Onium Ions. 18.[1] Static Protonated and Exchanging Diprotonated Ambivalent Heteroorganic Systems: Hydroxylamines, Acetone Oxime, and Dimethyl Sulfoxide

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Monoprotonated aliphatic hydroxylamines, acetone oxime, and dimethyl sulfoxide as their fluoroantimonate salts (prepared from the corresponding hydrochloric acid salts) in SbF_5–SO_2ClF (or SO_2) solution were studied to determine the site of protonation. Subsequently, diprotonation was also investigated in HSO_3F–SbF_5 (magic acid) solution. From the ^1H and ^{13}C NMR data of the static and exchanging species it was possible to determine the site of monoprotonation, as well as an indication of diprotonation. MINDO/3 calculations were also carried out on the parent, mono-, and diprotonated forms of dimethyl sulfoxide. The calculated and experimental results gave good agreement.

Weak bases (1) are protonated in strong acids of increasing strength. Whether a static protonated form (2) is observed depends primarily upon the relative acidity constant. In some cases, an equilibrium between 1 and 2 was observed in sulfuric and fluorosulfuric acid solutions, due to the very weak basicity of the studied compounds.[2,3] With the use of mixtures of fluorosulfuric acid and antimony pentafluoride (magic acid) the acidity constant H_0 can be greatly increased, allowing the complete protonation of weaker bases, forming the static protonated onium ions.[4]

$$\underset{1}{RX:} \overset{H^+}{\rightleftharpoons} \underset{2}{\overset{+}{R}XH}$$

When two or more heteroatoms are present in a molecule frequently more than one site can be protonated in magic acid solution, forming static heteroorganic dications. This is the case with some anilines,[5] trihydroxy- and trimethoxybenzenes,[6] dinitriles,[7] amino acids,[8] guanidines, ureas,[9] azobenzenes, and hydrazines.[5] Most of these compounds form highly stabilized systems where the two charges are usually separated by one or more atoms. An exception is the case of diprotonated hydrazines, where the two charged centers are adjacent to each other. Due to the ability of nitrogen to stabilize the charge, diprotonated hydrazines can even be isolated as stable salts from aqueous hydrochloric acid solutions.

Even in superacid media it is not expected that weak ambivalent bases will be completely diprotonated, forming a stable static species. An even more unlikely possibility would be the formation of the geminally doubly protonated perhydronium ion (4) via protonation of the hydronium ion (3). However, such a species could be involved in an exchange process in superacidic media.

$$\underset{3}{HA} + \underset{3}{H_3O^+:} \rightleftharpoons \underset{4}{H_4O^{2+}} + A^-$$

In the present study we have investigated, by ^1H and ^{13}C NMR spectroscopy, monoprotonated hydroxylamines, acetone oxime, and dimethyl sulfoxide as their fluoroantimonate salts prepared from the hydrochloric acid salts in SbF_5–SO_2ClF solution and determined the site of monoprotonation. Subsequently, we also studied the possible diprotonation in HSO_3F–SbF_5 solution. Since the sites of possible diprotonation are adjacent to each other, the possibility of diprotonation was investigated in terms of basicity of the sites being protonated. We also carried out MINDO/3 calculations of the heat of formation and charge distributions for dimethyl sulfoxide and its mono- and diprotonated derivatives. The results were compared with the experimental (NMR) results.

Results and Discussion

When hydroxylamine hydrochloride is dissolved in a solution of SbF_5–SO_2ClF, the formed fluoroantimonate salt shows two absorptions in the ^1H NMR spectrum at −80 °C at δ_{1H} (Me_4Si) 6.87 and 8.47 (Table I). From the multiplicities of the

$$NH_2OH{\cdot}HCl \xrightarrow[-80\ °C]{SbF_5\text{–}SO_2ClF} \overset{+}{H_3N}\text{–}OH\ Sb_2F_{10}Cl^-$$

coupling patterns and integration of the peak areas, the resonances were assigned to the hydroxyl and ammonium protons, respectively. When the temperature of the solution was raised, the doublet due to the ammonium group further broadened due to the ^{14}N quadruple effect. The quartet of the hydroxyl group, however, remained unaffected by change of temperature.

