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FTIR Spectra of Dialkyl Sulfide and Alkanethiol Complexes with Hydrogen Fluoride in Solid Argon

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Hydrogen-bonded complexes of dialkyl sulfides and alkanethiols with HF have been prepared by condensing the argon-diluted reagents at 12 K. Infrared spectra of the $(CH_3)_2S$--HF complex revealed a ν_s(HF) mode at 3382 cm^{-1}, which suggests that the latter has a weaker hydrogen bond than the $(CH_3)_2O$--HF complex. The two HF librational modes at 631 and 622 cm^{-1} exhibit considerably less separation than the ν_l modes for the ether complex, which indicates less asymmetry in the sulfide librational potential. The ν_l modes for $(CH_3)_2S$--HF are considerably lower in value than modes for $(CH_3)_2O$--HF, which is characteristic of a less rigidly bound complex. The larger sulfide base has a higher proton affinity but is too diffuse in electron density to bind HF as strongly as the smaller oxide base. Similar results were obtained for the diethyl sulfide, methanethiol, and ethanethiol complexes with hydrogen and deuterium fluorides. Complexes involving one sulfide and two HF submolecules appear to be dominated by the chain structure.

Introduction

The matrix-isolation technique has proven valuable in the characterization of hydrogen-bonded complexes between hydrogen fluoride and small base molecules. Information about structure and bonding for complexes involving such base molecules as NH_3, H_2O, PH_3, and H_2S has been obtained.[1-4] The purpose of this study is to characterize complexes between hydrogen fluoride and sulfide bases and to compare these results to those for analogous oxygen complexes. Gas-phase studies using infrared[5,6] and photoelectron spectroscopy[7,8] have provided evidence for the formation of both 1:1 and 1:2 complexes with $(CH_3)_2S$ and HF. The analogous $(CH_3)_2O$ and HF complexes have been studied in several laboratories in the gas phase[6,9-11] and in solid argon.[12] Infrared spectra of complexes of hydrogen fluoride with several sulfide molecules in solid argon will be described below.

Experimental Section

The vacuum, cryogenic, and spectroscopic techniques used have been described in detail elsewhere.[1,4,12] All spectra were recorded with a Nicolet 7199 Fourier-transform infrared spectrometer between 4000 and 400 cm^{-1} at 1-cm^{-1} resolution. A single-beam spectrum of the CsI window at 12 K was recorded and ratioed as a background to a single-beam spectrum of the matrix to produce a simulated double-beam spectrum for each experiment. Reported frequency values were rounded to the nearest wavenumber.

Hydrogen fluoride (Matheson) was purified by pumping at 77 K and deuterium fluoride was produced by the reaction of F_2 (Matheson) with D_2 (Air Products) at low pressures in a passivated stainless-steel vacuum system. Methanethiol (Matheson) was frozen and evacuated to remove volatile impurities. Dimethyl sulfide, $(CD_3)_2S$, ethanethiol, and diethyl sulfide (Aldrich) were purified through fractional distillation on a vacuum line.

The acid and base samples were diluted betwen 150:1 and 500:1 mole ratios and argon (Air Products) and codeposited on the CsI window at approxmately 2 mmol/h for 15 h or approximately 6 mmol/h for 5 h. After deposition the samples were annealed to between 16 and 26 K for 10 min and recooled to 12 K. Spectra were recorded before, during, and after sample preparation and annealing. Blank samples were prepared and annealed for each reagent separately.

