2000 cm^{-1} bear a 1:1 correspondence with the spectra of KSO_3F and $K(HS_2O_7)$, respectively.

Normal-Coordinate Analysis.—A normal-coordinate analysis was performed for the Se_4^{2+} D_{4h} model using Wilson's *FG*-matrix method.[14]

The symmetry coordinates are

$$S_r^{A_{1g}} = {}^1/_2(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_r^{B_{1g}} = {}^1/_2(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_\alpha^{B_{2g}} = {}^1/_2(\Delta \alpha_1 - \Delta \alpha_2 + \Delta \alpha_3 - \Delta \alpha_4)$$

$$S_r^{E} = \frac{1}{\sqrt{}}(\Delta r_1 - \Delta r_3)$$

$$S_\alpha^{E_u} = \frac{1}{\sqrt{2}}(\Delta \alpha_1 - \Delta \alpha_3)$$

where the Δr and $\Delta \alpha$ terms refer to small increments in the Se–Se bond lengths and the SeSeSe angles, respectively.

A Urey–Bradley (UB) force field was employed since there is not sufficient vibrational data for evaluating a general potential function. The UB potential is given by

$$2V = \sum_i [2K'r\Delta r_i + K(\Delta r_i)^2] + \sum_{i<j} [2H'r^2\Delta\alpha_{ij} + Hr^2(\Delta\alpha_{ij})^2] + \sum_{i<j}[2F'q\Delta q_{ij} + F(\Delta q_{ij})^2]$$

where K and H are the bond stretching and valence angle bending force constants, respectively. F and F' are the UB interaction constants associated with the displacements (Δq_{ij}) in the equilibrium distance[9] between adjacent nonbonded atoms. The linear displacement constants K' and H' can be neglected because of the equilibrium condition that $\partial V/\partial r = 0$ and $\partial V/\partial \alpha = 0$. The F-matrix elements in Wilson's method were expressed in terms of K, H, and F (F' was put equal to $-0.1F$) using the technique described by Overend and Scherer.[15] Four linear equations are obtained relating the force constants to the vibrational frequencies, any three of which can be solved directly for K, H, and F.

From the data for A_{1g} (327 cm^{-1}), E_u (306 cm^{-1}), and B_{2g} (188 cm^{-1}) we arrive at $K = 2.2$, $H = 0.12$, and $F = 0.15$ mdyn/Å. The B_{1g} mode is then predicted to occur at 306 cm^{-1} which is in reasonable agreement with either of the assignments discussed for this vibration.

As far as we are aware, the only other Se–Se stretching force constants available for comparison are those for the $^{80}Se_2$ molecule ($k = 3.498$ mdyn/Å, $r_e = 2.1661$ Å)[16] and for dimethyl diselenide. For $(CH_3)_2Se_2$, the value of $k = 1.674$ mdyn/Å has been estimated on the basis of a modified valence force field calculation. We feel that our value of 2.2 mdyn/Å is significantly larger despite the fact that it relates to a different potential function. This presumably indicates that there is some degree of multiple bonding in the Se_4^{2+} ion. A simple Hückel-type MO calculation gives an Se–Se bond order of 1.5.[3] The UB constants H and F may be compared with those for ClSSCl ($H_{SSCl} = 0.21$, $F_{SCl} = 0.19$ mdyn/Å) and BrSSBr ($H_{SSBr} = 0.15$, $F_{SBr} = 0.16$ mdyn/Å).[17]

Acknowledgment.—We thank the National Research Council of Canada for financial support of this work.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

The Fluorosulfuric Acid Solvent System. VII. The Behavior of Some Extremely Weak Bases in the Superacid System HSO_3F–SbF_5–SO_3

BY R. J. GILLESPIE AND G. P. PEZ

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Nitrogen, oxygen, neon, xenon, hydrogen, nitrogen trifluoride, and carbon monoxide all have a very small solubility in the HSO_3F–SbF_5–SO_3 system and do not appear to be protonated. Carbon dioxide has a moderate solubility and sulfur dioxide has a high solubility in this superacid solvent but neither is protonated to any significant extent. The very weak base 1,3,5-trinitrobenzene appears to be completely protonated.