When antimony pentafluoride was replaced with magic acid, the proton absorption due to the hydroxyl group broadened and displayed no fine coupling. The ammonium group's absorption collapsed to a broadened singlet. When the temperature was raised the hydroxyl peak broadened and eventually merged into the baseline. This effect is reversible with no decomposition occurring and indicates an exchange process through diprotonated hydroxylamine (see subsequent discussion).

$$\overset{+}{H_3}NOH \underset{}{\overset{HSO_3F\text{–}SbF_5\text{–}SO_2ClF}{\rightleftharpoons}} \overset{+}{H_3}N\text{–}\overset{+}{O}H_2$$

The same temperature dependence effects are observed for *N*-methylhydroxylamine hydrochloride, trimethylamine oxide hydrochloride, and acetone oxime hydrochloride. In the ^1H NMR spectra the hydroxyl absorption in each of the above cases is observed even at −80 °C. Lowering the temperature results in a broad absorption at the same ^1H NMR chemical shift as observed in SbF_5–SO_2ClF solution (Table I).

The hydrogen chloride salt of dimethyl sulfoxide is stable and can be isolated from an ethereal solution.[10,11] When this salt was dissolved in a solution of SbF_5–SO_2, the formed fluoroantimonate displayed two sharp singlets in the ^1H NMR spectrum at δ_{1H} 6.26 (s) and 3.18 (s), corresponding to the absorptions of the hydroxyl and methyl groups, respectively. The ^1H NMR spectrum of the solution showed no temperature dependence between −20 and −80 °C.

When dimethyl sulfoxide is dissolved in a solution of

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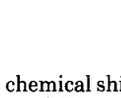
Table I. ^{1}H NMR Parameters of the Hydroxylamines, Acetone Oxime, and Dimethyl Sulfoxide in Strong Acid Solution

Registry no.	No.	Species	Solvent	Temp, °C	δ_{1H} (Me$_4$Si) NH$_3$	OH	CH$_3$
5470-11-1	5	NH_3^+OH Cl^-	SbF_5–SO_2ClF	−80	8.47 (bd)	6.87 (q)	
			HSO_3F–SbF_5–SO_2ClF	−80	8.53 (bs)	7.00 (b)	
					NH_2		
4229-44-1	6	$CH_3N^+H_2OH$ Cl^-	SbF_5–SO_2ClF	−20	8.60 (b)	7.18 (t)	3.66 (t)
			HSO_3F–SbF_5–SO_2ClF	−80	8.65 (bs)		3.53 (t)
				−100	8.73 (b)	7.30 (b)	3.60 (b)
7651-88-9	7	$(CH_3)_3N^+OH$ Cl^-	SbF_5–SO_2	−38		7.42 (s)	3.59 (s)
			HSO_3F–SbF_5–SO_2	−60			3.86 (s)
				−100		7.30 (bs)	3.60 (s)
					=NH		
4154-71-6	8	$HON^+H{=}C(CH_3)_2$ Cl^-	SbF_5–SO_2ClF	−80	11.13 (bs)	8.20 (s)	2.80 (s), 2.86 (s)
127-06-0		$HON{=}C(CH_3)_2$	HSO_3F–SbF_5–SO_2ClF	−10			2.88 (s), 2.80 (s)
				−60	11.21 (bs)		2.88 (s), 2.81 (s)
				−100	11.32 (bs)	8.40 (vb)	2.85 (b)
26394-12-7	9	$(CH_3)_2S{=}OH^+$ Cl^-	SbF_5–SO_2	−20		6.26 (s)	3.18 (s)
67-68-5	10	$(CH_3)_2S{=}O$	HSO_3F–SbF_5–SO_2	−20			3.36 (s)
				−100		6.53 (s)	3.38 (s)

Table II. ^{13}C NMR Chemical Shifts [a] of Protonated (Methylated) Heteroorganic Compounds

