Isolation and Characterization of Acetyl Hypofluorite[1]

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Abstract: Acetyl hypofluorite, $H_3CC(O)OF$, has been prepared by passage of diluted fluorine through solid $KOAc \cdot 2HOAc$ and isolated by trapping at −78 °C. It is a slightly yellow liquid (mp ca. −96 °C) with a vapor pressure of about 4 torr at −40 °C. Vapor-pressure measurements between −64 and −20 °C lead to an enthalpy of vaporization of 35.6 ± 2.4 kJ/mol and an extrapolated normal boiling point of 53 ± 6 °C. At −78 °C, in 1:1 (v/v) CCl_4:$CDCl_3$, its ^{19}F NMR shift is 168.3 ppm vs. $CFCl_3$. Its mass spectrum has been measured, as has its infrared spectrum in a solid argon matrix, and these support its identification. The vapor absorbs in the far ultraviolet, with an absorption maximum at 210 nm ($\epsilon \sim 103$ L/mol·cm). The compound is of limited stability, particularly in the liquid phase, which sometimes explodes. The vapor is more stable, with a 2-h half-life at room temperature in Kel-F. The half-life is much shorter in Monel. Decomposition is inhibited by O_2. Decomposition in a Kel-F container gives nearly quantitatively a 1:1 mixture of CH_3F and CO_2, but in a Monel apparatus or in the presence of O_2, substantial amounts of $H_3COC(O)F$ are formed.

It is rather unusual for the chemical behavior of a compound to be explored in detail before the compound itself has been isolated or even positively identified. Such, however, appears to be the case with acetyl hypofluorite, $H_3CC(O)OF$. Unlike its perfluorinated analogue, $F_3CC(O)OF$, which has been known since 1953,[3] acetyl hypofluorite has only recently come upon the scene. The synthesis of this compound was first reported to result from passage of a fluorine–nitrogen mixture through a suspension of sodium acetate in a mixture of acetic acid and $CFCl_3$ at −78 °C.[4] Subsequent preparations have been effected by passage of nitrogen-diluted fluorine through solutions of ammonium or alkali acetates in glacial acetic acid at room temperature[5,6] and through the solid compound $KOAc \cdot 2HOAc$.[7] In none of these cases was the hypofluorite isolated. Either a reactive organic substrate was added directly to the reaction mixture or the hypofluorite was transferred via a stream of nitrogen into a solution of the substrate. The identity of the hypofluorite was deduced from the nature of the reaction products. In this way, acetyl hypofluorite has become established as a useful reagent for organic fluorinations and particulary for the preparation of ^{18}F-labelled compounds for positron-emission tomography, even though it cannot be said that its identity has been incontrovertibly established.[8]

Although the reaction chemistry that has been elucidated strongly supports the identification of the reagent as acetyl hypofluorite, it can be argued that the evidence is not entirely conclusive, and it is to resolve this ambiguity that we have undertaken the present study. The solvent-free preparative technique developed by Jewett et al.[7] seemed especially suited to an effort to make neat acetyl hypofluorite, and we took this procedure as the starting point for our synthesis.

(1) Work performed under the auspices of the Office of Basic Energy Sciences, Divisions of Chemical and Materials Sciences, U.S. Department of Energy.

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(8) While the present paper was in preparation, two manuscripts describing the ^{19}F NMR spectrum of acetyl hypofluorite were submitted for publication: (a) Diksic, M.; Farrokhzad, S.; Colebrook, L. D. *Can. J. Chem.*, in press. (b) Hebel, D.; Lerman, O.; Rozen, S. *J. Fluorine Chem.*, in press. Diksic et al. measured the spectrum in acetic acid at ambient temperature; Hebel et al. measured it in $CFCl_3$ at −78 °C. Hebel et al. also measured the ^1H NMR spectrum of the same solution and the decomposition to CH_3F and CO_2. Both groups obtained results that are entirely concordant with ours.

Experimental Section

Reagents. Fluorine was a commercial product of technical grade (Air Products Corp.), purchased as a 20% v/v mixture in nitrogen. Nitrogen and argon were of prepurified grade, and oxygen was ultra high purity grade. Potassium acetate, acetic acid, and other chemicals were commercial products of analytical reagent grade.

