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Conjugate Brönsted–Lewis superacids in fluorosulfuric acid—Hammett acidity function and electrical conductivity studies of Ta(V), Nb(V) and Sb(V) Lewis acids

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Abstract

Conjugate Brönsted–Lewis superacids in fluorosulfuric acid are studied by two techniques. Hammett acidity function studies on HSO_3F–$Ta(SO_3F)_5$ in the concentration range of 0–3.4 mol% of Lewis acid are reported. The conjugate system HSO_3F–$Ta(SO_3F)_5$ shows in this range of Lewis acid concentration acidities equal or higher to those of HSO_3F–$3SO_3$–SbF_5, which is commonly assumed to be the strongest conjugate protonic acid. Electrical conductivities of the neat Lewis acids of the type $MF_n(SO_3F)_{5-n}$, $n=3$ or 4, M = Nb or Ta, and of their solutions in HOS_3F over the complete concentration range are studied and compared to conductivities of SbF_5 in HSO_3F and in anhydrous HF. All conjugate superacids in HSO_3F are found to be highly conducting and strongly ionizing over the entire concentration range.

Keywords: Brönsted–Lewis; Conjugate; Protonic acid

1. Introduction

Among the very strong protonating and ionizing solvents, the highest proton acidities are encountered in conjugate Brönsted–Lewis acids [1–3]. These solvent systems are composed of a strong protonic or Brönsted acid—or superacid—as solvent,[1] HA, and a molecular Lewis superacid,[2] Y as solute. The self-ionization or proton-transfer of HA according to:

$$2HA \rightleftharpoons H_2A^+_{solv} + A^-_{solv} \qquad (1)$$

will be, in the simplest case, affected by the addition of Y in two ways: (i) the acidium ion H_2A^+ concentration will be increased, and (ii) the nucleophilicity of the base ion A^- will be reduced by complexation to Y to give the less basic, complex anion $[AY]^-$:

$$2HA + Y_{solv} \rightleftharpoons H_2A^+_{solv} + [AY]^-_{solv} \qquad (2)$$

The Hammett acidity function, $-H_0$ [8], is commonly used as a measure of acidity and procedures have been developed to apply $-H_0$ determinations to conjugate superacids [4–6]. A critical evaluation of acidity determinations of highly acidic conjugate systems with $-H_0$ values of ≥20 has appeared [9].

Of the simple protonic superacids of the type HA, fluorosulfuric acid HSO_3F [7,10,11] and anhydrous HF [12] have emerged as the strongest proton donors with identical $-H_0$ values of 15.1 [4–6,13]. For Lewis superacids, a number of methods have been employed to arrive at a ranking according to their acceptor ability [2,14]. It is, however, generally agreed that Sb(V) fluoride, SbF_5, ranks as the strongest Lewis superacid of those compared [2,14]. It should hence follow that the conjugate superacids HF–SbF_5 and HSO_3–SbF_5 or 'Magic Acid' [1,2,15,16] should display the very highest acidities, and estimates of $-H_0$ up to 30 (or about 15 orders of magnitude more acidic than HF or HSO_3F) have been made [1,2]; however, accurate measurements beyond $-H_0$, values of 23 are experimentally very demanding and open to criticism [9].

Of the protonic superacids, fluorosulfuric acid, because of its large liquid range (−89 to 167.7°C), its compatibility with glass, the availability of purification methods [17] and its outstanding solvent characteristics [7,10,11] offers clear

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[1] Brönsted superacids are defined as protonic acids of higher acidity than 100% H_2SO_4. See the work of Gillespie and Peel [4,5], Gillespie et al. [6] and Gillespie [7].

[2] Lewis superacids are defined as stronger electron pair acceptors than $AlCl_3$ (see the work of Olah et al. [1,2]). Note: the term is restricted to molecular Lewis acids and does not include atomic Lewis acids H^+ or M^{n+}.