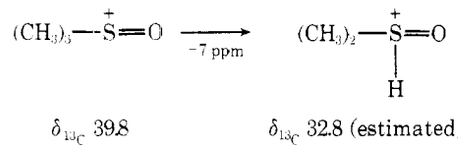
Registry no.	No.	Species	δ_{13C} (Me$_4$Si) 1	2	3	4
1184-78-7	11	$(CH_3)_3\overset{+}{N}{-}O^-$	62.1			
	7	$(CH_3)_3\overset{+}{N}{-}OH$	58.3			
	10	$(CH_3)_2S{=}O$	37.1			
	9	$(CH_3)_2S{=}\overset{+}{O}H$	34.3			
47987-92-8	12	$(CH_3)_3\overset{+}{S}{=}O$	39.8			
22396-69-6	13	$(CH_3)_2S{=}\overset{+}{O}CH_3$	32.7		60.4	
75-18-3	14	$(CH_3)_2\overset{+}{S}$	16.3			
18683-32-4	15	$(CH_3)_2\overset{+}{S}H$	19.5			
676-84-6	16	$(CH_3)_3S^+$	26.5			
67-71-0	17	$(CH_3)_2SO_2$	41.5			
26428-10-4	18		40.7			
65465-71-6	19		38.7		63.4	
67-64-1	20 [b]	$(CH_3)_2\overset{4}{C}{=}\ddot{O}$	30.2			205.1
43022-03-0	21 [c]		30.2	31.6		248.5
41798-19-0	22 [c]		27.0	32.2	68.8	245.1
	23		16.1	22.8		156.1
	24		18.2	21.8		181.8

[a] All of the ^{13}C NMR chemical shifts are referenced from external Me$_4$Si. All of the measurements were performed at −60 °C except where indicated otherwise. [b] These chemical shifts were obtained from ref 22. [c] The ^{13}C NMR data was measured in ref 17.

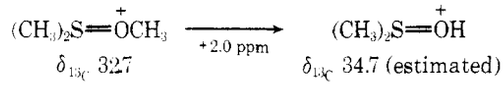
HSO_3F–SbF_5–SO_2 at −20 °C, the hydroxyl absorption is not observed in the ^{1}H NMR spectrum. On cooling the solution to −100 °C a slightly broadened singlet is observed at δ 6.53. The fact that there is no coupling with the methyl hydrogens led Modena[12] to assign the absorption at δ_{1H} 6.26 to the OH group (O-protonation) rather than to the SH group, as suggested in our preceding work.[13] However, since the absorption at δ 6.26 is broadened, it could indicate the possibility of coupling or an exchanging system.

It also appeared difficult to determine the site of protonation on the basis of ^{13}C NMR chemical shift data.[12] In order to estimate the ^{13}C NMR shifts of S- and O-protonated dimethyl sulfoxide, the ^{13}C NMR spectra of protonated and methylated dimethyl sulfide and dimethyl sulfone were used as models for the S and O derivatives of dimethyl sulfoxide, respectively. Table II shows that the replacement of the methyl group of trimethylsulfonium iodide by hydrogen results in a shielding of the methyl carbon resonance by 7.0 ppm.

Applying this value to the chemical shift of the trimethylsulfoxonium iodide[10,14] we could estimate the ^{13}C NMR resonance of S-protonated Me_2SO as $\delta_{^{13}C}$ (Me_4Si) 32.8. The *O*-



methyl derivative of dimethyl sulfone was slowly formed (1 h) when the sulfone was treated with an equimolar amount of CH_3F–SbF_5 in SO_2 at −30 °C. The methyl carbons bound to sulfur were shielded by 2.0 ppm relative to the protonated sulfone. Based on the ^{13}C NMR absorption of the O-methylated Me_2SO,[5] it is possible to estimate the carbon resonance of O-protonated Me_2SO as $\delta_{^{13}C}$ (Me_4Si) 34.7. Thus, the ex-



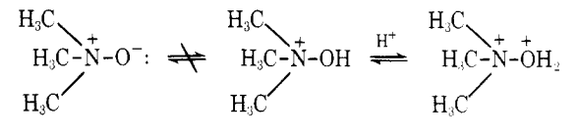
perimentally observed shift of $\delta_{^{13}C}$ 34.3 is close to the estimated value of the O-protonated form, but the S-protonated form deviates only slightly. The ^{13}C NMR chemical shifts in Table II are those of the static species indicated and are not in equilibrium.

