contributions to the paramagnetic shielding, B, mainly determine the rhodium chemical shifts. This parallels the result found for similar platinum complexes.[16] Likewise, substitution of the carbonyl group for a phosphine group in the rhodium(I) complexes seems to produce a red shift in the absorption spectra. If the ΔE term is dominant, then the rhodium nucleus should be less shielded in the carbonyl complex than in the tris-triphenylphosphine complex. The carbonyl complex is observed at higher field, again indicating a greater dependence of σ on the other terms in eq 1.

Obviously an estimate of the other factors which could effect the paramagnetic shielding of the rhodium and phosphorus nuclei is difficult at this time. These experimental results may, however, give some insight into the shielding mechanism. Further experimental, as well as theoretical, studies are in progress in the hope of further understanding these parameters.

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Formation and Fluorine-19 Nuclear Magnetic Resonance Spectra of the Polyfluorosulfuric Acids, $H(SO_3)_nF$. Existence of the Polyfluorosulfuric Acids in SbF_5–HSO_3F

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Abstract: Direct evidence for the formation of the polyfluorosulfuric acids, HS_2O_6F, HS_3O_9F, . . . , $HS_7O_{21}F$, in solutions of SO_3 in HSO_3F or HSO_3F–SO_2ClF has been obtained by the observation of separate ^{19}F nmr signals from each of these species at low temperature. Recent evidence for the formation of these acids in HSO_3F–SbF_5 systems is shown to be incorrect.

The Raman and room temperature ^{19}F nmr spectra of solutions of SO_3 in HSO_3F have been studied previously[1] and the results have been interpreted as providing evidence for the formation of the polyfluorosulfuric acids $H(SO_3)_nF$. New lines that appear in the Raman spectrum on addition of SO_3 to HSO_3F could be satisfactorily interpreted as being due to the formation of HS_2O_6F and HS_3O_9F and further changes in the Raman spectrum at high SO_3 concentrations indicated, but did not prove, the existence of higher members of the series of polyfluorosulfuric acids. On addition of SO_3 to HSO_3F, only a single line was observed in the room temperature ^{19}F nmr spectrum, but it showed a large shift to low field with increasing concentration of SO_3. This large shift could only be reasonably interpreted as indicating the formation of a series of polyfluorosulfuric acids, but separate signals from the different acids were not obtained.

A recent ^{19}F nmr and Raman spectroscopic study by Commeyras and Olah[2] of concentrated solutions of SbF_5 in HSO_3F has provided evidence for the formation of SbF_6^- and $Sb_2F_{11}^-$ anions in these systems. The formation of these anions had not been observed in the more dilute solutions previously investigated by Thompson, *et al.*,[3] in which it was shown that the following equilibria are set up.

$$SbF_5 + 2HSO_3F \rightleftarrows H_2SO_3F^+ + SbF_5(SO_3F)^-$$

$$2SbF_5 + 2HSO_3F \rightleftarrows H_2SO_3F^+ + (SbF_5)_2SO_3F^-$$

In order to account for the formation of SbF_6^- and $Sb_2F_{11}^-$, Commeyras and Olah proposed the following additional equilibria, including the formation of the polyfluorosulfuric acids HS_2O_6F and HS_3O_9F.

$$HSO_3F \rightleftarrows SO_3 + HF$$

$$SbF_5 + HF \rightleftarrows HSbF_6$$

$$2SbF_5 + HF \rightleftarrows HSb_2F_{11}$$

$$SO_3 + HSO_3F \leftrightarrows HS_2O_6F$$

$$2SO_3 + HSO_3F \leftrightarrows HS_3O_9F$$

In support of this scheme they attributed lines at approximately -69 and -32 Hz from HSO_3F in their 56.4 MHz ^{19}F nmr spectra to the species HS_2O_6F and HS_3O_9F, respectively. The scheme seems unlikely as there is no evidence for any appreciable dissociation of fluorosulfuric acid into SO_3 and HF.[4] Furthermore it has been shown that SbF_6^- and $Sb_2F_{11}^-$ are also formed in the SbF_5–H_2O and SbF_5–H_2SO_4 systems in solution in SO_2.[5] Hence it is clear that the additional fluoride required to convert SbF_5 to SbF_6^- or $Sb_2F_{11}^-$ need not come from dissociation of the HSO_3F, and it has been demonstrated that the SbF_6^- and $Sb_2F_{11}^-$ can arise *via*

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(1) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 675 (1962).

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(4) R. J. Gillespie, J. B. Milne, and R. C. Thompson, *ibid.*, **5**, 468 (1966).

(5) P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, **91**, 7264 (1969).