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advantages over anhydrous HF both in its applications and in the use of physical measurements. In particular, electrical conductivity measurements [17,18], ^{19}F NMR studies at variable temperatures [7,10,11] and Hammett function studies [4,6,5] are more easily performed in this solvent than in HF. This is best illustrated by the $-H_0$ values of HF, which is not directly measured, but rather obtained by interpolation methods [13]. The interpolated value of $-H_0 = 15.1$ differs dramatically from the measured value of ~ 11 [1,2]. On the other hand, the 'heteroleptic' [18] conjugate superacid HSO_3F–SbF_5 or 'Magic Acid' suffers from considerable complexity because of F vs. SO_3F^- redistribution, apparent in the reported ^{19}F NMR spectra [18,19]. There has hence been some effort spent on the development of 'homoleptic' [18] conjugate superacids in HSO_3F which would involve binary fluorosulfates as Lewis acids. Four such conjugate superacid systems, HSO_3F–$Au(SO_3F)_3$ [20,21], HSO_3F–$Pt(SO_3F)_4$ [22], and HSO_3F–$M(SO_3F)_5$, M = Nb or Ta [23], have been developed and studied by various methods, among them conductometry [20–23]. More recently, the potential system HSO_3F–$Sb(SO_3F)_5$ has come into focus with the isolation and characterization of $Cs[Sb(SO_3F)_6]$ [21]a. In addition a number of well defined fluoride–fluorosulfates of Nb(V) and Ta(V) with the composition $MF_n(SO_3F)_{5-n}$, with $n = 3$ or 4 [24], which are found to be miscible with HSO_3F at any concentration. In contrast, NbF_5 and TaF_5 have only limited solubility in either HF or HSO_3F, [1,2] presumably due to their tetrameric structures [25].

Due to this excellent solubility, electrical conductometric studies at 25°C are now possible for the $MF_n(SO_3F)_{5-n}$, $n = 3$ or 4, species in HSO_3F solutions over the entire concentration range and allow a comparison to the HSO_3F–SbF_5 system. An electrical conductance study over the entire concentration range has been reported only for the HF–SbF_5 system [26,27].

For a Hammett acidity function study according to:

$$H_0 = pK_{BH^+} - \log[BH^+]/[B] \qquad (3)$$

the indicator base ratio BH^+/B is determined spectrophotometrically as discussed previously [4–6]. The noble-metal systems HSO_3F–$Au(SO_3F)_3$ [20,21] and HSO_3F–$Pt(SO_3F)_4$ [22] are unsuited for this purpose because both are intensely coloured, possibly on account of ligand-to-metal charge transfer transitions [20–22]. Hence, the homoleptic system HSO_3F–$Ta(SO_3F)_5$ [23] is chosen, with the Lewis acid $Ta(SO_3F)_5$ prepared in situ by the oxidation of Ta by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$ [28,29]. The conjugate system HSO_3F–$Nb(SO_3F)_5$ appears to be a weaker protonic acid as judged by a conductometric study in HSO_3F up to concentrations of ~ 0.04 mol kg^{-1} [23].

This study is expected to increase our insights into novel and useful conjugate superacid systems of Sb(V), Ta(V) and Nb(V) Lewis acids. The conductivity measurements over the entire concentration range of the HA–Y systems move from the traditional dilute solution studies (up to 0.05 mol kg^{-1}) to ranges that are used in practical applications of superacids [1–3].

2. Experimental

2.1. Chemicals

The Lewis acids $Ta(SO_3F)_5$ [23], $TaF_3(SO_3F)_2$ [24], $TaF_4(SO_3F)$ [24], $NbF_3(SO_3F)$ [24], and $NbF_4(SO_3F)$ [24] were synthesised according to published methods. The fluorides TaF_5, NbF_5, and SbF_5 were obtained from AtoChem North America (formerly Ozark-Mahoning). The former two were of a quoted purity of 99% and were used without further purification. Sb(V) fluoride was purified by repeated distillation. The pure product, recognizable by its high viscosity, was obtained by a final trap-to-trap distillation. Details on the purification and manipulation of SbF_5 were published recently [30]. Fluorosulfuric acid of technical grade (Orange County Chemicals) is purified by double distillation at atmospheric pressure as described previously [17]. Bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, was obtained by the catalytic fluorination (AgF_2) of SO_3. An improved procedure has recently been published [29]. Ta and Nb metal powders were obtained from Matthey and Johnson. The indicator bases 2,4-dinitrofluorobenzene (DNBF) (Matheson, Coleman Bell) and 2,4,6-trinitrotoluene (TNT) (Eastman Organic Chemicals) were obtained commercially. Both were recrystallized from methanol and dried in vacuo over P_4O_{10}. They and their monoprotonated cations, $DNFBH^+$ and $TNTH^+$, were employed in this study.

2.2. Measurements

Hammett acidity function measurements followed published precedents [6,5]. Our equipment to measure electrical conductivities [20,21], the conductivity cell design [17,18], cell calibration procedures [17,18,20,21], and the constant-temperature bath [20,21] operating at 25.0°C have all been described. Conductivity measurements on Lewis acid–HSO_3F solutions were started with measurements of the neat Lewis acids. HSO_3F was gradually added from a graduated, pre-weighed burette inside a drybox (Vacuum Atmosphere, Hawthorne, CA) model DL-001-S-G filled with dry N_2. Measurements were made about 30 min after mixing.