Recent Raman spectroscopic studies by Spiekermann and Schrader[15] have indicated that the mono-O-protonated structure is formed in magic acid solution containing dimethyl sulfoxide. This is in accord with the general chemical background of acid-catalyzed reactions of dimethyl sulfoxide, indicating that a proton adds at oxygen, as well as the NMR spectroscopic data of Modena and the data described in the present work. Observed temperature-dependent behavior in superacid media raised the question of whether or not the diprotonation of dimethyl sulfoxide is involved in an exchange process.

When the hydrochloride salts of hydroxylamines, acetone oxime, and dimethyl sulfoxide were dissolved in a solution of antimony pentafluoride–sulfuryl chloride fluoride (or sulfur dioxide), the corresponding monoprotonated fluoroantimonate salts were obtained. The ^1H NMR spectra were usually not temperature dependent, and the site of protonation could be unequivocally determined from the spectra. When the same precursors were dissolved in a solution of HSO_3F–SbF_5–SO_2ClF (or SO_2), the NMR spectra were temperature dependent and did not display sharp absorptions or fine coupling. As the temperature of the solutions was lowered, the absorptions corresponding to the monoprotonated species started to be resolved in the ^1H NMR spectra. Thus, it appears that in the strong superacidic system an exchange reaction is taking place.

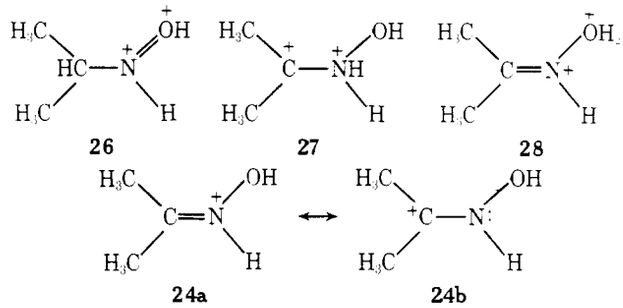
The observed exchange of the hydroxyl proton can be best explained through the intermediacy of an N,O (S,O) diprotonated species. In the ^1H NMR spectra of the monoprotonated species in SbF_5–SO_2ClF (or SO_2) (not a proton source) no exchange is observed. Thus, the exchange phenomenon with HSO_3–SbF_5 cannot be due to deprotonation to the neutral species followed by reprotonation. Although it can be concluded that exchange occurs through a diprotonated species, these obviously unstable (through charge–charge repulsion) species have not been directly observed under nonexchanging conditions.

In HSO_3F–SbF_5 solution trimethylamine oxide hydrochloride (**7**) is not in equilibrium with trimethylamine oxide (**11**). Rather, the basicity of the oxygen of **7**, despite the adjacent ammonium center, allows it to be protonated in HSO_3F–SbF_5, forming the diprotonated ion **25**. However, even the strong acidity of HSO_3F–SbF_5 is not large enough to



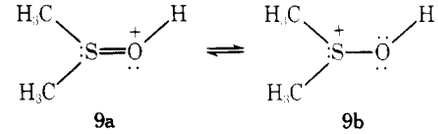
completely protonate **7**, which results in an equilibrium between **7** and **25**. As the temperature of the solution is lowered, the absorptions for the thermodynamically more stable monoprotonated ion **7** are observed in the ^1H NMR spectrum. Even at −120 °C some exchange is still taking place as evidenced by the slightly broadened absorptions. N-Protonated hydroxylamine (**5**) and N-methylated hydroxylamine (**6**) exhibit the same temperature-dependent behavior in their ^1H NMR spectra. In each case the second protonation can take place only on the nonbonded electron pair of the oxygen atom. This is not the case, however, for acetone oxime and dimethyl sulfoxide.

For N-protonated acetone oxime there are conceivably three possible sites for a second protonation: the iminium carbon (**26**), the nitrogen (**27**), and the oxygen (**28**). N-Pro-



tonated acetone oxime (**24**) is stabilized primarily by two resonance structures similar to those described for iminium ions.[16] Thus, due to their basicities, protonation at carbon (**26**) or nitrogen (**27**) is not considered feasible. This is confirmed by the NH absorption in the ^1H NMR spectrum and by the ^{13}C NMR shift of the iminium carbon. The hydroxyl absorption of $\delta_{^1H}$ 8.2 is shielded by 6 ppm from that of protonated acetone, indicating that the former site is more basic. Again diprotonation at the oxygen atom leads to exchange.