Introduction

Considerable use has been made in the past few years of the extremely high acidity of solutions of antimony pentafluoride in fluorosulfuric acid in the study of the protonation of a variety of weak organic bases.[1-3] Conductivity and nmr measurements[4] have shown that these solutions contain the acid $H[SbF_5(SO_3F)]$ which is partly ionized according to

$$H[SbF_5(SO_3F)] + HSO_3F \rightleftharpoons H_2SO_3F^+ + SbF_5(SO_3F)^-$$

thus giving a moderately high concentration of the fluorosulfuric acidium ion $H_2SO_3F^+$ and consequently a rather highly acidic medium. It has also been shown that the high acidity of this system can be further in-

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[1] R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968).

[2] G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3586 (1967); G. A. Olah and R. H. Schlosberg, *ibid.*, **90**, 2726 (1968).

[3] M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, **89**, 1735 (1967).

creased by the addition of sulfur trioxide.[4] Conductivity and ^{19}F nmr measurements indicate that the partly ionized acid $H[SbF_5(SO_3F)]$ is replaced by the fully ionized acid $H[SbF_2(SO_3F)_4]$ in a mixture containing SO_3 in the $SO_3:SbF_5$ mole ratio of >3.

$$H[SbF_2(SO_3F)_4] + HSO_3F \longrightarrow H_2SO_3F^+ + SbF_2(SO_3F)_4^-$$

Thus the concentration of $H_2SO_3F^+$ is raised to a high value and this mixture would appear to be the most highly acidic medium that has yet been studied.[5] It was considered worthwhile therefore to investigate the possibility that a number of species that are not ordinarily regarded as bases might be protonated in this medium. The behavior of hydrogen, nitrogen, oxygen, xenon, neon, nitrogen trifluoride, carbon monoxide, carbon dioxide, sulfur dioxide, and 1,3,5-trinitrobenzene has been examined.

Experimental Section

Materials.—Fluorosulfuric acid, antimony pentafluoride, and potassium fluorosulfate were purified as described previously.[4,6] The superacid mixture $HSO_3F-SbF_5-SO_3$ was prepared by mixing the first two components and adding to this a 20% w/w solution of SO_3 in HSO_3F. All transfer operations were done in a dry nitrogen atmosphere. Eastman Kodak 1,3,5-trinitrobenzene (mp 121.8–122.0°) was used. The gases He, Xe, Ne, O_2, N_2, CO, CO_2, and SO_2 were high-purity commercial samples which were purified by low-temperature trap-to-trap distillation when possible. Nitrogen trifluoride (minimum purity 95%) was obtained from K & K Chemicals, New York, N. Y. All of the gases were stored in glass bulbs over P_2O_5 for several days before use.

Solubility Measurements.—Gas solubilities in the superacid system were measured by following gas-pressure changes accompanying dissolution on a simple volume-calibrated vacuum system. For each determination the solvent was kept at $20 \pm 0.3°$. Ideal gas behavior was assumed.

Conductivity Measurements.—The apparatus used for the conductivity determinations has been previously described.[6] Measurements were made in an oil thermostat at $25 \pm 0.002°$ or in a trichloroethylene bath at −83.6°.

Results

Each of the gases nitrogen, oxygen, carbon monoxide, neon, xenon, hydrogen, and nitrogen trifluoride has a solubility of less than 1 ml of gas/100 ml of the superacid solvent HSO_3F-SbF_5 (0.36 *m*)–SO_3 (1.06 *m*). This is of the same order as their solubilities in water which strongly indicates that they do not undergo protonation in this medium. The electrical conductivity of the acid remained unchanged when it was allowed to come to equilibrium with an atmosphere of helium, nitrogen, or oxygen at 1 atm pressure. Any base behavior would have reduced the concentration of the acid cation $H_2SO_3F^+$ and hence would have reduced the conductivity of the solution.