2.3. Ultraviolet/visible optical cells and equipment

To allow various manipulations of solutions without exposing them to the atmosphere, 1-mm quartz Spectrosil precision optical cells were attached via a Pyrex bridge to a 25-ml round-bottom flask fitted with a B19 cone. In addition, the apparatus was fitted with a Kontes Teflon stem stopcock and a sidearm attached to a B10 cone. A matching adaptor consisting of a Kontes Teflon stem stopcock between a B10 cone and a B19 socket was also provided. Sample solutions were usually loaded into the solvent-containing flask in the drybox, mixed thoroughly and then transferred into the optical cell chamber by tilting the apparatus. Reproducibility was tested by repeating the above mixing procedure a few times between readings. On some occasions, it was adequate to use 10-mm Spectrosil precision optical cells, fitted with Teflon plugs and sealed with Teflon tape.

Electronic spectra were recorded on a Hewlett Packard single-cell mode array spectrophotometer, Model 8452A, incorporating HP Vectra computer hardware and a HP Think Jet printer. Software was available for internal sample referencing.

3. Results and discussion

3.1. The acidity of the HSO_3F–$Ta(SO_3F)_5$ superacid

High concentrations of Lewis acid are not suitable for study due to various experimental restrictions, among them problems encountered when trying to quickly dissolve more Ta metal powder in the $S_2O_6F_2/HSO_3F$ mixtures. The reaction times needed are too long, leading to contamination from a slow leakage of air into the reactor or from trace amounts of grease dissolved in the media. It is found that only reactions of less than about 5 days duration give reproducible H_0 values.

The Hammett acidity values for $Ta(SO_3F)_5$ in HSO_3F at select concentrations studied are given in Table 1. The plot of $-H_0$ vs. mol% Lewis acid is shown in Fig. 1 for $Ta(SO_3F)_5$, and for the two strong Lewis acids SbF_5 ('Magic Acid') and $SbF_2(SO_3F)_3$ [4–6]. The principal feature of the plot is that beyond a concentration of about 1 mol%, $Ta(SO_3F)_5$ appears to be at least as strong as $SbF_2(SO_3F)_3$. The second striking feature worth noting is that compared to either SbF_5 or $SbF_2(SO_3F)_3$, the rate of $-H_0$ increase is considerably less for $Ta(SO_3F)_5$ in the 0–1 mol% range, whereas beyond this concentration, it is equal or even greater than for the other two solutions.

Both features of the $Ta(SO_3F)_5$ acidity can be explained. Its unexpectedly high value at concentrations beyond ~ 1 mol% (~ 0.1 m) has already been predicted by the conductance results [23], which revealed the oligomeric nature of this system in addition to a 10-fold increase of its acidic dissociation constant with a similar increase in concentration (from 0.01 to 0.1 m). By extrapolation of the conductivity results, the acidic dissociation constant, K_a, for $Ta(SO_3F)_5$ should be of the order of 2×10^{-2} m at 1 mol% and 1×10^{-1} m at 5 mol%. From the previously estimated concentration of $H_2SO_3F^+$ in 100% HSO_3F and its $-H_0$ value, the idealized Eqs. (4) and (5) can be used to estimate K_a for $Ta(SO_3F)_5$ in HSO_3F at any given concentration. $[H_2SO_3F^+]$ is equal to $[Ta(SO_3F)_6]$ in the latter equation.

$$-H_0 = \log[H_2SO_3F^+] + 18.79 \tag{4}$$

$$K_a = \frac{[H_2SO_3F^+][Ta(SO_3F)_6]}{[Ta(SO_3F)_5]} \text{ mol kg}^{-1} \tag{5}$$

Table 1
The Hammett acidities of $Ta(SO_3F)_5$ in HSO_3F at 20°C

$[Ta(SO_3F)_5]$, mol%	$-H_0$	Indicator
0	15.07	DNFB, TNT
0.055	15.55	DNFB, TNT
0.154	16.07	TNT
0.318	16.73	TNT, DNFBH+
0.913	18.03	DNFBH+
1.25	18.36	DNFBH+, TNTH+
1.80	18.58	TNTH+
2.11	18.71	TNTH+
3.37	18.91	TNTH+