Preparation and Purification of Acetyl Hypofluorite. *CAUTION: Liquid acetyl hypofluorite is an unpredictably explosive material. In our work explosions have occurred even at temperatures below −80 °C. To minimize the explosion hazard, we recommend that preparations of neat acetyl hypofluorite be limited to 0.2 mmol or less.*

Acetyl hypofluorite was made and handled in an apparatus fabricated from Teflon or Kel-F, with the exception of the Monel vacuum line and pressure gauge used for pressure measurements. Our preparations made use of the method of Jewett et al.[7] Our 20% v/v F_2 in N_2 was diluted further, with use of mass flowmeters to control the dilution, and passed through 20–30 g of $KOAc \cdot 2HOAc$ contained in a Teflon PFA in-line filter assembly (Savillex Corp.) between two Teflon filter discs of coarse porosity. Although no great effort was made to optimize the yield of product, we did find that dilution with oxygen instead of nitrogen increased yields substantially, particularly when higher fluorine concentrations were used. Thus the use of oxygen as a diluent allowed us to obtain respectable yields of acetyl hypofluorite with fluorine concentrations at least as high as 5% v/v, whereas when nitrogen was used, as noted by Jewett et al.,[7] good yields could only be obtained with fluorine concentrations below 1%. The crude product was collected in a Kel-F U-tube cooled with dry ice. It was contaminated with a small quantity of acetyl fluoride and larger amounts of acetic acid. The acetyl fluoride was removed by pumping on the sample from a dry ice bath in high vacuum while monitoring the mass spectrum, until the peak at $m/e = 62$ became small relative to the one at $m/e = 78$. (This is a very sensitive test, since 62 is a major peak of acetyl fluoride, whereas 78 is a minor peak of acetyl hypofluorite.) The product was freed from acetic acid by distilling it in high vacuum through a U-tube cooled in a chloroform slush (−65 °C) and collecting it in a U-tube cooled with liquid nitrogen. This redistillation usually resulted in considerable loss of product by decomposition. A more convenient, though slightly less thorough method of removing acetic acid entails placing a suitable cold trap upstream of the product-collecting U-tube during the preparation. The optimal temperature for this trap is a function of the fluorine concentration in the gas stream, since it should be the lowest temperature that will not hold up product. For a gas stream that is 2% in fluorine, a carbon tetrachloride slush (−23 °C) is appropriate.

Mass Spectrometry. The mass spectrum of acetyl hypofluorite and qualitative mass spectra of its decomposition products were obtained with a Finnigan Model 400 quadrupole mass spectrometer. Samples were introduced through a Kel-F inlet line protruding directly into the ion source. In the case of acetyl hypofluorite itself, the best spectra were obtained by sampling the vapor while pumping on a sample held in a dry ice bath. Precision measurement of ratios of decomposition products were carried out with a Consolidated Model 21-620 magnetic sector mass spectrometer.

NMR Spectrometry. NMR spectra were measured on a Bruker Model AM 300 spectrometer. ^{19}F spectra were referenced against an internal $CFCl_3$ standard. Upfield shifts are indicated as negative. Acetyl hypofluorite samples were measured at −78 °C in a 1:1 (v/v) mixture

Table I. Vibrational Bands of Acetyl Hypofluorite

obsd freq, cm^{-1}	assgnt[a]	approx descrpn[a]	other contribns
2950 w	$\nu_1(A')$, $\nu_{13}(A'')$	asym C–H str	
2910 vw	$\nu_2(A')$	sym C–H str	
1839 vs⎫ 1817 vs⎭	$\nu_3(A')$	C=O str (71)	C–C str (11)
1789 m	?		
1434 m⎫ 1424 sh⎭	$\nu_4(A')$	sym CH$_3$ wag [C–C–H bend (36); H–C–H bend (30)]	C–C str (18)
1372 sh⎫ 1368 s⎭	$\nu_5(A')$, $\nu_{14}(A'')$	asym CH$_3$ wag	
1203 s⎫ 1164 vs⎭	$\nu_6(A')$	C–O str (28)	C–C–O/C–C=O bend (20), C–C–H bend (20), H–C–H bend (14), C–C str (13)
1043 sh⎫ 1034 m⎭	$\nu_{15}(A'')$	CH$_3$ rock (80)	
1015 sh⎫ 1005 m⎭	$\nu_7(A')$	CH$_3$ rock (64)	O–F str (16)
900 m⎫ 840 s⎭	$\nu_8(A')$	O–F str (64)	C–C–H bend (15), C–C str (13)
790 m	$\nu_9(A')$	C–O str (40)	C–C str (20), C=O str (17)
665 s⎫ 625 s⎭	$\nu_{16}(A'')$	C=O bend (80)	
590 m⎫ 550 w⎭	$\nu_{10}(A')$	C–C=O bend (56)	C–C str (21), C–O–F bend (11)
490 w⎫ 430 w⎭	$\nu_{11}(A')$	C–C–O bend (41)	C–C=O bend (25), O–F str (12), C–O str (11)