Table I. Absorptions (cm^{-1}) Produced on Codeposition of Dimethyl Sulfide and Hydrogen Fluoride with Excess Argon

absorptions				
$(CH_3)_2S$ + HF	$(CH_3)_2S$ + DF	$(CD_3)_2S$ + HF	$(CD_3)_2S$ + DF	assignt
3598	2655	3594	2642	2
3514	2595	3514	2593	2
3445	2550	3442	2549	ν_s(site)
3415	2530	3414	2529	ν_s(site)
3382	2506	3379	2505	ν_s
3324	2467	3324	2463	A
3290	2430	3290	2425	A
a	2195	2850	2195	2
a	2150		2170	2
1141	861	1143	863	$2\nu_l$
879		882		A
820		*a*		2
775		780		A
746		740		2
631	461	629	462	ν_l
622	455	621	456	ν_l
597		596		2
580		580		2
551		550		A
517		517		A

[a] Obscured by precursor absorption.

Results

Fourier-transform matrix infrared studies of HF and HF–DF mixtures with dimethyl sulfide and other sulfide bases will be described in turn.

Dimethyl Sulfide. Three experiments were conducted with hydrogen fluoride and dimethyl sulfide codeposited at 12 K. In the most dilute experiment the spectrum, displayed in Figure 1a, showed HF monomer, dimer, and water bands (labeled HF, D, and W),[13] absorptions due to N_2--HF and H_2O--HF complexes (labeled N and W^c),[2,14] bands for water–dimethyl sulfide complexes (labeled WS), as verified from experiments with added water, and strong precursor absorptions.[15] New product absorptions included a strong sharp band at 3382 cm^{-1} (A = absorbance = 0.38, labeled ν_s), a single absorption (labeled $2\nu_l$) at 1140 cm^{-1}, and a sharp doublet (labeled ν_l) at 631 (A = 0.07) and 622 cm^{-1} (A = 0.11). The matrix was annealed to 24 K and

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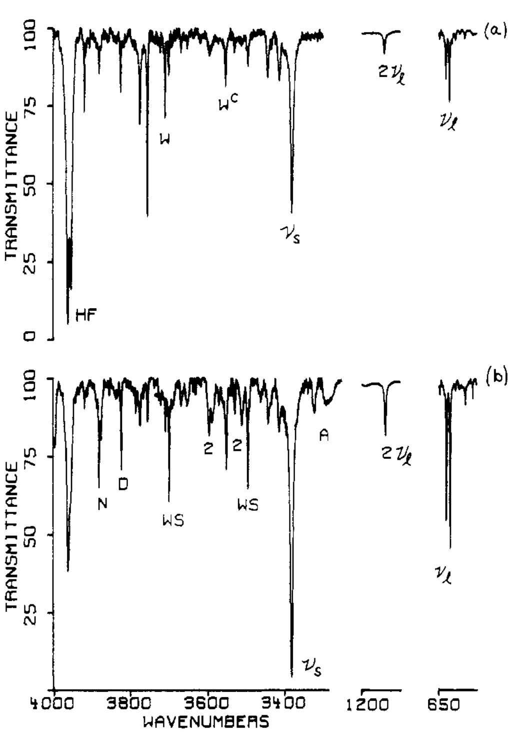


Figure 1. Infrared spectra of dimethyl sulfide and hydrogen fluoride samples (500:1): (a) after codeposition of 22 mmol of each sample at 12 K for 4 h; (b) after warming to 26 K and recooling to 12 K.

recooled, and another spectrum was recorded (Figure 1b), which showed that hydrogen fluoride monomer decreased, dimer and impurity complexes increased, all the new bands identified in Figure 1a increased in intensity by a factor of 3, and new absorptions labeled **2** and A grew in at 3598, 3514, 3324, and 3290 cm^{-1}. Weak satellite features on precursor bands appeared in the precursor blank and cannot be attributed to HF complexes. In experiments at higher concentrations the above bands were considerably stronger, and new bands (labeled **2**) increased markedly. Other new bands (labeled A for higher aggregate) appeared in the regions above and below the ν_l modes as listed in Table I.