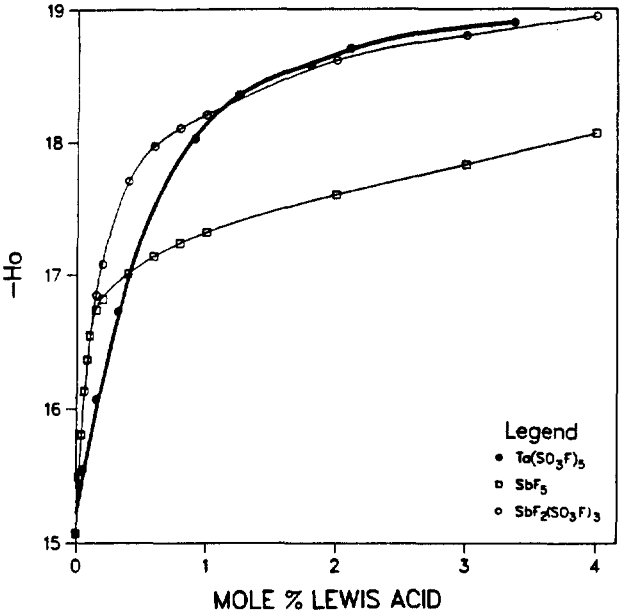

Fig. 1. Hammett acidity of $Ta(SO_3F)_5$, SbF_5 [4–6] and $SbF_2(SO_3F)_3$ [4–6] in HSO_3F at ambient temperature.

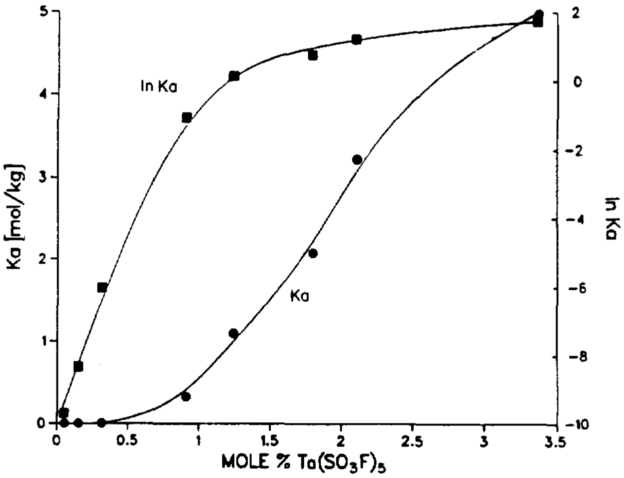

Fig. 2. Dependence of the acidic dissociation constant, K_a, on $Ta(SO_3F)_5$ concentration in HSO_3F at ambient temperature.

A plot of K_a vs. $Ta(SO_3F)_5$ concentration is shown in Fig. 2. K_a increases steeply at greater than ~1 mol%, up to a value of ~5 m at the maximum concentration, indicating virtually complete dissociation of the acid. Furthermore, this value is an order of magnitude greater than the K_a value of ~0.1 m predicted at this concentration from the conductivity studies. The K_a vs. concentration curve is deceiving, however, since the rate of K_a increase at the lower concentrations is hidden by the scale of the plot. For this reason, a plot of $\ln K_a$ vs. concentration is also shown in Fig. 2, which indicates that the greatest *logarithmic rate of* K_a *increase* is at concentrations of less than about 1 mol%. Following this 'critical point', the rate quickly decreases and $\ln K_a$ approaches a constant value. Extrapolation of the $\ln K_a$ plot to infinite dilution leads to a very approximate K_a value of 8×10^{-5} mol kg^{-1}, which is about an order of magnitude less than that estimated from the conductivity measurements. This suggests a large dependence of the acidic dissociation constant shown in Eq. (4) on concentration, which in turn implies that it is not a very accurate representation of the system's acidity, as was already indicated from the conductivity measurements [23].

The increase in magnitude of this system's acidic dissociation constant with concentration can be partially attributed to formation of stronger polymeric acids at higher concentrations, as suggested for the SbF_5 systems [4–6]. The slope difference between the three systems' $-H_0$ vs. concentration curves (Fig. 1) at ≤ 1 mol% Lewis acid concentration reflects the lower initial K_a value of the Ta system.

The formation of $H_x[Ta(SO_3F)_{5+x}]$ (with $x > 1$) type acids (and/or oligomeric analogs) in solution at higher $Ta(SO_3F)_5$ concentrations is not inconceivable, since $Cs_2[Ta(SO_3F)_7]$ is isolable. This could result in 2 or even 3 mol of $H_2SO_3F^+$ forming per mole $Ta(SO_3F)_5$ upon acidic dissociation, leading to an approximate two- or three-fold increase in the acidity expected from simple acidic dissociation, and thus further contributing to the magnitude of the $-H_0$ values at higher concentrations. Species of this type are not known to exist in either the SbF_5 or $SbF_2(SO_3F)_3$ systems. However, it must be stressed that the conductometric titration results do not provide any evidence for such polybasic acids in the *neutral* range.

