shown in eq 5 requires very little opening of the unbroken Al–C–Al bond angle to facilitate rotation. However, in **4**, the bond angle must be opened further to allow attack by a TMA monomer. This is consistent with the slightly higher activation energy and the more negative entropy of activation found for the exchange between **1** and **3** and compared to the exchange in TPTA.

Registry No. TPTA dimer, 17439-80-4; TMTA dimer, 56030-41-2; TMA dimer, 15632-54-9; tetramethyldi-*p*-tolylaluminum, 17439-75-7; pentamethyl-*p*-tolylaluminum, 17439-77-9.

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Raman Spectra of Trifluoromethylsulfinyl Fluoride, Trifluoromethylsulfinyl Chloride, and Sulfinyl Chloride Fluoride

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Gas-phase infrared (2000–400 cm^{-1}) and liquid-phase Raman spectra (2000–100 cm^{-1}) for $CF_3S(O)F$, $CF_3S(O)Cl$, and $FS(O)Cl$ are reported, and vibrational analyses are made for the three molecules. Depolarization ratio measurements indicate that the compounds belong to symmetry species C_1 and thus are pyramidal in agreement with lone-pair repulsion considerations.

Introduction

A relatively large number of sulfinyl halides have been synthesized and characterized by vibrational spectral analyses.[1-7] We report here the infrared and Raman spectra and vibrational assignments for the unsymmetrical sulfinyl halides $CF_3S(O)F$, $CF_3S(O)Cl$, and $FS(O)Cl$.

Although the assignments for $FS(O)Cl$ are tentative due to the impurity of the sample, comparative analyses of the spectra for all three compounds gave rise to consistent results. The structures of the three compounds have not been determined; however, a pyramidal geometry is predicted from lone-pair repulsions. The three molecules may belong to point group C_s (planar) or to point group C_1 (pyramidal). Related sulfinyl compounds $S(O)F_2$,[8] $(CF_3)_2SO$,[9] and $S(O)Cl_2$[10] have been shown to be pyramidal.

Experimental Section

Bis(trifluoromethyl)disulfane (PCR, Inc.) was allowed to react with AgF_2 at 0° for 12 hr to give good yields of CF_3SF_3.[11] The CF_3SF_3 was then carefully hydrolyzed to give quantitative yields of $CF_3S(O)F$. Pure $CF_3S(O)F$ was obtained by gas chromatography using a column constructed of 0.25-in. o.d. copper tubing packed with 25% FS 1265 on Chromosorb P. When HCl was allowed to react with $CF_3S(O)F$ for 1 hr at 25°, good yields of $CF_3S(O)Cl$[12] were obtained. It was also purified by gas chromatography using the same column.

$FS(O)Cl$ was obtained from the reaction between equimolar quantities of ClF (Ozark-Mahoning) and $SOCl_2$ at −78° over a period of 12 hr. Yields of $FS(O)Cl$ approached 50%. The $FS(O)Cl$ was purified somewhat by low-temperature distillation.

Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrometer. Gas-phase infrared spectra were obtained by using a 7-cm glass cell equipped with KBr windows (pressures from 5 to 35 Torr). A Jarrell-Ash Model 25-300 Raman spectrometer equipped with a Coherent Radiation Model CR-MG krypton–argon laser (4880 Å for $CF_3S(O)F$ and $CF_3S(O)Cl$ and 5308 Å for $FS(O)Cl$) was used to record the Raman spectra. Samples for liquid-phase Raman spectra were sealed in 0.4-cm o.d. Pyrex tubes. Rotation of a half-wave plate by 45° turned the direction of the electric vector of the incident light through 90°, allowing the measurement of depolarization ratios.

Discussion and Results

For both $CF_3S(O)F$ and $CF_3S(O)Cl$, 14 of the expected 15 fundamentals are observed in the Raman spectrum, while all six fundamentals are observed in the case of $FS(O)Cl$. For C_1 symmetry, all bands in the Raman spectrum are expected to be polarized, and this is observed. All bands are both infrared and Raman active. In Figure 1 are the Raman spectra of $CF_3S(O)F$ and $CF_3S(O)Cl$. The Raman and infrared spectral data and the assignments for $CF_3S(O)F$ and $CF_3S(O)Cl$ are given in Table I. The Raman and infrared spectra and band assignments for $FS(O)Cl$ are found in Table II. The small number of bands observed in the infrared spectrum is a result of complete absorption by the KBr windows below 400 cm^{-1}.