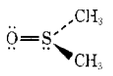
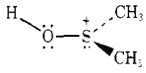
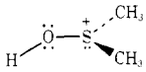
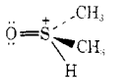
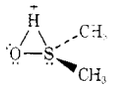
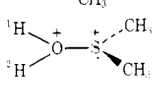
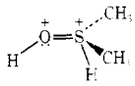
There is considerable evidence from IR, Raman, and NMR data of the various salts and strong acid solutions of dimethyl sulfoxide pointing toward O-protonation. Since the hydrochloric acid salt of dimethyl sulfoxide forms the static monoprotonated fluoroantimonate **9** in SbF_5–SO_2 solution (evidenced by the temperature independence of the ^1H NMR spectrum), it is possible to attain unequivocal structural information from its ^1H and ^{13}C NMR spectra. Resonance forms **9a** and **9b** contribute to the overall structure. In comparison



with the previously discussed protonated oximes, imines,[16] and ketones[17] (Tables I and II), it might have been expected that **9a** should be a major contributor to the overall structure, resulting in restricted rotation about the S–O bond. However, the ^1H and ^{13}C NMR spectra show only one methyl absorption, indicating free rotation about the S–O bond. Thus, the hydroxysulfonium ion (**9b**) is the major contributor to the overall structure of monoprotonated dimethyl sulfoxide (**9**).

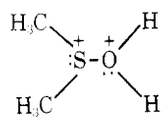
O-Protonated dimethyl sulfoxide is comparable to the *N*-hydroxytrimethylammonium ion (**7**) except that one of the methyl groups on nitrogen is replaced by a nonbonded pair

Table III. MINDO/3 Calculations of Heats of Formation, Bond Order, and Charge Densities for Dimethyl Sulfoxide and its Mono- and Diprotonated Ions

No.	Species	Geometry: Bond lengths, Å		Geometry: Angles, deg		ΔH_f, kcal/mol	S–O bond order	Charge density	
10		O–S	1.48	OSC	106.7	−47.7 (−46.9)[a]	0.791, 0.380, 0.447	−0.617	+0.853
		S–C	1.81	HCS	107.5				
		C–H	1.09						
9		H–O	0.936	HOS	144.2	80.1	0.603, 0.241, 0.279	−0.461	+0.865
9		H–O	0.935	HOS	131.3	83.2	0.678, 0.174, 0.282	−0.461	+0.775
30		H–S	1.40	HSO	237.8	153.2	0.705, 0.474, 0.365	−0.486	+1.168
31		H–O	1.33	HOS	56.2	183.0	0.733, 0.101, 0.258	−0.370	+0.666
		H–S	1.33	OHS	67.6				
29[b]		S–O	1.61	HOS[1]	133.2	370.7	0.583, 0.131, 0.130	−0.238	+0.667
		H–O[1]	0.966	HOS[2]	121.9				
		H–O[2]	0.980						
32		H–O	0.936	HOS	144.2	429.7	0.623, 0.277, 0.215	−0.458	+1.06
		H–S	1.40	HSO	237.8				

[a] Experimental value: *Natl. Bur. Stand. (U.S.), Circ.*, **500** (1952). [b] Registry no.: **29**, 65465-72-7.

of electrons. It is thus expected that the second protonation, as implied by the larger contribution of **9b** to **9**, will occur on oxygen, forming **29**. This is confirmed by the ^1H NMR spec-