Previous acidity studies with the HSO_3F–SbF_5 [4,6,5,18] systems have shown that acidity increases steadily with the number of moles of SO_3 added, but a maximum of only 3 mol SO_3 could be inserted into the Sb–F or As–F bonds. Hence, the presence of an unprecedented five fluorosulfate groups per metal center may also be partly responsible for the high acidity of $Ta(SO_3F)_5$.

Since there are strong indications from comparative electrical conductivity studies [23] that HSO_3F–$Ta(SO_3F)_5$ is a considerably stronger acid than HSO_3F–$Nb(SO_3F)_5$, acidity function studies of the latter system were not undertaken.

3.2. Specific electrical conductivities of Lewis acids

3.2.1. Specific conductivities of neat compounds

Selected data for element fluoride fluorosulfates and for binary fluorides, both formed by group 5 and group 15 elements, are collected in Table 2. Data on two oxyfluorosulfates $SeO(SO_3F)_2$ [36] and ClO_2SO_3F [37] are added for purpose of reference. The latter is found to act as a base in HSO_3F to produce the $[ClO_2]_{(solv)}^+$ cation [37]. The remaining system of group 5 and 15 are Lewis acids and can produce conjugate superacids in HSO_3F.

As far as appearance is concerned, all compounds listed in Table 2 are viscous liquids, frequently of limited volatility. Evidence from vibrational spectra has been collected to suggest the presence of fluoride- or fluorosulfate bridged oligomers at room temperature [24,35,37]. A heterolytic cleavage of those oligomers to give conducting ionic fragments is suggested. In all instances, where measurements over a limited temperature range have been carried out, the specific conductivities are found to rise with increasing temperature, which is consistent with the proposed ionic dissociation as cause for the observed electrical conductivities. There is one exception: Sb(V) fluoride exhibits extremely low specific conductivities even at slightly elevated temperatures and

Table 2
Specified electrical conductivities K in Ω^{-1} cm^{-1} of selected fluoride–fluorosulfates

Compound class	Compounds	K (Ω^{-1} cm^{-1})	T (°C)	Ref.
Element fluorides	SbF_5	$<4 \times 10^{-9}$	25	[26,27]
	VF_5	2.43×10^{-4}	25	[31,32]
	NbF_5	2.33×10^{-5}	93.8	[33,34]
	TaF_5	1.53×10^{-5}	92.6	[33,34]
Element fluoride-fluorosulfates	$TaF_4(SO_3F)$	1.10×10^{-5}	25	this work
	$NbF_4(SO_3F)$	5.80×10^{-5}	25	this work
	$AsF_3(SO_3F)_2$	5.85×10^{-5}	25	[35]
	$TaF_3(SO_3F)_2$	1.28×10^{-4}	25	this work
	$NbF_3(SO_3F)_2$	1.76×10^{-4}	25	this work
Element oxy fluorosulfates	$SeO(SO_3F)_2$	1.59×10^{-5}	25	[36]
	$ClO_2(SO_3F)$	7.51×10^{-2}	25	[37]

homolytic rather than heterolytic dissociation at elevated temperatures [26,27] seems to occur.

Two other exceptions are TaF_5 and NbF_5, which at room temperature are crystalline solids with ordered tetrameric structures [25]. On heating beyond their respective melting points, conducting liquids form. In spite of the higher temperatures (92.6 and 93.8°C—all other measurements are taken at 25°C), an approximate order of decreasing electrical conductivities emerges: $VF_5 > NbF_3(SO_3F)_2 > TaF_3(SO_3F)_2 > AsF_3(SO_3F)_2, \sim NbF_4(SO_3F) > TaF_4(SO_3F) > NbF_5 > TaF_5 \gg SbF_5$. For any composition, Nb(V) compounds appear to show higher conductivities than the corresponding Ta(V) systems. Furthermore, conductivities appear to increase with substitution of fluoride by fluorosulfate. The actual values, measured at 25°C, are in the range of 10^{-5} to 10^{-4} Ω^{-1} cm^{-1} which corresponds to the specific conductivity of HSO_3F (1.085×10^{-4} Ω^{-1} cm^{-1}) [10,17], where on account of the proton jump mechanism the self-ionization ions $H_2SO_3F^+$ and SO_3F^- contribute substantially to the measured value [10]. Anion jump, or in this case SO_3F^- jump, appears to be a probable contributor to the conductivities of the element fluoride fluorosulfates, as the SO_3F-group is well capable of bridge formation. The relatively high conductivity of VF_5 may be due to its linear fluorine-bridged polymeric structure in both the solid and the liquid state [38], which differs from that of NbF_5 and TaF_5 [25].