Three experiments were conducted with DF–HF mixtures. The absorptions observed in the HF experiments were again present, and new absorptions specific to the DF system were observed at 2506 cm^{-1} ($A = 0.76$, labeled ν_s), at 861 cm^{-1} (labeled $2\nu_l$), and at 462 and 456 cm^{-1} (labeled ν_l). The matrix was annealed stepwise to 24 K and recooled to 12 K, and the resulting spectrum is shown in Figure 2. The bands identified above doubled in absorbance, and new absorptions labeled 2 and A appeared in the DF stretching region as listed in Table I. Another more concentrated DF experiment gave stronger bands, particularly those growing on the annealing cycles. No perturbed base submolecule modes could be attributed to product complexes in these experiments.

Table II. Absorptions (cm^{-1}) Produced on Codeposition of Diethyl Sulfide and Hydrogen Fluoride in Excess Argon

absorptions		
$(C_2H_5)_2S$ + HF	$(C_2H_5)_2S$ + DF	assignt
3598	2671	2
3562	2656	2
3526		2
3474	2569	2
3366	2495	ν_s
3352	2485	ν_s(site)
3315	2462	ν_s(site)
3218	2425	A
3195	2417	A
a	2160	2
a	2120	2
1140	863	$2\nu_l$
658	480	ν_l(site)
647	473	ν_l
637	467	ν_l(site)
620	455	ν_l
876	*b*	2
592	*b*	2
586	*b*	2

[a] Obscured by precursor. [b] Not observed.

Four experiments were done with $(CD_3)_2S$ using the faster spray-on rate, and the spectrum appeared much like that in Figure 1a, with small displacements in the bands as listed in Table I. Annealing produced stronger absorptions at 3594 and 3514 cm^{-1} than at 2900 cm^{-1}, and more concentrated samples gave stronger absorptions as described above. An experiment with a DF–HF mixture produced DF counterparts of the product bands; more growth of the new bands labeled 2 was noted than for those marked A in this experiment.

Diethyl Sulfide. Experiments were conducted for diethyl sulfide over the same concentration ranges and annealing conditions employed for dimethyl sulfide. The spectra in Figure 3 and Table II summarize the results. The only obvious difference between dimethyl and diethyl sulfide appears in the site splittings for the ν_s and ν_l modes for the larger sulfide base. Annealing at 25 K for 10 min produced new bands labeled 2 and A; in particular note the new bands labeled 2 at 2160 and 2120 cm^{-1}.

Methanethiol. Similar studies were done with methanethiol, and the results are presented in Figure 4 and Table II. The sample revealed strong ν_s and weak ν_l bands and a 965-cm^{-1} satellite on the 955-cm^{-1} CH_3 rock of CH_3SH after deposition;[16] these bands

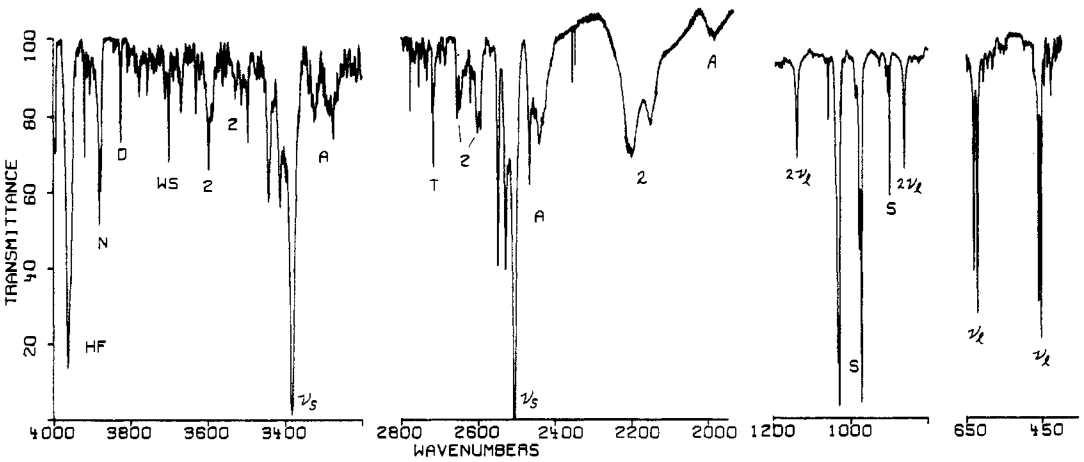


Figure 2. Infrared spectrum of dimethyl sulfide and HF:DF samples (300:1, 40 mmol each, 80% DF) codeposited at 12 K and annealed at 24 K. S denotes methyl sulfide base absorptions.