[a] Numbers in parentheses are % contributions of valence force constants to the potential energy of each vibrational mode (minor contributions not indicated). A' vibrations are in-plane; A'' vibrations are out-of-plane.

of CCl$_4$ and CDCl$_3$ contained in a tube sealed under ca. 0.5 atm of oxygen to retard decomposition. The methyl fluoroformate decomposition product was measured in CDCl$_3$ at room temperature in an evacuated and sealed tube. A few measurements of the acetyl hypofluorite resonance were also made at room temperature in glacial acetic acid containing 0.15 M potassium acetate, and an attempt was made to measure it in D$_2$O.

Matrix Preparation and Optical Spectrophotometry. Matrices in argon were deposited on a CsI disc cooled to ca. 17 K by means of a closed-cycle helium refrigerator (CTI Cryogenics). The cooled disc was mounted in a vacuum shroud fitted with cesium iodide windows for infrared measurements and a fused silica window for photolysis. Acetyl hypofluorite matrices were prepared by passing argon at ca. 6 std cm^3/min through a U-tube containing the acetyl hypofluorite at –78 °C and then through a Kel-F inlet tube directed at the cooled CsI disc. Matrices of methyl fluoroformate decomposition product were prepared similarly. Matrices of the CO$_2$–CH$_3$F decomposition product mixture were prepared by diluting this mixture 100-fold with argon and then depositing the diluted mixture at a rate of ca. 6 std cm^3/min. To facilitate interpretation of the infrared spectrum of the acetyl hypofluorite matrix, it was subjected to photolysis with radiation from a 200-W high-pressure mercury lamp that was filtered through water. Infrared bands of acetyl hypofluorite decreased on photolysis, while those of CH$_3$F and CO$_2$ increased. Infrared spectra were measured with a Beckman Model IR 4260 spectrophotometer. Ultraviolet spectra were measured with a Cary 14 spectrophotometer. Samples for gas-phase measurements were contained in a Kel-F cell of 52 cm^3 volume and 10 cm light path. Silver chloride windows were used for infrared measurements; sapphire windows were used for the ultraviolet.

Vapor Pressure of Acetyl Hypofluorite. The instability of liquid acetyl hypofluorite necessitated an unusual method of measuring its vapor pressure. The effluent from the reactor in which the compound was prepared was passed through a cold trap that consisted of a Kel-F U-tube packed with Teflon Raschig rings. The Kel-F gas-phase spectrophotometer cell described above was evacuated and filled with the effluent from this cold trap, and the ultraviolet absorption spectrum of the acetyl hypofluorite was measured as a function of trap temperature. Particular reliance was placed on measurements at 220 nm, where the absorption by acetyl hypofluorite was near its maximum and that of possible impurities and decomposition products was quite low. The extinction coefficient of the acetyl hypofluorite was determined (with an uncertainty of 5–10%) by measuring the UV absorption of a sample in an oxygen atmosphere, pumping the oxygen away through a U-tube cooled with liquid nitrogen, removing any initially present CH$_3$F and CO$_2$ by taking vapor heads at –78 °C, allowing the sample to warm up and decompose, and finally measuring the pressure of the decomposition products.