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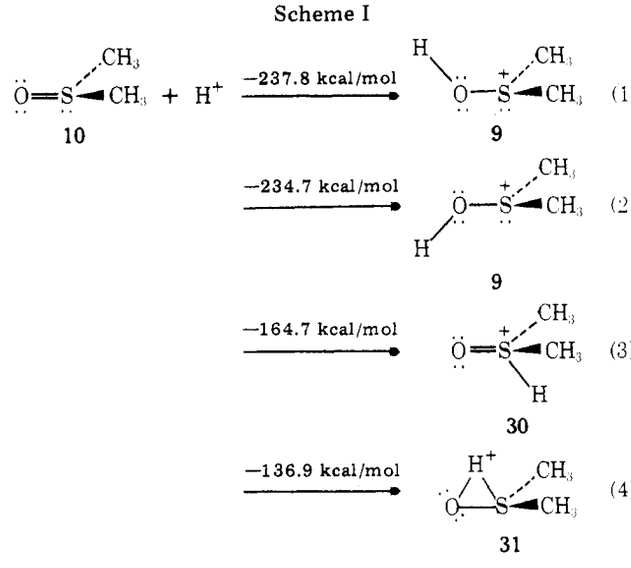
trum in HSO_3F–SbF_5, which only showed the temperature dependence of the hydroxyl absorption.

MINDO/3 Calculations of Mono- and Diprotonated Dimethyl Sulfoxide. Since the experimental evidence suggests that mono- and diprotonation of dimethyl sulfoxide take place in strong acid solutions on the oxygen atom, MINDO/3 calculations were carried out on the various possible structures of mono- and diprotonated dimethyl sulfoxide to investigate the most stable cations and to relate the energetics of the possible forms. The MINDO program was calibrated with respect to the heat of formation of dimethyl sulfoxide and its S–O bond length. Indeed, the required constants for the S–O bond were not available in the original QCPE 279 version of the MINDO program. The two parameters, α and β, required to evaluate the core repulsion integral and the resonance integral, respectively, were determined by a two-dimensional variation procedure that led to the values $\alpha_{SO} = 1.8$ and $\beta_{SO} = 0.51$. The results of the MINDO/3 calculations for the model compound Me_2SO and its protonated derivatives are summarized in Table III.

From the heats of formation in Table III it is possible to estimate the energetics of the sites of mono- and diprotonation of dimethyl sulfoxide. In Scheme I the monoprotonation reactions are given. As can be seen from the data, O-protonation of dimethyl sulfoxide is an extremely favorable process compared to either the formation of S-protonated or hydrogen-bridged structures. It is interesting to note that there are two relative minima for O-protonation with an energy difference of only 3.1 kcal/mol for the syn and anti forms. Thus, the O-protonated cation is the most stable species, as observed experimentally. This is reasonable if the charge densities of the

Scheme I

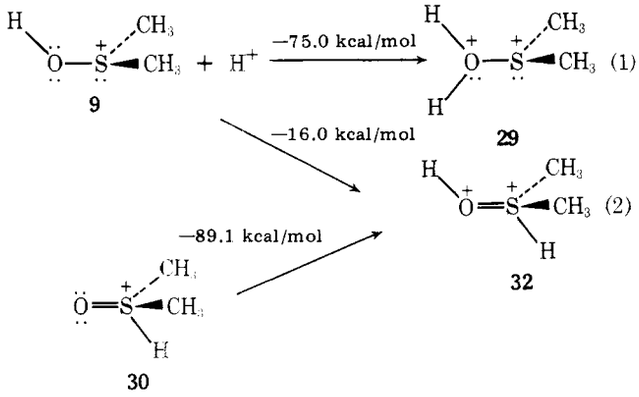


oxygen and sulfur atoms are considered before and after protonation. In dimethyl sulfoxide the charge on oxygen is −0.617 and on sulfur it is +0.853. After O-protonation the charge on oxygen increased to −0.461 while that on sulfur remained approximately the same. With S-protonation the charge on sulfur increased substantially to +1.168, whereas it remained approximately the same on oxygen. Upon O-protonation there is a lessening of the dipole of the S–O bond, whereas the charge difference in S-protonation increases, indicating a less stable system. Electrostatic addition to oxygen is thus favored.

From the data of Table III, Scheme II depicts the energetics of the formation of syn-O-protonated dimethyl sulfoxide and the diprotonated species. From the syn-O-protonated dimethyl sulfoxide, O-protonation is again found to be the most favorable. From the relative charges on sulfur and oxygen the electrostatic addition to oxygen to form **29** is expected.