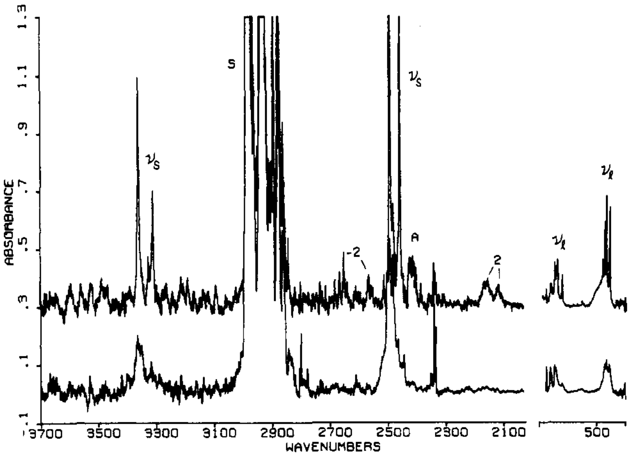


Figure 3. Infrared spectrum of Ar:$(C_2H_5)_2S$ = 300:1 and Ar:(DF + HF) = 150:1 (90% DF) samples codeposited at 12 K with absorbance scale at bottom. Spectrum displaced at top recorded after annealing to 25 K. S denotes ethyl sulfide absorptions.

Table III. Absorptions (cm^{-1}) Produced on Codeposition of Alkanethiols and Hydrogen Fluoride in Excess Argon

absorptions				
CH_3SH + HF	CH_3SH + DF	C_2H_5SH + HF	C_2H_5SH + DF	assignt
3677	2698	3654	2690	2
3617	2665	3611	2661	3
		3535	2610	ν_s(site)
3514	2594	3513	2594	ν_s
		3506	2589	ν_s(site)
		3493	2580	ν_s(site)
		3444	2549	3
3320	2468	3349	2475	3
3157	2352	3150	2347	2
2900	2165	*a*	2169	3
632	482			2
582	455	595	457	ν_l
577	450	565	446	ν_l(site)
562	415	573	421	ν_l
		552	410	ν_l(site)

[a] Obscured by precursor.

doubled on annealing to 24 K, and new bands appeared that are labeled 2 and 3 in Figure 4. An additional experiment with double the acid concentration gave much stronger ν_s and ν_l bands, and the bands labeled 2 and 3 were observed. Annealing had little effect on the ν_s and ν_l bands, but the band 2 absorptions increased and the band 3 absorptions increased markedly.

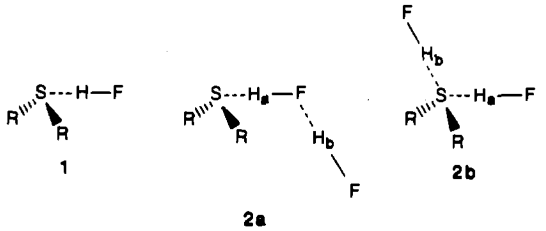
Ethanethiol. Parallel experiments with ethanethiol gave results similar to those for methanethiol; the product band positions are listed in Table III. The major difference is the multiplicity of site splittings for ν_s, that was not observed with the smaller methanethiol base. On annealing, the absorptions labeled **2** and **3** grew to strong bands, in agreement with the CH_3SH studies.

Discussion

The new product absorptions will be identified, and vibrational assignments will be made. Structure and bonding in the sulfide complexes will be compared to structure and bonding in similar oxygen complexes.