Other Measurements. Pressures of the decomposition products of acetyl hypofluorite were measured in a Monel vacuum line, using a

Monel Bourdon gauge with a resolution of approximately 1 torr. The melting point of acetyl hypofluorite was measured in a Kel-F tube under an atmosphere of oxygen to retard decomposition. Thermometers were calibrated against a copper–constantan thermocouple.

Results

At low temperature acetyl hypofluorite is a white solid, melting at –96 ± 1 °C to a pale yellow liquid. At –78 °C the compound's ^{19}F NMR spectrum, measured in 1:1 (v/v) CCl$_4$/CDCl$_3$, shows a single line with a shift of 168.3 ppm vs. CFCl$_3$. When an oxygen stream containing acetyl hypofluorite was passed into a room-temperature solution of 0.15 M potassium acetate in glacial acetic acid, a relatively broad line (half-width ca. 800 Hz) was seen with a shift of 163 ppm. The same resonance was observed, though at much lower intensity, when the oxygen stream contained 2% v/v fluorine, but no acetyl hypofluorite. The resonance in acetic acid is not stable but decays substantially over 15–30 min. A strong resonance was observed to grow in at –267.6 ppm, along with weaker ones at –18.7 and –115.4 ppm. The first two of these were assigned respectively to CH$_3$F and H$_3$COC(O)F (methyl fluoroformate),[9,10] while the third was not identified. When an oxygen stream containing acetyl hypofluorite was passed into D$_2$O, no hypofluorite ^{19}F resonance was detectable in the solution 5–10 min after addition of the reagent.
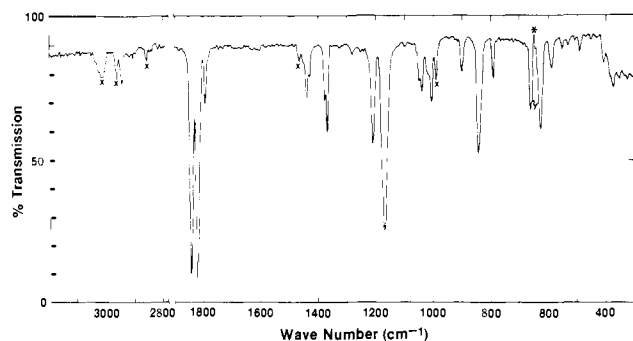
The mass spectrum of acetyl hypofluorite is dominated by peaks at m/e = 43 (CH$_3$CO$^+$, 100%) and 15 (CH$_3^+$, 67%), with smaller peaks at 14 (CH$_2^+$, 14%), 29 (HCO$^+$, 10%), and 45 (HC(O)O$^+$, 7%). The acetyl hypofluorite molecular ion peak at m/e = 78 is only present to the extent of about 3%. Minor and variable peaks attributable to CH$_3$F and CO$_2$ are seen at m/e = 33, 34, and 44 and are probably the result of decomposition, though they could also result in part from rearrangement during fragmentation.

Acetyl hypofluorite vapor absorbs in the far ultraviolet, with an absorption maximum at 210 nm ($\epsilon \sim 103$ L/mol·cm). The infrared spectrum of matrix-isolated acetyl hypofluorite is shown in Figure 1, and the principal vibrational bands are tabulated in the first column of Table I.

The vapor pressure of acetyl hypofluorite is presented in Table II. The results indicate an enthalpy of vaporization of 35.6 ± 2.4 kJ/mol and imply a normal boiling point of 53 ± 6 °C, where

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Figure 1. Infrared spectrum of acetyl hypofluorite in an argon matrix at ca. 17 K. Resolution 2–3 cm⁻¹ above 650 cm⁻¹; 8–15 cm⁻¹ between 650 and 550 cm⁻¹; 5–7 cm⁻¹ below 550 cm⁻¹. Vertical scale of spectrum above 2800 cm⁻¹ has been expanded two-fold. Bands marked X are assigned to CH_3F; band marked Y is assigned to CO_2; feature marked * is an instrumental artifact. Bands of CH_3F and CO_2 are assigned on the basis of a reference spectrum obtained after depositing an argon matrix that was ca. 0.5% v/v in each of these compounds. Deposition of another reference matrix containing $H_3COC(O)F$ indicated that no bands belonging to this species were present in the acetyl hypofluorite matrix.