The MINDO/3 results agree well with the experimental observation in strong acids. The values for the heat of reaction from Schemes I and II are not expected to agree experimen-

Scheme II



tally due to the solvation effect of the proton. The heat of formation of the proton (+365.5 kcal/mol) should be considerably lower[18] since the de facto protonating agent is $H_2O_3{}^+SF$ and not the naked proton itself. This will make the reactions less favorable energetically, but the relative energies of different O- and S-protonated species should not be affected.

Conclusions

The solutions of the hydrochloric acid salts of *N*-hydroxylamines, acetone oxime, and dimethyl sulfoxide in SbF_5–SO_2ClF (SO_2) gave the monoprotonated fluoroantimonates. Their ^1H and ^{13}C NMR spectra allowed the determination of the site of protonation. In HSO_3–SbF_5–SO_2ClF (or SO_2) it was possible from the ^1H NMR data to show that a second protonation takes place, resulting in exchange with the monoprotonated species. Since oxygen is the only basic site in the *N*-hydroxytrimethylammonium ion, it was unequivocally shown that the second protonation occurs on oxygen. When considering all of the possible sites for the second protonation of acetone oxime, it was concluded from the ^1H NMR data that exchange was occurring through protonation on oxygen. In the case of dimethyl sulfoxide, it was also determined from the ^1H NMR data that a second protonation on oxygen causes exchange of the hydroxyl proton. MINDO/3 calculations were also carried out on dimethyl sulfoxide and its mono- and diprotonated ions. The results in all cases showed mono- and diprotonation at oxygen to be most favorable, in agreement with the experimental data.

It was thus possible to demonstrate that diprotonated species can be formed in superacidic media. Such species could be involved in some acid-catalyzed reactions.

Experimental Section

Starting Materials. Hydroxylamine hydrochloride and dimethyl sulfoxide were commercially available of highest purity (Baker Chemical Co.), as were trimethylamine oxide dihydrate, dimethyl sulfone, and dimethyl sulfide (Eastman Chemical Co.) and acetone oxime (Air Products).

Trimethylamine oxide (2 g) was prepared by heating the dihydrate under vacuum (~1 mm) at 150 °C for 2 h. Trimethylamine oxide hydrochloride was prepared from the dihydrate as reported.[20]

The hydrochloride salts of acetone oxime[21] and dimethyl sulfoxide were prepared by dissolving equimolar amounts of dry HCl and the precursor in dry diethyl ether. The salt, which immediately precipitates out of solution, was filtered under a dry nitrogen atmosphere and stored in a desiccator.

Preparation of Solutions. The precursors (~0.5 g) were dissolved in SO_2 or SO_2ClF solutions and then carefully added to a solution of HSO_3F–SbF_5 or SbF_5 (~2 g), dissolved in SO_2ClF or SO_2 (~2 g) to give approximately 10% solutions. All of the solutions were kept in a dry ice–acetone bath.

Nuclear Magnetic Resonance Studies. The ^1H NMR spectra were obtained on a Varian Associates Model A-56/60 spectrometer equipped with a variable temperature probe and controller.

The ^{13}C NMR studies were performed on a Varian XL-100-15 spectrometer equipped for proton decoupling, with a variable temperature unit and a 620L computer with 16K data points. The instrument was run in the Fourier transform pulse mode with either proton decoupling or the fully coupled experiment with some nuclear Overhauser effect. The pulse width (H_1 field) in typical experiments was 2–15 μs, where a 42-μs pulse is equivalent to a 90° pulse. Acquisition times were between 0.3 and 0.8 s with pulse delays of 0–9 s depending on the experiment. The total number of transients for a suitable signal to noise ratio for each absorption varied from 100 to 7000 passes. The radio frequency was 25.16 MHz, with the absorption referenced from external Me_4Si in CCl_3F.

MINDO/3 Calculations. The experimental geometry of dimethyl sulfoxide[11] was used in all calculations of the parent compound and its protonated derivatives. For the protonated species all of the bond lengths, angles, and dihedral angles involving the attacking proton were completely optimized. In addition to these parameters, the S–O bond length was optimized for the O-diprotonated species.

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