Identification. The new product absorptions listed in Table I–III were not observed in argon matrix samples of the sulfur compounds or hydrogen fluoride alone. However, these bands were produced with high yields when the reagents were mixed during condensation. Three groups of product absorptions can be identified on the basis of sample concentration and annealing behavior. Absorptions of the first group were strong after sample condensation and increased by a factor of 2 or 3 on annealing. Absorptions of the second group were weak following reagent condensation but grew markedly (>6-fold) on annealing, and the third group was characterized by even greater growth on annealing, particularly in more concentrated samples.

Chart I



The first group of absorptions with labels ν_s and ν_l were intense after sample deposition, indicating that they belong to the primary product species. This group of bands maintained constant relative intensities over several experiments and on sample annealing. These observations indicate that the first group of absorptions can be assigned to the 1:1 complex **1** (see Chart I) between the sulfide base and HF. The second group of product absorptions exhibited a higher order concentration dependence on HF which characterizes 1:2 complexes **2**, and the third group appears to have a still higher order reagent dependence; these bands are attributed to 2:2 or 1:3 complexes.

Assignments. The strong, sharp primary product absorptions labeled ν_s exhibited DF counterparts with HF:DF ratios of 1.349 to 1.355, which characterize the fundamental vibration of the acid ligand in the primary complex **1**. The very small shift in these modes when CH_3 was replaced by CD_3 shows that a dimethyl sulfide–HF complex is formed and again verifies the H–F nature of this vibration. These bands are appropriately displaced from the 3919-cm^{-1} HF fundamental in solid argon[13] owing to the hydrogen-bonding interaction. The ν_l bands are assigned to the two librational motions of the HF submolecule in the 1:1 complex arising from the two rotational degrees of freedom from the diatomic. In the case of dimethyl sulfide–HF, the two bands are sharp and clearly resolved for the two libration directions, and the HF:DF ratios (1.359, 1.367) are almost identical. A single overtone band was observed for one of the two ν_l modes with overtone:fundamental ratios of 1.808 or 1.834, depending on the assignment. In the case of methanethiol–HF, the upper ν_l mode is split into a 584, 577 cm^{-1} doublet, and the lower ν_l mode appeared at 562 cm^{-1}; the upper doublet exhibited an HF:DF ratio (1.283 ± 0.001) different from that of the lower band (1.354). The splitting and different isotopic ratios point to different potential surfaces for the two librations. One clearly involves an interaction the other lacks, and it is tempting to suggest that the ν_l doublet involves a motion that approaches the unique thiol hydrogen and the single ν_l mode is orthogonal and does not.

Comparisons of Bonding and Structure. The structures of the 1:1 sulfide-HF complexes are presumed to follow that of the H_2S--HF complex where HF is hydrogen-bonded to a lone pair on sulfur, giving a right-angle pyramidal structure.[17] The two librational modes in the $(CH_3)_2S$--HF complex, then, involve libration of the HF submolecule in the plane bisecting the C–S–C angle and in the perpendicular plane containing the HF submolecule. The ν_s and ν_l modes, which are most characteristic of bonding and structure, are compared in Table IV for sulfide and oxide bases. The major difference in the spectra are splittings in these bands due to different matrix packing around the complexes, particularly for the larger bases.

Although the intermolecular interactions that result in the red-shift of the H–F fundamental in a 1:1 complex are complicated;[18] in general, the larger displacement in ν_s from the isolated