Although mixing of some of the fundamentals may occur, group theory provided a basis for at least first approximations of band assignments. It was most convenient in this study to

Table I. Raman and Infrared Spectra for $CF_3S(O)F$ and $CF_3S(O)Cl^a$

$CF_3S(O)F$		$CF_3S(O)Cl$		
Infrared (gas), cm^{-1}	Raman (liquid), cm^{-1}	Infrared (gas), cm^{-1}	Raman (liquid), cm^{-1}	Assignment
1267 vs	1257 m	1242 s	1205–1260 w, sh	S=O str
1226 vs	1227 w	1218 s	1190 m	CF_3 str
1213 vs	1217 w	1123 s	1120 w	CF_3 str
1152 vs	1142 w	1096 mw	1100 vw	CF_3 str
	757 vs	751 m	752 s	CF_3 def
749 s, br	745–710 m, sh			S–F str
590 m	587 w	577 w	574 w	CF_3 def
555 vw	550 w	551 w	553 w	CF_3 def
		489 m	489 s	S–Cl str
480 m	480 m	461 w	463 m	C–S str
409 m	413 s		346 vs	S=O wag
	342 m			S–F wag
	289 vs		301 s	CF_3 rock
			267 m	S–Cl wag
	220 m		211 w	CF_3 rock
	192 w		163 m	C–S wag
	Not obsd		Not obsd	CF_3 torsion

[a] Key: sh, shoulder; w, weak; m, medium; s, strong; vs, very strong.

Table II. Raman and Infrared Spectra for FS(O)Cl

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
1293 vs	1276 m	S=O str
751 vs	739 m	S–F str
514 s	493 s	S–Cl str
435 w	444 vs	S=O wag
	347 s	S–F wag
	314 vs	S–Cl wag

consider the spectra in terms of the bands due to CF_3X (X = S(O)F or S(O)Cl) and the bands due to XS(O)F or XS(O)Cl (X = CF_3 or F). In this way a common basis for detailed vibrational analysis was obtained. That is, the six fundamental vibrations of FS(O)Cl may be described roughly as three stretching modes, SO, SF, and SCl; two wagging modes, SF and SCl; and the FS(O)Cl deformation mode (or SO wagging mode). Analogously, the 15 fundamentals for $CF_3S(O)F$ ($CF_3S(O)Cl$) can be pictured as 9 CF_3X modes (3 stretchings, 3 deformations, 2 rockings, and 1 torsional) and 6 XS(O)F (X = CF_3) modes (SO, SF, and SC stretching; SF, SC, and SO wagging).

Sulfur(IV)–oxygen stretching frequencies assigned previously in the literature include $S(O)F_2$ (1333 cm^{-1}),[1] $(CF_3)_2SO$ (1242 cm^{-1}),[9] $S(O)Cl_2$ (1229 cm^{-1}),[3] and $S(O)Br_2$ (1121 cm^{-1}).[4] We have assigned the SO stretching frequency in $CF_3S(O)F$, $CF_3S(O)Cl$, and FS(O)Cl to bands at 1267, 1242, and 1276 cm^{-1}, respectively. It appears that the SO stretching frequency is related approximately to the electron-withdrawing ability of the atoms or groups attached to the sulfur, and this trend is reflected in the assignments we have made; e.g., the sulfur–oxygen stretching mode occurs at the highest frequency in $S(O)F_2$, and the trend is $S(O)F_2$ > FS(O)Cl > $CF_3S(O)F$ > $(CF_3)_2SO$ ~ $CF_3S(O)Cl$ > $S(O)Cl_2$ > $S(O)Br_2$. A similar order, due primarily to an increasing mass effect, is observed for bands assigned to the sulfur–oxygen wagging motion: $S(O)F_2$ (526 cm^{-1}),[1] $(CF_3)_2SO$ (373 cm^{-1}),[8] $S(O)Cl_2$ (344 cm^{-1}),[3] $S(O)Br_2$ (267 cm^{-1}),[4] and, including the compounds studied here, $S(O)F_2$ > FS(O)Cl (444 cm^{-1}) > $CF_3S(O)F$ (413 cm^{-1}) > $(CF_3)_2SO$ > $CF_3S(O)Cl$ (346 cm^{-1}) ~ $S(O)Cl_2$ > $S(O)Br_2$. The sulfur–oxygen wagging mode in $S(O)F_2$ had been assigned to a band in the spectrum at 326 cm^{-1};[3] however, force constant calculations[7,13] have supported the assignment of the band at 526 cm^{-1}.