Table II. Vapor Pressure of Acetyl Hypofluorite

temp, °C	optical density[a]	vapor pressure, torr	
		obsd	calcd[b]
−64.1	0.029	0.55	0.49
−60.1	0.033	0.62	0.71
−49.2	0.100	1.89	1.90
−40.0	0.213	4.0	4.0
−30.4	0.454	8.6	8.3
−20.4	0.885	16.7	16.8

[a] Of vapor saturated at indicated temperature, measured at 220 nm through 10 cm light path. [b] From equation: $\ln p(\text{torr}) = 19.763 - 4282/T(\text{K})$. Correlation coefficient is −0.9983.

uncertainties are indicated as 2σ.

At −78 °C acetyl hypofluorite usually shows little or no decomposition (*but see cautionary note in Experimental Section*), and in a Kel-F container the vapor is reasonably stable even at room temperature, a typical initial half-time for decomposition being of the order of 2 h. Decomposition is much more rapid when the vapor is exposed to a Monel apparatus. The liquid appears to be much less stable than the vapor, and rapid (*and sometimes violent*) decomposition can take place rather unpredictably even at low temperature. Both liquid and vapor, however, are stabilized greatly by the presence of oxygen. In a Kel-F vessel containing ca. 0.5 atm of O_2, the initial decomposition half-time of 20 torr of vapor at room temperature is approximately 20 h.

The decomposition in Kel-F produces a gaseous product over 97% of which has a large vapor pressure at −78 °C. This highly volatile product consists principally of an equimolar mixture of CH_3F and CO_2, along with traces of C_2H_6 and CH_2F_2. In a typical decomposition experiment, a 25.9-mg sample (0.332 mmol as $H_3CC(O)OF$) decomposed to yield 14.74 cm³ of gaseous material at STP (0.658 mmol). This material was found by mass spectrometric analysis to consist of 50.3 mol % CH_3F and 49.7 mol % CO_2. The very small amount of less volatile product appears from its mass spectrum to consist primarily of methyl acetate, along with some residual acetic acid impurity.

When decomposition takes place in Monel or in the presence of oxygen, a great deal more material of lower volatility is formed, constituting ca. 20% of the gaseous product. This material was identified as methyl fluoroformate, $H_3COC(O)F$, by its ¹⁹F NMR and gas-phase infrared spectra, which agree with those reported in the literature,[10,11] and by its mass spectrum, which appears not to have been hitherto reported: m/e = 78 (M⁺, 4.6%), 77 ([M

− 1]⁺, 9%), 47 (FCO⁺, 42%), 31 (H_3CO^+, 100%), 29 (HCO⁺, 40%), 15 (CH_3^+, 30%).

Discussion

The physical properties and mode of decomposition of the material that we have synthesized clearly establish it as acetyl hypofluorite. The mass spectral fragmenting pattern is reasonable for such a compound, and the ¹⁹F NMR shift is in the same region as those of other hypofluorites.[12] From the NMR spectrum, we may also conclude that our product is the same as the one that results from passage of fluorine through acetic acid containing alkali acetate.[6,8a]
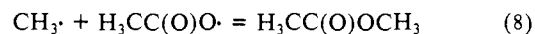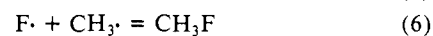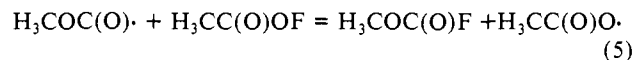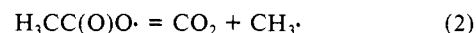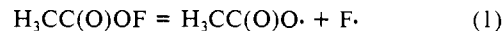
The infrared spectrum of acetyl hypofluorite shows distinct similarities to that of the isoelectronic peroxyacetic acid, $H_3CC(O)OOH$.[13] We have carried out a preliminary normal coordinate analysis of the acetyl hypofluorite molecule,[14] using valence force constants taken from other molecules of similar structure and assuming that the skeleton of the molecule is planar. The latter assumption appears to be justified in the case of the peroxyacids.[15] The resulting *tentative* assignments of the principal vibrational bands are given in Table I. We were unable to interpret the band at 1789 cm⁻¹. Three of the expected low-frequency fundamental vibrations were not observed: the C–O–F bend ν_{12}, expected at 250–300 cm⁻¹, and the C–O and C–C torsions ν_{18} and ν_{19}, expected at 100–200 cm⁻¹. As can be seen from Table I, the simple valence modes are mixed in many of the fundamentals, often to such an extent that the bands defy straightforward description.