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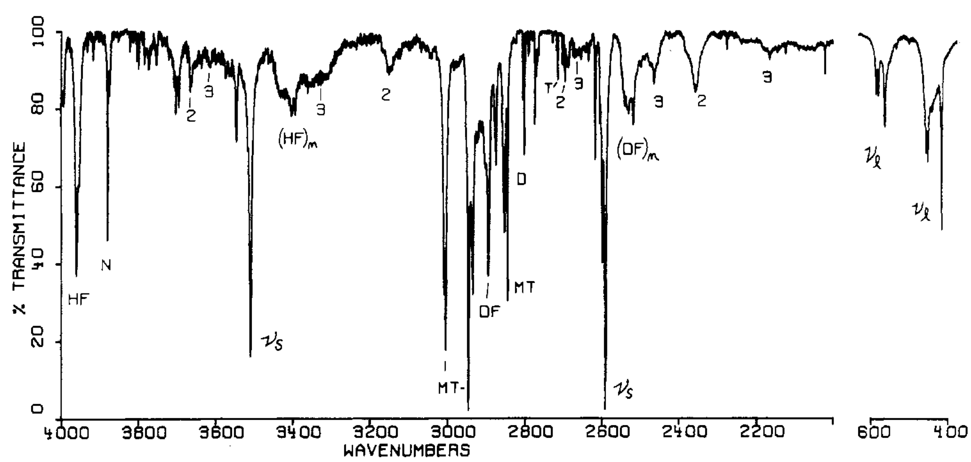

Figure 4. Infrared spectrum of methanethiol and hydrogen fluoride samples (300:1 each, 80% DF) codeposited at 12 K and annealed to 24 K. MT denotes methanethiol absorptions.

Table IV. Comparison of H–F Stretching and Librational Modes (cm^{-1}) for Sulfur and Oxygen Base Complexes[a]

	H_2O	H_2S	CH_3OH	CH_3SH	C_2H_5OH	C_2H_5SH	$(CH_3)_2O$	$(CH_3)_2S$	$(C_2H_5)_2O$	$(C_2H_5)_2S$
ν_s(H–F)	3554	3652	3438	3514	3412	3513	3350	3382	3322	3367
ν_l(H–F)	721	508	747	584	757	595	801	631	791	647
ν_l(H–F)	614	481	656	562	669	552	687	622	696	620
	(167)[b]	(170)	(182)	(187)	(188)	(191)	(192)	(200)	(200)	(205)

[a] References in text. [b] Proton affinity (kcal/mol) from ref 19.

molecule value follows a stronger interaction and results in a greater hydrogen-bond strength. Stronger hydrogen bonds are usually more rigid and are reflected in higher ν_l modes. As shown in Table IV, increasing methyl substitution increases the displacement in ν_s and increases the ν_l modes, and these trends indicate an increased hydrogen-bond strength. This increase in hydrogen-bond strength follows an increase in proton affinity[19] in each column, but not between the oxides and sulfides, where the sulfide has the higher proton affinity but the weaker hydrogen bond compared to the oxide. The larger sulfide base, although more receptive to a proton, apparently is too diffuse in electron density to bind HF as strongly as the smaller oxide base. This observation fits well with the general principles of hard and soft acids and bases.[20]

The librational modes reflect on the diffuse nature of the lone pair density in dimethyl sulfide as compared to dimethyl ether. Even though the ν_s modes are very similar, the ν_l modes are substantially lower for the sulfide base and are split over only 9 cm^{-1}. This splitting reflects the lower anisotropy of the lone-pair density on the sulfur, which is much closer to the cylindrical symmetry of PH_3 (degenerate ν_l modes)[3] than the considerable anisotropy of dimethyl ether (114-cm^{-1} splitting).[12] The lower ν_l modes indicate less ridigity for the complex, which arises from a more diffuse lone-pair-binding site for the HF ligand. Lower frequency librational modes have been found for the heavier members of the series of methyl halide–HF complexes.[21] The ν_l overtone also exhibits a lower overtone:fundamental ratio than found for the ether complex (1.88, 1.87);[12] this indicates more anharmonicity in the librational potential for the larger base. A similar relationship was found for NH_3 and PH_3 complexes with HF.[3]

It should be mentioned that the dimethylsulfide–hydrogen chloride 1:1 complex has been studied in solid argon[22,23] and exhibits a larger fractional shift in the HCl fundamental (0.210) than does the hydrogen fluoride complex (0.137). This may reflect the greater polarizability of the HCl submolecule.

