which is converted to 1-fluoro-2-methoxycyclooctane (**12**).[12]

Discussion

The mass, infrared, and NMR spectra reported here for our new substance, in combination with its chemical behavior and the identity of its decomposition products, leave little doubt that we are dealing with a molecule (CH_3OF) analogous to the well-known trifluoromethyl hypofluorite (CF_3OF). The identification is also supported by the high volatility of the compound, which is much more volatile than HOF,[4] though less so than CF_3OF.[16] This volatility and the compound's unexpectedly high degree of kinetic stability have combined to make its isolation, purification, and characterization relatively uncomplicated. (*But see the discussion of the explosion hazard in the Experimental Section.*)

The mass spectrum of methyl hypofluorite shows a prominent peak associated with the molecular ion. In this respect, CH_3OF resembles HOF[4] but differs from CF_3OF and acetyl hypofluorite.[6,17] The infrared spectrum can be accounted for satisfactorily from consideration of the spectra of CH_3OH and CF_3OF,[13,14] although the two bands considered as candidates for the O–F stretch are, respectively, somewhat lower and somewhat higher in frequency than the O–F stretching bands of other hypofluorites.[2]

The ^{19}F NMR shift of 120 ppm implies a substantially deshielded fluorine atom, as would be expected for a fluoroxy compound.[2] The shift is somewhat less than in the perfluoroalkyl hypofluorites (CF_3OF, 147 ppm; C_2F_5OF, 139 ppm)[2] or in acetyl hypofluorite (168 ppm).[6,18] We may note that all of these shifts

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(14) Wilt, P. M.; Jones, E. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2933–2948.
(15) Smardzewski, R. R.; Fox, W. B. *J. Fluorine Chem.* **1975**, *6*, 417–425.
(16) Porter, R. S.; Cady, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 5628–5631.
(17) Huston, J. L.; Studier, M. H. *J. Fluorine Chem.* **1979**, *13*, 235–249.
(18) Hebel, D.; Lerman, O.; Rozen, S. *J. Fluorine Chem.* **1985**, *30*, 141–146.

are considerably more positive than that of hypofluorous acid (21 ppm).[19] Ghibaudi et al.[20] have attempted to correlate the ^{19}F NMR shifts in hypofluorites with the O–F bond energies, but their effort suffers from the use of an obsolete value for the energy of the O–F bond in HOF. If we update their correlation, we may conclude that CH_3OF should have an O–F bond energy between 200 and 205 kJ/mol, stronger than that of any hypofluorite other than HOF (211 kJ/mol).[21]

The vicinal H–F coupling through carbon and oxygen is unique to the CH_3OF molecule; the value of $^3J_{HF} = 45\text{–}46$ Hz is substantially larger than typical three-bond H–F couplings through two carbon atoms or through carbon and nitrogen.[22,23] The geminal C–F coupling through oxygen ($^2J_{CF} = 11$ Hz) may be compared with the value of 7 Hz found for CF_3OF.[24]

The addition of CH_3OF across double bonds to form α-fluoro methoxy compounds constitutes behavior expected for an alkyl hypofluorite and is analogous to the reactions of CF_3OF.[25,26] The fact that the simple products obtained from the reactions with styrene and 1,1-diphenylethene seem not to have been previously described in the literature illustrates the absence of general methods for the preparation of β-fluoro ethers and suggests that CH_3OF may find significant application as a synthetic reagent. (See also, however, ref 12.) The failure of irradiation to accelerate reaction in these systems implies that the CH_3OF is reacting by an ionic mechanism characteristic of many fluoroxy compounds.[25,27]

The stereospecificity of CH_3OF is much lower than that of other electrophilic fluorination reagents, which are characterized by an unstable α-fluorocarbocation intermediate that leads to predominantly syn addition.[28,29] This difference could be understood if the fluorine atom in CH_3OF were much less electrophilic than those of other OF-containing reagents, so that the attack of the olefin's π electrons would be concentrated mainly on the relatively electron-depleted oxygen atom. The resulting α-oxycarbocation, with its resonant cyclic oxonium form, would not constitute a very tight ion pair and would have a good chance to lose its stereoselectivity (Scheme II). Diffusion of the fluoride ion out of the ion pair cage is even more conspicuous in the case of acenaphthylene (**9**), for which no rotation around the central σ bond is possible. This rationalization is consistent with the regioselectivity of the reactions of CH_3OF with the unsymmetrical olefins **1** and **3**, in which the reagent resembles HOF[30] more than it does CF_3OF.[25]

In view of the conventional wisdom that it would be difficult, if not impossible, to bond an OF moiety directly to a hydrogen-bearing carbon atom, the relative ease with which CH_3OF can be prepared, isolated, and handled is somewhat unexpected. In fact, CH_3OF appears to be somewhat more kinetically stable than either HOF or acetyl hypofluorite. And what is perhaps especially remarkable is that a compound that is so easily made could have remained unknown for so long.

Taking into consideration recent developments in the field of hypofluorite chemistry, there appears to be little reason left to discourage researchers from attempting the synthesis of hypofluorites of almost any sort. Rozen and Hebel[7] have undertaken to develop a rationale for predicting which acyl hypofluorites can be synthesized, based on the presence or absence of electronegative groups in the 2-position and on the spatial proximity of the hypofluorite fluorine atom to hydrogen atoms in the molecule. It remains to be determined whether such considerations will prove to be useful predictors for the preparation of other types of hypofluorites. In any case, determined efforts may be expected to lead to the identification of a wide variety of further examples of these interesting compounds, at least some of which are likely to have useful properties as synthetic and analytical reagents.

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(26) Addition of the elements CH_3O and F across double bonds is not in itself compelling evidence for the existence of a CH_3OF molecule, since such addition can also be accomplished with use of methanol as solvent for the reaction of an olefin or acetylene with a source of electrophilic fluorine such as F_2, CF_3OF, $FClO_3$, $CsSO_4F$, or XeF_2. The methanol can capture the intermediate fluorocarbocation to produce fluoro methoxy adducts: (a) Merritt, R. F. *J. Am. Chem. Soc.* **1967**, *89*, 609–612. (b) Merritt, R. F. *J. Org. Chem.* **1967**, *32*, 4124–4126. (c) Barton, D. H. R.; Hesse, R. H.; Jackman, G. P.; Pechet, M. M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2604–2608. (d) Djuric, S. W.; Garland, R. B.; Nystead, L. N.; Pappo, R.; Plume, G.; Swenton, L. *J. Org. Chem.* **1987**, *52*, 978–990. (e) Shellhamer, D. F.; Curtis, C. M.; Hollingsworth, D. R.; Ragains, M. L.; Richardson, R. E.; Heasley, V. L.; Heasley, G. E. *Tetrahedron Lett.* **1982**, *23*, 2157–2160. (f) Shellhamer, D. F.; Curtis, C. M.; Dunham, R. H.; Hollingsworth, D. R.; Ragains, M. L.; Richardson, R. E.; Heasley, V. L.; Shackelford, S. A.; Heasley, G. E. *J. Org. Chem.* **1985**, *50*, 2751–2758. In their first paper, Shellhamer et al. actually claimed the formation of CH_3OF, but this claim was withdrawn in their second paper. For reactions involving $CsSO_4F$, see ref 11.

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