A number of the bands show marked splittings. These seem too large to be accounted for solely by differences in site symmetry, and we suggest that they may reflect the presence of rotational isomers in which the fluorine atom is either cis or trans to the carbonyl oxygen. Our preliminary calculations indicate that such rotational isomerism about the C–O bond could indeed account for the observed splittings. A similar explanation has been suggested for some of the splittings observed in the infrared spectrum of fluorocarbonyl hypofluorite, $FC(O)OF$.[16] We may note that in the case of peroxyacetic acid the intramolecular hydrogen bond may be expected to lock the molecule into the cis conformation.

A detailed study of the molecular spectra of acetyl and trifluoroacetyl hypofluorites is now being undertaken.

As might have been anticipated, acetyl hypofluorite is considerably less volatile than its perfluorinated derivative, $F_3CC(O)OF$.[3] If we take our value of 35.6 kJ/mol for the enthalpy of vaporization and estimate that it may decrease as much as 10% to ca. 32 kJ/mol at the extrapolated normal boiling point of 53 °C (326 K), we obtain a Trouton's constant of 98 J/mol·K. The difference from the "normal" value of 88 seems barely significant and may reflect association in liquid acetyl hypofluorite.

The dominant mode of decomposition of acetyl hypofluorite is to CH_3F and CO_2, but the formation of ethane and methyl fluoroformate, as well as the catalysis by metal and inhibition by oxygen, point to a free-radical mechanism as opposed to a simple unimolecular decomposition. The methyl fluoroformate presumably results from rearrangement of an initially formed acetate radical. A possible reaction scheme is the following:

$$H_3CC(O)OF = H_3CC(O)O\cdot + F\cdot \tag{1}$$

$$H_3CC(O)O\cdot = CO_2 + CH_3\cdot \tag{2}$$

$$H_3CC(O)O\cdot = H_3COC(O)\cdot \tag{3}$$

$$CH_3\cdot + H_3CC(O)OF = CH_3F + H_3CC(O)O\cdot \tag{4}$$

$$H_3COC(O)\cdot + H_3CC(O)OF = H_3COC(O)F + H_3CC(O)O\cdot \tag{5}$$

$$F\cdot + CH_3\cdot = CH_3F \tag{6}$$

$$2CH_3\cdot = C_2H_6 \tag{7}$$

$$CH_3\cdot + H_3CC(O)O\cdot = H_3CC(O)OCH_3 \tag{8}$$

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Rearrangement 3 would appear to be catalyzed by metal surfaces.

The stabilizing action of molecular oxygen presumably results from its reaction with atoms and free radicals to produce less reactive peroxy species. The role of oxygen in enhancing the yield of methyl fluoroformate is not clear. It may have the effect of stabilizing the acetate radical, allowing more time for rearrangement 3 to take place.

The analogous decomposition of trifluoroacetyl hypofluorite to CF_4 and CO_2 has also been found to be catalyzed by metal and inhibited by oxygen.[17] Hexafluoroethane is a minor product of this decomposition, though trifluoromethyl fluoroformate is not. However, carbonyl fluoride is formed. It may be that in the trifluoroacetyl system, the reaction analogous to reaction 5 produces two molecules of COF_2 instead of a molecule of F_3COC-(O)F.

The authors of the first report on acetyl hypofluorite took special note of the fact that it was the only hypofluorite to contain an unfluorinated alkyl radical.[4a] Indeed, aside from HOF itself, it is the only hypofluorite that contains hydrogen. This fact, however, appears to be of considerably less significance for acetyl hypofluorite than for HOF. Decomposition of HOF proceeds with elimination of O_2 and formation of HF;[18] the analogous decomposition of acetyl hypofluorite to HF, CO_2, and C_2H_4 does not take place. The decomposition of acetyl hypofluorite appears to be closely analogous to that of trifluoroacetyl hypofluorite, and at least to a first approximation, there is no reason to expect their stabilities to be grossly different. In fact, the two compounds do appear to be of very roughly comparable stability.