Finally, the $(CH_3)_2S$- -HF complex has been observed in the gas phase under low resolution[6] with ν_s and ν_l band centers at 3502 and 575 cm^{-1}. The argon matrix solvates the complex, sharpens the bands, and red-shifts ν_s to 3382 cm^{-1}, but the matrix blue-shifts ν_l to a resolved doublet at 622 and 631 cm^{-1} due to the matrix cage, which is repulsive to the large-amplitude librational motion.

The structure of the 1:2 sulfide–2HF compelxes could be a chain, as shown in **2a** and/or bifid, as in **2b**. Even though calculations have shown that **2a** is more stable than **2b**, photoelectron spectroscopic evidence has been presented for both structure **2a** and **2b**, and the infrared spectrum has been cited for **2a** in the gas phase.[6,8] Clearly, the union of $(CH_3)_2S$ and $(HF)_2$ would produce **2a**, but the addition of another HF to **1** could result in **2b** as well as **2a**, and the **2b** structure might be more competitive for the larger sulfide base than for the smaller ether base. It is important to note that the vibrational characteristics of **2a** and **2b** are distinctly different; in **2a** the H_a–F vibration is of lower frequency than ν_s in **1** due to the fluoride affinity of H_b–F, whereas the H_b–F vibration is of higher frequency than ν_s, and in **2b** the H_a–F and H_b–F bands may be of higher frequency than ν_s since each of the two hydrogen bonds to a common sulfide base could be weaker than the single such bond in **1**. The present experiments show bands in both diagnostic regions that grow on annealing and point to the formation of 1:2 complexes. In some of these experiments (particularly for $(CD_3)_2S$), the band 2 intensity in the 3500–3600-cm^{-1} region exceeds the band intensity in the 2800–2900-cm^{-1} region. Using acetone–2HF complexes as a model,[24] the absorbance of the H_a–F motion should at least equal the H_b–F absorbance, so additional absorbance in the upper region could be taken as evidence for **2b**, which does not absorb in both regions like **2a**. It is believed that both structures **2a** and **2b** probably exist in these matrix samples.[25] Even though **2a** is more stable than **2b** steric factors can prevent their equilibration in the matrix cage. The spectra in Figures 2 and 3 show absorption in the 2100–2200-cm^{-1} region that requires a DF analogue of **2a**, and **2b** could contribute to the absorbance in the 2580–2680-cm^{-1} region, and thus species **2b** cannot be ruled out. In the $(CD_3)_2S$ and HF experiments, the much stronger product absorptions for

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(25) The same rationale may apply to the 1:2 ether- -$(HF)_2$ compelx reported in ref 12; i.e., both bifid and chain structures could be formed in the matrix. Weak interaction between the terminal fluorine and the alkyl substituent in structure **2a** is likely.

2 in the 3500–3600-cm^{-1} region as compared to the 2800–2900-cm^{-1} region strongly suggest the presence of **2b**. Finally, it is possible that HF prefers the **2b** structure and that DF prefers **2a**, since DF preferentially bonds to HF rather than the reverse.[26]

The bands identified as 3 in these experiments are due to higher aggregates. In the methyl and ethyl sulfide experiments, the broad, strong absorptions in 3300-cm^{-1} region could be due to a dimer of dimers, i.e. two 1:1 complexes or some higher polymer such as a 1:3 complex. In the thiol experiments, the third hydrogen could participate in higher clusters, but the clear trend in H–F modes coming just below the 1:1 complex and 1:2 complex values suggest a chain type 1:3 complex following a chain type 1:2 complex.