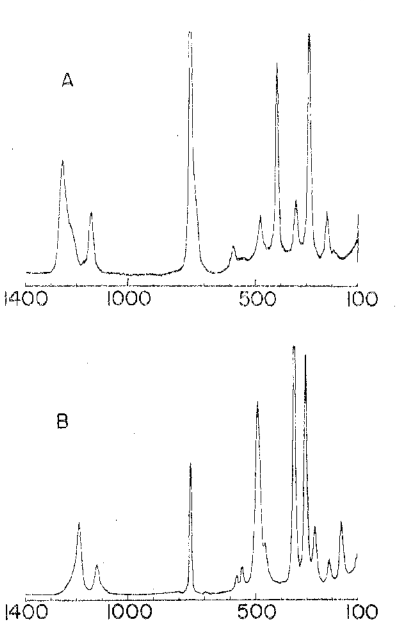

Figure 1. Raman spectra of $CF_3S(O)F$ (A) and $CF_3S(O)Cl$ (B) (cm^{-1}).

The SF stretching frequency in FS(O)Cl is assigned readily at 739 cm^{-1}. This compares to the SF_2 symmetrical stretching mode in $S(O)F_2$[1] at 801 cm^{-1} and the two SF_4 antisymmetric stretching vibrations[14] at 867 and 728 cm^{-1}, respectively. However, for $CF_3S(O)F$ the SF stretching mode is not immediately apparent. The broad band in the infrared spectrum centered at 749 cm^{-1} might be assigned to one of the CF_3 deformation modes, but it is much more intense than a similar band observed in $CF_3S(O)Cl$ (751 cm^{-1} in the infrared spectrum). CF_3 deformation modes around 750 cm^{-1} appear to be sharp and strong in the Raman spectra.[9] The expanded Raman spectrum of $CF_3S(O)F$ between 700 and 800 cm^{-1} shows clearly two bands in the 750-cm^{-1} region. The strong, sharp band at 757 cm^{-1} is assigned to one of the CF_3 deformation modes and a shoulder of medium intensity from 745 to 710 cm^{-1} is assigned to the SF stretch. The latter band is not present in the spectrum of $CF_3S(O)Cl$.

An alternate, and perhaps more realistic, explanation is that mixing of symmetry coordinates occurs for fundamentals such as these having the same symmetries with frequencies in close proximity. The intense Raman band at 757 cm^{-1} would result from a symmetric combination and the medium band at 745–710 cm^{-1} from an antisymmetric combination of the symmetry coordinates.

Among the S–Cl stretching frequencies which have been reported in the literature are SO_2Cl_2 (symmetrical 406 cm^{-1}),[15] $S(O)Cl_2$ (symmetrical 490 cm^{-1}),[3] SCl_2 (525 cm^{-1}),[16] S_2Cl_2 (460 cm^{-1}),[16], and CF_3SSCl (490 cm^{-1}).[17] There are only two possibilities for the SCl stretch in $CF_3S(O)Cl$, the bands at 346 and 489 cm^{-1}. Both are strong bands in the Raman spectrum; however, we assigned the band at 346 cm^{-1} to the SO wagging mode, since it fits the trend for other reported SO wagging motions more closely than does the band at 489 cm^{-1}. Thus the latter must be assigned to the S–Cl stretching frequency. Similar reasoning was used to differentiate between the two possibilities in FS(O)Cl. The band at 493 cm^{-1} was assigned to the SCl stretching frequency and the band at 444 cm^{-1} to the SO wagging mode.

The SF wagging mode was assigned to the band at 342 cm^{-1} for $CF_3S(O)F$ and to 347 cm^{-1} for FS(O)Cl. Previously, S–F wagging fundamentals for SF_6[18] and SO_2FBr[3] had been assigned to bands at 344 and 320 cm^{-1}, respectively. FS(O)Cl exhibits an SCl wagging mode at 314 cm^{-1}, while in $CF_3S(O)Cl$ the analogous mode was assigned to a band at 267 cm^{-1}. The value for the SCl wagging motion in SF_5Cl is reported to be 270 cm^{-1}.[19]

Recently several CF_3S-containing molecules have been studied, and the C–S stretching frequency was reported to be 475 cm^{-1} for CF_3SCF_3,[9] 468 cm^{-1} for $CF_3S(O)CF_3$,[9] and 446 cm^{-1} for CF_3SSCF_3.[9,20] Thus, we have assigned the C–S stretch in $CF_3S(O)F$ and $CF_3S(O)Cl$ to the bands of medium intensity at 480 and 463 cm^{-1}, respectively.