In view of its instability, the isolation of acetyl hypofluorite may be of only limited significance for its use as a synthetic reagent.

For such applications, it would appear safest to continue to use the compound without isolation, either by addition of substrate to a dilute solution of the reagent or by carrying the reagent with a gas stream into a solution of a substrate. In the latter case, our observations indicate that it will be advantageous to use oxygen rather than nitrogen as a carrier.

Finally, it seems worthwhile to note that hazards may exist even if the acetyl hypofluorite is not explicitly isolated. Fluorination of acetates in Freon at low temperatures can, at least in principle, produce dangerously high concentrations of acetyl hypofluorite, and delivery of acetyl hypofluorite in a gas stream into a cold reaction medium can lead to condensation of the reagent. An explosion resulting from the latter conditions has already been reported.[19]

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Effect of Thiolate vs. Nitrogen-Base Ligands on O_2 Stretching Frequencies of (Oxytetraphenylporphyrinato)cobalt

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Abstract: The resonance Raman spectra of model compounds of oxycytochrome P-450, $K^{Cr}[Co(TPP)(SC_6H_5)^{16}O_2]$ (K^{Cr}: potassium 18-crown-6 ether) and its $^{18}O_2$ analogue were located at 1122 and 1058 cm⁻¹, respectively, in CH_2Cl_2 solution at ~185 K with 457.9-nm excitation. The $\nu(^{16}O_2)$ of this compound is lower by 22 cm⁻¹ than that of a model compound of oxyhemoglobin, $Co(TPP)(1-MeIm)^{16}O_2$ (1144 cm⁻¹), measured under similar conditions. The observed shift has been attributed to the presence of lone-pair electrons on the thiolate sulfur atom which donate extra electron density to dioxygen via π overlap. The $\nu(O_2)$ of $K^{Cr}[Co(TPP)(SCH_2C_6H_5)^{16}O_2]$ and its $^{18}O_2$ analogue are observed at 1120 and 1055 cm⁻¹, respectively, by 476.5-nm excitation. The small shift of $\nu(O_2)$ observed by replacing the $SC_6H_5^-$ with $SCH_2C_6H_5^-$ ion indicates that the degree of total electron donation to dioxygen via σ and π overlap is similar for these two compounds. When a CH_2Cl_2 solution of crystalline $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ is saturated with dioxygen at ~185 K and warmed to ~225 K, a new $\nu(O_2)$ band appears at 1137 cm⁻¹ which is assigned to $[Co(TPP)(HSC_6H_5)O_2]$. The electronic spectrum of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ in CH_2Cl_2 solution exhibits the α and β bands at 620 and 522 nm, respectively, and a split Soret band at 468 and 423 nm. The excitation profile of the $\nu(O_2)$ (1122 cm⁻¹) suggests that the 468-nm component contains substantial Co–O_2 character.

It is generally recognized that the active site of oxycytochrome P-450 during the reaction cycle[1] is a six-coordinate iron protoporphyrin (low spin) in which dioxygen is coordinated trans to the thiolate sulfur of a cysteinyl residue (structure I). This

$$
\begin{array}{cc}
\text{O}_2 & \text{O}_2 \\
| & | \\
-\text{Fe}- & -\text{Fe}- \\
| & | \\
\text{SR}^- & \text{N(Im)} \\
\text{I} & \text{II}
\end{array}
$$

structure is similar to that of oxyhemoglobin (low spin) except that the group trans to its dioxygen in oxyhemoglobin is the imidazole nitrogen of the proximal histidine (structure II). In cytochrome P-450, the O–O bond is cleaved after one-electron reduction by NADH, and the activated oxygen thus produced or released from the ferryl (FeO) bond is utilized for hydroxylation of a substrate.[2] On the other hand, hemoglobin binds dioxygen reversibly without the O–O bond cleavage. It is, therefore, of great interest to compare the effect of these two axial ligands on the bound dioxygen.

(1) For example, see: Alexander, L. S.; Goff, H. M. *J. Chem. Educ.* **1982**, *59*, 179.

(2) Groves, J. T.; McClusky, G. A. "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 277.