3.2.2. Specific conductivities of the conjugate superacids

The specific conductivities of solutions of the Nb(V) and Ta(V) fluoride–fluorosulfates of the type $MF_n(SO_3F)_{5-n}$, M = Nb or Ta, $n = 3$ or 4, are shown in Fig. 3, plotted against the Lewis acid concentration in mol%. All four materials are completely miscible with HSO_3F and the resulting solutions are more highly conducting than are the individual components [7,10,11] (see also Table 2). While the electrical conductivity increases with increasing SO_3F-content, the relative order of the specific conductivities is now different. The Ta(V) Lewis acids appear to give higher specific conductivities than their Nb(V) counterparts. The reverse had been observed for the neat compounds.

As a consequence, the highest conductivities are observed for $TaF_3(SO_3F)_2$. For this system, only conductometric titrations at very low Lewis acid concentration (~0.05 mol kg^{-1}) are possible with KSO_3F as standard base.

Also included in Fig. 3 are the conductivities of SbF_5 in HSO_3F. Even though liquid SbF_5 is poorly conducting (see Table 2), its solutions are more conducting than those of $TaF_3(SO_3F)_2$ near the maximum by a factor of 3 to 4. One has to be careful however, when including data from the HSO_3F–SbF_5 system, also known as Magic Acid [1,2]. A recent re-investigation of the system by ^{19}F NMR [39,19] has shown that SbF_5 is extensively solvolysed in HSO_3F to produce HF in addition to various oligomeric Sb–F–SO_3F containing anions. Hydrogen fluoride, which can cause enhanced conductivity, is also found to react with glass and at high SbF_5 concentrations (>30 mol%), crystalline $[H_3O][Sb_2F_{11}]$—its structure has recently been reported by us [40]—forms over a period of several weeks.

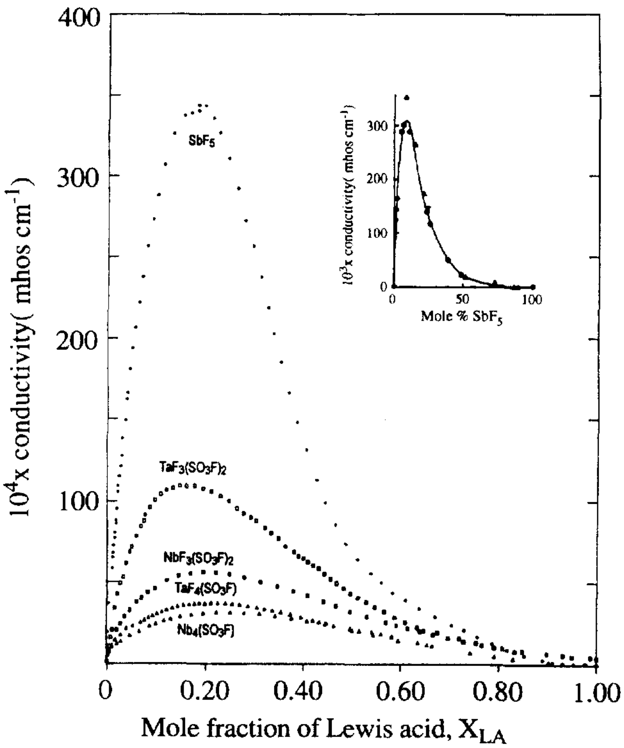

Fig. 3. Specific conductivities of $MF_{5-x}(SO_3)_x$ (M = Nb, Ta; $x = 1,2$) and SbF_5 in HSO_3F at ambient temperature (insert: specific conductivity of SbF_5 in HF at ambient temperature [26,27]).

It hence seems, that processes in HSO_3F–SbF_5 are complex and will produce various conducting ions, among them H_3O^+, and a number of monomeric and oligomeric anions (15 different species have been observed [39,19]). In the oligomeric anions, SO_3F-bridging takes precedent over F-bridging [39,19] in departure of previous views [41,42]. While the complexity in the HSO_3F–SbF_5 system can at least qualitatively explain the higher conductivity in HSO_3F than found for solutions of $MF_n(SOF)_{5-n}$, M = Nb or Ta, $n = 3$ or 4, it is interesting to note in Fig. 3 that for all five Lewis acids, a maximum in electrical conductivity is observed at Lewis acid concentrations of about 20 mol%.

The exact positions of the conductivity maxima are listed in Table 3 together with the maximum conductivities found in each system. The resulting plots are similar in shape for all five systems and are best described as rather asymmetric bell-shaped curves, with the conductivities trailing off at the high Lewis acid concentrations. As a consequence, all five solutions are highly conducting media over the whole Lewis acid concentration range.