Table I. ^{19}F Chemical Shifts of the Polyfluorosulfuric Acids and Equilibrium Compositions of SO_3–HSO_3F Mixtures

Solution		1	2^a	3^a
SO_3:HSO_3F ratio		0.241	1.12	1.94
^{19}F chemical shift (Hz) and (in parentheses) percentage total fluorine for each acid	HSO_3F	0 (80)	0 (29)	0 (14)
	HS_2O_6F	−182 (20)	−167 (53)	−158 (49)
	HS_3O_9F		−318 (17)	−312 (27)
	$HS_4O_{12}F$		−402 (3)	−400 (8)
	$HS_5O_{15}F$		−429 (1)	−427 (2)
	$HS_6O_{18}F$		−454 (∼0.2)	∼−448 (∼0.2)
	$HS_7O_{21}F$			∼−453 (∼0.1)
Percentage of initial SO_3 present in solution as free SO_3		15%	10%	28%

[a] Solutions in excess SO_2ClF.

ligand redistribution of the type

$$2SbF_5X^- \rightleftharpoons SbF_6^- + SbF_4X_2^-$$

We have therefore reinvestigated the ^{19}F nmr spectra of the HSO_3F–SO_3 system at low temperatures in an attempt to obtain the ^{19}F nmr spectra of the polyfluorosulfuric acids.

Results and Discussion

Temperatures of −100° or below are necessary to observe the ^{19}F nmr spectra of the polyfluorosulfuric acids. Solutions of SO_3 in HSO_3F alone are rather viscous at such temperatures but satisfactory spectra can be obtained from dilute solutions. Using the inert diluent SO_2ClF it is possible to obtain solutions with much larger SO_3/HSO_3F ratios which also have greatly reduced viscosities at low temperatures.

The −110° ^{19}F nmr spectrum of a solution in which SO_3:HSO_3F:SO_2ClF = 1.94:1.00:2.85 shows a single line from the diluent and, in addition, seven lines in the region expected for the $-SO_3F$ group, as shown in Figure 1. The highest field line is due to HSO_3F, and it seems reasonable to assign the other six to an equilibrium mixture of the polyfluorosulfuric acids, $H(SO_3)_nF$, with n = 2–7 and n increasing toward lower applied fields. (The spectrum also shows a small sharp line at −423 Hz from HSO_3F due to an unidentified impurity or reaction product which does not undergo rapid fluorine exchange at higher temperatures, as do the polyfluorosulfuric acids.) This assignment is consistent with the observed diminished intensity of the lower field lines with respect to the higher, as the ratio SO_3:HSO_3F decreases, as illustrated by the results in Table I. At approximately −60°, the lines from fluorosulfate-containing species merge, and at room temperature only a single averaged line is observed as has been previously observed.[1] The chemical exchange must occur through dissociations of the type illustrated by (1). From the

$$S_2O_6F^- \rightleftharpoons SO_3F^- + SO_3 \qquad (1)$$

compositions of the solutions and the relative amounts of the polyfluorosulfuric acids, it is possible to calculate the percentage of the total added SO_3 which is free in the solutions; the amount is seen to be appreciable (Table I), in agreement with the conclusions of a previous Raman study of SO_3–HSO_3F.[1] It is also clear that the amount of free sulfur trioxide is sensitive to the presence of the inert solvent SO_2ClF. Previous workers[6] have shown that a monomer–trimer equilibrium exists in solutions of SO_3 in inert solvents; presumably a shift in this equilibrium in the present case is responsible for the apparent discrepancy between the results for solutions 1 and solutions 2 and 3.

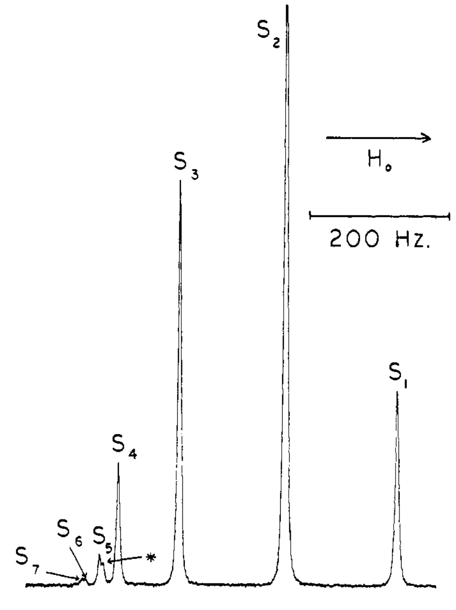

Figure 1. ^{19}F nmr spectrum (−110°, 56.4 MHz) of solution 3 (* = impurity peak).