As mentioned previously, there should be nine bands associated with the CF_3X portion of the $CF_3S(O)Cl$ and $CF_3S(O)F$ molecules. Three of these should be stretching bands. These three vibrations should lie in the range 1100–1400 cm^{-1}.[21-23] There are four bands in this region in the infrared and Raman spectra of each of these compounds. One of these (the highest frequency band in each case) has been assigned to the SO stretching frequency. The others, very strong in the infrared spectra and weak in the Raman spectra, may be assigned to the three CF_3 stretching fundamentals. Although the values of the CF_3 stretching frequencies for $CF_3S(O)F$ and $CF_3S(O)Cl$ are quite different, the shift of the frequencies of the latter to lower energy causes the positions of the absorbance bands in this region of the spectrum to be nearly identical with that of $(CF_3)_2SO$[9] which is reasonable.

The three expected CF_3 deformation modes are observed and are easily assigned by comparison to assignments made for $CF_3S(O)CF_3$ (753, 591, and 558 cm^{-1})[9] and CF_3SSCF_3 (760, 573, and 545 cm^{-1}).[9] Thus, we have assigned the three bands at 757 (see discussion of S–F stretching mode), 587, and 550 cm^{-1} to the CF_3 deformation modes of $CF_3S(O)F$ and those at 752, 574, and 553 cm^{-1} to analogous vibrations in $CF_3S(O)Cl$. By similar comparisons, the CF_3 rocking modes were assigned to the bands at 289 and 220 cm^{-1} for $CF_3S(O)F$ and 301 and 211 cm^{-1} for $CF_3S(O)Cl$. CF_3 rocking modes had been assigned previously as high as 490[21] and as low as 149[24] cm^{-1}. According to Haas and coworkers,[25-27] an intense band around 300 cm^{-1} (289 and 301 cm^{-1}) is characteristic of CF_3 rocking motions.

Finally, the CF_3 torsional mode is not observed in either case and probably falls below 100 cm^{-1} in the Raman effect.[28,29] It has been observed at 75 cm^{-1} in the case of CF_3SCF_3 and $CF_3S(O)CF_3$.[9]

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Registry No. $CF_3S(O)F$, 812-12-4; $CF_3S(O)Cl$, 20621-29-8; $FS(O)Cl$, 14177-25-4; CF_3SF_3, 374-10-7; ClF, 7790-89-8; $SOCl_2$, 7719-09-7.

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Reaction of Sodium 2,2,2-Trifluoroethoxide with Hexachlorocyclotriphosphazene[1,2]

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The reaction between sodium 2,2,2-trifluoroethoxide and hexachlorocyclotriphosphazene (I) yielded nine cyclotriphosphazenes of the formula $N_3P_3(OCH_2CF_3)_nCl_{6-n}$ where $n = 1$–6. Nuclear magnetic resonance analysis indicated that these products were compounds II–X. This constitutes the first isolation and identification of a complete series of alkoxychlorocyclophosphazenes. The reaction was found to follow almost exclusively a trans-nongeminal pathway, and a steric rather than an electronic "cis effect" is postulated to account for this pattern. Dipole moments were measured, but these were shown to be unsuitable for isomer identification, presumably because of the presence of the bulky, nonrigid trifluoroethoxy groups and a nonvanishing ring moment. The applicability of these results to related high molecular weight polyphosphazene systems is discussed.

Introduction

The syntheses of several fluoroalkoxycyclophosphazenes, including hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (X), were first reported in 1959 and 1962.[3,4] Later, the synthesis of tris-, tetrakis-, and pentakis(trifluoroethoxy)chlorophosphazene trimers was reported,[5] and the NMR spectrum of trifluoroethoxypentachlorocyclotriphosphazene (II) was described.[6] Apparently no attempts were made to identify the geometric isomers formed when alternative structures were possible.

The current interest in high molecular weight polyorganophosphazenes[7-15] has generated a need for new information about the replacement patterns that exist when alkoxy substituent groups replace chlorine atoms in phosphazene systems. The present study was undertaken in an effort to synthesize, separate, and identify the stereoisomers