A differently shaped conductivity vs. SbF_5 concentration plot is reported for HF–SbF_5, [29,30] shown as an insert into Fig. 3. The curve is considerably sharper with the maximum at 3.5 mol% SbF_5, where the electrical conductivity is

Table 3
Conductivity maxima in HSO_3F at 25°C

Lewis acid	mol%	$10^2 \times$ Conductivity (cm^{-1})
SbF_5	9.3–19.7	3.4
$TaF_3(SO_3F)_2$	17.7	1.1
$TaF_4(SO_3F)$	22.2–22.6	0.37
$NbF_3(SO_3F)_2$	19.4	0.56
$NbF_4(SO_3F)$	22.3	0.31

$\sim 300 \times 10^3\ \Omega^{-1}\ cm^{-1}$ and thus larger than in the HSO_3F–SbF_5 Magic Acid by a factor of 10. In the high Lewis acid concentration range, electrical conductivity drops off sharply [26] and measurements become difficult [27].

Considering the difference in reported ion mobilities of the acidium ions (λ° for $H_2SO_3F^+$ is 135 [10] vs. 350 for H_2F^+ [27]), it is expected that at very low SbF_5 concentrations where the proton jump mechanism is active [10,26,27], HF–SbF_5 should be more conducting than the HSO_3F–SbF_5 system. The absence of side reaction in HF–SbF_5 contributes as well to higher conductivities, while in HSO_3F–SbF_5 the formation of H_2O followed by protonation to give H_3O^+ [39,19,40] will reduce the overall acidity of the system and decrease the $H_2SO_3F^+$ concentration. Finally, oligomerization of the Lewis acids becomes a competing process to the generation of acidium ions by removal of the base ions, F^- or SO_3F^-. Oligomerization via fluorosulfate bridges is more likely in the HSO_3F–SbF_5 system than the formation of F-bridges in the HF–SbF_5 system. These three reasons may be given to explain the steep increase in conductivity at low to intermediate SbF_5 concentrations for the conjugate acid HF–SbF_5 and the rather slow gradual increase in all superacid systems in HSO_3F.

At intermediate Lewis acid concentration, conductivity via the proton jump mechanism becomes less likely as the bulk solvent (HF and HSO_3F) decreases and hydrogen bonding between the solvent as well as its self-ionization becomes less probable than hydrogen bonding between solvent and solute anions. Hence, the electrical conductivity goes to a maximum and starts to decline. In addition, the increased viscosity impedes the migration of conducting ions in the conductivity experiment.

At very high Lewis acid concentrations, the $MF_n(SO_3F)_{5-n}$, M = Nb or Ta, $n = 3$ or 4, systems are good conductors for reasons discussed in Section 3.2.1. Solvolysis of SbF_5 in HSO_3F appears to generate in addition to HF similar $SbF_n(SO_3F)_{5-n}$ [39,19] species. This, of course, is not possible in the conjugate HF–SbF_5 system. The suggested break-up of oligomers into conducting species for the mixed fluoride–fluorosulfate appears to be aided by the gradual addition of HSO_3F.

Thus, it seems to us that at least two different mechanisms may be active over the entire concentration range, as discussed above.

4. Summary and conclusions

In solvent systems like the conjugate superacids discussed here, the corrosiveness of the systems and the ever present problem of contamination by water and other extrenuous materials make precise measurements rather difficult. The Lewis acids of the $MF_n(SO_3F)_{5-n}$ type used present additional problems. We have recently concluded [43] that many of the viscous and oligomeric element fluoride fluorosulfates are phases which frequently are non-stoichiometric rather than well defined molecular compounds. The Nb and Ta compounds are all carefully purified by distillation [24] and their composition is confirmed by microanalysis and spectroscopy [24]. Nevertheless, composition may vary within limits from one batch to the next. Hence, care must be taken when interpreting results of the conductivity measurements described here and only general trends can be recognized. For these reasons, we also have decided not to report tabulated conductivity data in this publication.

The complete miscibility of the fluoride fluorosulfates with HSO_3F allows measurements over the whole concentration range rather than only in the very low region (up to molalities of ~ 0.05 mol kg^{-1}). This is not possible for MF_5, M = Nb or Ta, which show limited solubility in both HF and HSO_3F [1–3], and consequently new applications are anticipated for the ternary Lewis acids discussed here.

It is also important to obtain information on conjugate superacids at concentrations which are actually used in synthetic chemistry and in superacid catalysis [1–3]. It is clear now that in this region of equimolar amounts of HSO_3F and Lewis acid, highly conducting media are encountered, which may favor the formation of reactive cations not just by protonation. The observed maxima in electrical conductivity in HSO_3F suggest further work and applications at these concentrations of around 20 mol% Lewis acid (see Table 3).

Finally, we would like to draw some attention to conjugate superacids involving Ta(V) Lewis acids that are less likely to act as oxidizing agents than, for example, SbF_5 or AsF_5 [1–3].