A statistical mechanical treatment[7,8] has shown that all equilibria such as (2), in which unbranched chain

$$H(SO_3)_nF \rightleftharpoons H(SO_3)_{n-1}F + H(SO_3)_{n+1}F \qquad (2)$$

molecules react to give unbranched chains as products, should have an equilibrium constant, K_n, of unity when the equilibrium distribution of chain sizes is statistically random. The present data are necessarily rather limited by the compositions of mixtures homogeneous below −100°. However the values of the equilibrium constants calculable from the tabulated results, K_2 = 0.14–0.16, K_3 = 0.55–0.54 (solutions 2 and 3, respectively), and $K_4 \approx 0.8$ (solution 3), are clearly not unity, but appear to be approaching this value with increasing chain length. A similar deviation of K_n from unity in the case of the dimethyl polysulfates, has been interpreted[8] as meaning that the thermodynamic properties of the polymer units are not independent of the position of the unit with respect to the

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[6] R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2189 (1961).

[7] D. W. Scott, *J. Amer. Chem. Soc.*, **68**, 2294 (1946).

[8] J. R. Van Wazer, D. Grant, and C. H. Dungan, *ibid.*, **87**, 3333 (1965).

end of the chain; it follows that the largest deviations will occur for the shortest chains. The same explanation must be applicable to the polyfluorosulfuric acids.

It is interesting to compare the chemical shifts in the series of polyfluorosulfuric acids with those observed previously in the polysulfuryl fluorides (Table II).

Table II. The ^{19}F Chemical Shifts of Polyfluorosulfuric Acids and Polysulfuryl Fluorides

	Chemical shift, Hz	
	-OH[a,c]	$-F$[b,c]
$F(SO_3)SO_2X$	-158	-880
$F(SO_3)_2SO_2X$	-312	-960
$F(SO_3)_3SO_2X$	-400	-989
$F(SO_3)_3SO_2X$	-427	-998
$F(SO_3)_4SO_2X$	-448	-1003
$F(SO_3)_5SO_2X$	-453	-1005.5

[a] This work. [b] From the data of R. J. Gillespie, J. V. Oubridge, and E. A. Robinson, *Proc. Chem. Soc.*, 428 (1961), referenced to SO_2F_2 using $\delta(S_2O_5F_2) - \delta(SO_2F_2) = 880$ Hz (this work). [c] Referred to either HSO_3F or SO_2F_2.

After a very large chemical shift between SO_2F_2 and $S_2O_5F_2$, the shifts between the next members of the series are smaller than for the corresponding polyfluorosulfuric acids, and the series converges more rapidly. In neither series could a separate signal be detected for S_8 or higher members of the series. Unfortunately no simple explanation of these chemical shifts appears possible at present.

It is clear from the chemical shifts of HS_2O_6F and HS_3O_9F (Table II) that the signals observed by Commeyras and Olah[2] at ~−68 and ~−32 Hz from HSO_3F cannot be attributed to these species. These lines may reasonably be assigned to the fluorosulfate groups in fluorosulfate-containing complexes of antimony which arise by ligand redistributions such as

$$SbF_5(SO_3F)^- \rightleftarrows SbF_6^- + SbF_4(SO_3F)_2^-$$

as discussed above.

Experimental Section

Nmr Measurements. Low-temperature nmr spectra were obtained using a Varian DA-60IL spectrometer, equipped with a Varian V4540 temperature controller and the variable temperature probe, and operating at 56.4 MHz in the center band mode.

The areas under various peaks were measured by recording several spectra, cutting out the peaks and weighing them.

Materials. Sulfur trioxide and fluorosulfuric acid were purified by the standard methods. Sulfuryl chlorofluoride was prepared from potassium fluorosulfinate and chlorine according to Seel and Riehl.[9]

Sample Preparation. In a circulating drybox a weighed amount of fluorosulfuric acid was transferred to a baked-out 5-mm nmr tube using a glass syringe with a platinum needle. The tube was closed with a detachable top and connected to a standard glass vacuum line. After degassing the acid, sulfur trioxide was condensed into the tube from a weighed container and the amount of SO_3 determined by difference. If no further material was to be added, the tube was then sealed; otherwise SO_2ClF was condensed in from the precalibrated vacuum line prior to sealing. The solutions were mixed by heating to *ca.* 50° with frequent shaking.

Acknowledgments. We thank the Directorate of Chemical Sciences of the U. S. Air Force Office of Scientific Research for generous financial assistance.

[9] F. Seel and L. Riehl, *Z. Anorg. Allgem. Chem.*, **282**, 293 (1955).