Carbon dioxide was found to be moderately soluble in the HSO_3F-SbF_5 (2.94 *m*) acid; a 0.2 *M* solution of CO_2 was obtained in this solvent at 20.3° and 1 atm pressure. The solubility was essentially the same in an acid mixture containing a higher concentration of SbF_5 and also SO_3 (HSO_3F-SbF_5 (6.10 *m*)–SO_3 (4.51 *m*)). In each case the gas dissolution closely obeyed Henry's law from 0 to 76 cm. When the atmosphere above an acid mixture having the composition HSO_3F-SbF_5 (0.36 *m*)–SO_3 (1.06 *m*) was changed from helium to carbon dioxide at 1 atm pressure, the conductivity decreased from 3.984×10^{-2} to 3.955×10^{-2} ohm^{-1} cm^{-1}. This decrease in conductivity could be attributed to a slight protonation of carbon dioxide and the consequent removal of the fluorosulfuric acidium ion $H_2SO_3F^+$

$$H_2SO_3F^+ + CO_2 \rightleftharpoons HCO_2^+ + HSO_3F$$

However, this very small drop in conductivity corresponds to less than 1% ionization of the carbon dioxide in the 0.2 *M* solution.

Conductivity measurements were also made at −86.4°. In this case the conductivity of the same $HSO_3F-SbF_5-SO_3$ solvent increased from 2.449×10^{-3} to 2.541×10^{-3} ohm^{-1} cm^{-1} when a nitrogen atmosphere was replaced by a carbon dioxide atmosphere and the carbon dioxide attained a concentration in the solution of approximately 0.3 *M*. The conductivity change is again extremely small and increases rather than decreases as at 25°; possibly the carbon dioxide causes a decrease in the viscosity of the solution which is quite appreciable at −86°. The infrared spectrum of carbon dioxide in fluorosulfuric acid has a broad band at 2400 cm^{-1} which is the only characteristic absorption observed in addition to those arising from the solvent. This presumably arises from the antisymmetric C–O stretching vibration observed at 2380 cm^{-1} in the gas. Thus the dissolution of carbon dioxide in fluorosulfuric acid produces little or no solvent shift in its infrared spectrum. Proton nmr spectra of CO_2 solutions having concentrations in the range 0.2–1 *M* in HSO_3F and HSO_3F-SbF_5 showed only the single solvent peak at all temperatures down to −85°. We can only conclude that there is no evidence for the protonation of carbon dioxide in these acid systems.

Sulfur dioxide is extremely soluble in the HSO_3F-SbF_5 and $HSO_3F-SbF_5-SO_3$ systems. In the acid HSO_3F-SbF_5 (6.45 *m*)–SO_3 (14.50 *m*) a 2 *M* solution of SO_2 was obtained at 60 cm. Measurements to lower pressures of SO_2 closely follow Henry's law and it appears unlikely therefore that there is any appreciable protonation of the sulfur dioxide. Conductivity measurements point to the same conclusion. A conductivity decrease from 3.980×10^{-2} to 3.946 ohm^{-1} cm^{-1} was observed when SO_2 was added to the acid mixture HSO_3F-SbF_5 (0.36 *m*)–SO_3 (1.06 *m*) up to a concentration of 0.25 *M* SO_2. The conductivity decrease is approximately the same as that produced by carbon dioxide in the same concentration range. Proton nmr spectra of solutions of SO_2 in the superacid mixture showed only the single solvent peak at all temperatures down to −85°. It was not possible to obtain infrared spectra of the dissolved sulfur dioxide because of strong background absorptions from SO vibrations of the acid. The position and intensity of the 2900-Å ultraviolet absorption band of dissolved SO_2 did not change when the following solvents were used: 100% H_2SO_4, 65%

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oleum,[7] HSO_3F, and HSO_3F–SbF_5 (10 mol %). We conclude that there is no evidence for the protonation of sulfur dioxide in HSO_3F, HSO_3F–SbF_5, or HSO_3F–SbF_5–SO_3.

It has been shown that 1,3,5-trinitrobenzene behaves as a very weak base in fluorosulfuric acid.[6] Its degree of ionization has not been measured with precision, but it is probably less than 1%. When 1,3,5-trinitrobenzene is added to an HSO_3F–SbF_5 (0.330 *m*)–SO_3 (1.182 *m*) superacid mixture, it causes a marked decrease in the conductivity which continues until approximately 1 mol of trinitrobenzene had been added for each mole of the acid $H[SbF_2(SO_3F)_4]$ orginally present. This indicates that trinitrobenzene is fully ionized in the superacid solvent. Comparison is made in Figure 1 with the behavior of the strong base KSO_3F. In the case of trinitrobenzene the conductivity does not increase after the stoichiometric end point because it is too weak a base to ionize appreciably in the HSO_3F solvent after the strong acid $H[SbF_2(SO_3F)_4]$ has been titrated whereas KSO_3F is a strong base of the fluorosulfuric acid solvent.