Conclusions

Dialkyl sulfide and alkanethiol complexes with HF have been prepared by condensing the reagents with excess argon at 12 K. Infrared spectra reveal strong sharp ν_s (H–F stretching) and two separate ν_l (H–F libration) modes for each 1:1 complex. Comparison with spectra of similar oxygen complexes shows weaker sulfide base–acid interactions and predicts weaker HF hydrogen bonding with sulfide bases. Lower librational modes for sulfide–HF complexes indicate less rigid complexes owing to more diffuse lone pairs on sulfur, and smaller separation between ν_l modes shows a more isotropic sulfur lone pair–HF interaction. Higher stoichiometry 1:2 complexes in these experiments appear to be dominated by the chain structure S- -H–F- -H–F.

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Hydrophobic and Steric Effects on the Ion-Pair Formation of Tris(1,10-phenanthroline)iron(II) and Arenesulfonate Ions. Kinetic Determination of the Formation Constants of the Ion Pairs and a ^{1}H NMR Study of Their Structures

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Ion-pair formation constants (K) for $Fe(phen)_3^{2+}$ and six kinds of arenesulfonate ions were obtained from kinetic studies of the aquation of the complex ion in aqueous sodium arenesulfonate solutions: $K = 5 \pm 1, 13 \pm 2, 28 \pm 5, 19 \pm 3, 8 \pm 2$, and 5 ± 1 mol^{-1} dm^3 for benzene-, 4-methylbenzene-, 4-ethylbenzene-, 2,4-dimethylbenzene-, 1-naphthalene-, and 2-naphthalenesulfonate, respectively. An arenesulfonate of greater hydrophobicity showed a larger formation constant, except that small formation constants were shown by bulky naphthalenesulfonates. The formation constant was smaller for an arenesulfonate than for an alkanesulfonate with the same number of carbon atoms. The ^{1}H NMR signal of arenesulfonate in the ion pair was found to shift upfield. Comparison of the observed shifts with those calculated on the basis of the current loop model supported a model of the ion pair in which the arenesulfonate ion lies in the hydrophobic cavity between two phenanthroline ligands of the complex ion with the sulfonate group directed outside the cavity.

Hydrophobic interaction plays an important role not only in biological systems but also in systems containing coordination compounds of aromatic nitrogen-donor ligands such as 1,10-phenanthroline and 2,2′-bipyridine.[2-8] We previously studied the effects of alkylammonium cations[9] and alkanesulfonate anions[10] on the rate of racemization and aquation of $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline). The complex ion was found to form ion pairs not only with alkanesulfonate ions but also with alkylammonium cations through hydrophobic interaction. In the present study, various arenesulfonate ions have been examined for the effect on the rate of aquation of the complex ion. This has disclosed how the molecular shape of the arenesulfonate ion effects the formation of the ion pair between $Fe(phen)_3^{+2}$ and an arenesulfonate ion. An ^{1}H NMR study was also carried out in order to clarify the structure of the ion pair.

Experimental Section

The sodium arenesulfonates were of reagent grade from Tokyo Kasei Kogyo Co., Ltd., except sodium 4-methylbenzene- and 2,4-dimethylbenzenesulfonate, which were synthesized from the sulfonic acids (Tokyo Kasei) and sodium carbonate. They were recrystallized three times from ethanol–methanol (5:1) solution and dried at 70 °C in vacuo after 5 h. First-order rate constants for the aquation of $Fe(phen)_3^{2+}$ were obtained at 25 °C from the changes i the absorbance at 510 nm of the solution containing 5×10^{-5} mol dm^{-3} $[Fe(phen)_3](ClO_4)_2$ and a sodium arenesulfonate. Nickel(II) perchlorate (5×10^{-4} mol dm^{-3}) was added as a scavenger of liberated phenanthroline. In measuring the ^{1}H NMR spectra tetramethylammonium bromide (0.002 mol dm^{-3}) was used as the internal reference. The other chemicals and procedures were the same as those described in a previous paper.[11]

Results

Kinetics of the Aquation of $Fe(phen)_3^{2+}$. The observed rate constants of the aquation are shown in Figure 1 as a function of

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