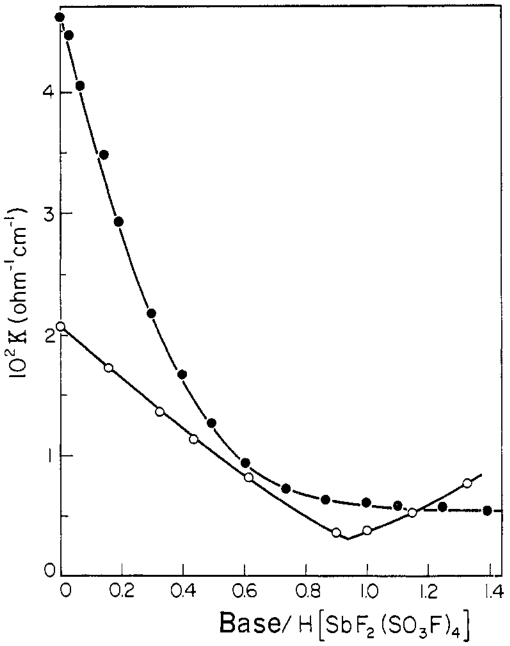

Figure 1.—Conductometric titrations of solutions of the acid $H[SbF_2(SO_3F)_4]$ in HSO_3F with 1,3,5-$C_6H_3(NO_2)_3$, ●, and with KSO_3F, ○.

Discussion

Despite the fact that the system HSO_3F–SbF_5–SO_3 is the most highly acidic system yet investigated, it is not a sufficiently strong proton donor to protonate nitrogen, oxygen, carbon monoxide, hydrogen, neon, xenon, carbon dioxide, and sulfur dioxide. It has, for example, been suggested that, because of its relatively high electronegativity, neon should be protonated to give NeH^+ in strong inorganic acids.[8] Recently nitrogen has been shown to form stable complexes with some transition metals.[9] Since our results show that nitrogen can have only extremely weak donor properties toward the proton, the formation and stability of the transition metal complexes must clearly be attributed largely to electron release from the metal into vacant orbitals on the nitrogen which also enhances the donor properties of the nitrogen lone pair. Substituting the hydrogens in ammonia with fluorine is expected to cause a large decrease in basicity but it is nevertheless somewhat surprising that NF_3 shows no basic properties at all in the superacid media. Substitution of the alkyl groups in a ketone by a doubly bonded oxygen clearly also causes a very great decrease in basicity as we have found no evidence for the protonation of carbon dioxide whereas ketones and aldehydes are in general completely protonated in various acid solvents such as H_2SO_4 and HSO_3F.[1]

The complete lack of protonation or any other form of interaction between sulfur dioxide and the superacid medium is also somewhat surprising particularly in view of its high solubility in these highly acidic media and the previously observed marked increase in the solubility between 100% H_2SO_4 and a concentrated oleum.[10] There is presumably some hydrogen-bonded interaction between the SO_2 and the solvent but this is apparently not strong enough to have any observable effect on the position and intensity of the ultraviolet absorption spectrum of sulfur dioxide.[7] It is interesting to note, however, that antimony pentafluoride is a sufficiently strong Lewis acid to form a stable acid–base complex with sulfur dioxide[11] despite the demonstration of the very weak basicity of sulfur dioxide toward the HSO_3F–SbF_5–SO_3 superacid.

As a part of an extensive but, as yet, incomplete series of measurements using nitro compounds as indicators on the Hammett acidity function of the HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3 systems a preliminary value of -15 has been obtained for the pK of 1,3,5-trinitrobenzene.[12] Since this base is fully ionized in the HSO_3F–SbF_5 (0.330 *m*)–SO_3 (1.182 *m*) superacid mixture the H_0 of this mixture must be at least -16.

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