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References

[1] G.A. Olah, G.K.S. Prakash, J. Sommer, Science 206 (1979) 13.
[2] G.A. Olah, G.K.S. Prakash, J. Sommer, Superacids, Wiley, New York, 1985, and refs. therein.

[3] T.A. O'Donnell, Superacids and Acidic Melts as Inorganic Chemical Reaction Media, VCH Publ., New York, 1993, and refs. therein.
[4] R.J. Gillespie, T.E. Peel, Adv. Org. Chem. 9 (1972) 1.
[5] R.J. Gillespie, T.E. Peel, J. Am. Chem. Soc. 95 (1973) 5173.
[6] R.J. Gillespie, T.E. Peel, E.A. Robinson, J. Am. Chem. Soc. 93 (1971) 5083.
[7] R.J. Gillespie, Acc. Chem. Res. 1 (1968) 202.
[8] L.P. Hammett, A.J. Deyrup, J. Am. Chem. Soc. 54 (1993) 2721.
[9] R. Jost, J. Sommer, Rev. Chem. Intermed. 9 (1988) 171 and refs. therein.
[10] R.C. Thompson, in: G. Nickless (Ed.), Inorganic Sulphur Chemistry, Elsevier, Amsterdam, 1968, p. 587.
[11] A.W. Jache, Adv. Inorg. Chem. Radiochem. 16 (1974) 177.
[12] M.F.A. Dove, A.F. Clifford, in: J. Jander, H. Spandan, C.C. Addison (Eds.), Chemistry in Non-Aqueous Ionizing Solvents, Vol. 2.1, Viehweg Publ., 1971.
[13] R.J. Gillespie, J. Liang, J. Am. Chem. Soc. 110 (1988) 6037.
[14] P.L. Fabré, J. Devynk, B. Tremillon, Chem. Rev. 82 (1982) 591 and refs. therein.
[15] A.A. Woolf, J. Chem. Soc. (1955) 433.
[16] G.A. Olah, M.B. Comisarow, C.A. Cupas, C.U. Pittmann, J. Am. Chem. Soc. 87 (1965) 2997.
[17] J. Barr, R.J. Gillespie, R.C. Thompson, Inorg. Chem. 3 (1964) 1149.
[18] R.C. Thompson, J. Barr, R.J. Gillespie, R.A. Rothenburg, Inorg. Chem. 4 (1965) 1641.
[19] D.L. Zhang, PhD Thesis, The University of British Columbia, Vancouver, Canada, 1995.
[20] K.C. Lee, F. Aubke, Inorg. Chem. 18 (1979) 389.
[21] K.C. Lee, F. Aubke, Inorg. Chem. 19 (1980) 119.
[22] (a) D. Zhang, S.J. Rettig, J. Trotter, F. Aubke, Inorg. Chem. 34 (1995) 3153; (b) K.C. Lee, F. Aubke, Inorg. Chem. 23 (1984) 2124.
[23] W.V. Cicha, F. Aubke, J. Am. Chem. Soc. 111 (1989) 4328.
[24] D. Zhang, F. Aubke, J. Fluorine Chem. 58 (1992) 81.
[25] A.J. Edwards, J. Chem. Soc. (1964) 3714.
[26] H.H. Hyman, L.A. Quaterman, M. Kilpatric, J. Katz, J. Phys. Chem. 65 (1961) 123.
[27] R.J. Gillespie, K.C. Moss, J. Chem. Soc. A (1966) 1170.
[28] F.B. Dudley, G.H. Cady, J. Am. Chem. Soc. 79 (1957) 513.
[29] D. Zhang, C. Wang, F. Mistry, B. Powell, F. Aubke, J. Fluorine Chem. 76 (1996) 83.
[30] C. Wang, S.C. Siu, G. Hwang, B. Bley, M. Bodenbinder, C. Bach, H. Willner, F. Aubke, Eur. J. Solid State Inorg. Chem. 33 (1996) 917.
[31] H.C. Clark, H.J. Emeléus, J. Chem. Soc. (1957) 21.
[32] H.C. Clark, H.J. Emeléus, J. Chem. Soc. (1958) 180.
[33] F. Fairbrother, W.C. Frith, A.A. Woolf, J. Chem. Soc. (1954) 1031.
[34] F. Fairbrother, G.H. Grundy, A. Thompson, J. Chem. Soc. (1965) 761.
[35] H. Imoto, F. Aubke, J. Fluorine Chem. 15 (1980) 59.
[36] H.A. Carter, PhD Thesis, University of British Columbia, 1970.
[37] H.A. Carter, F. Aubke, Inorg. Nucl. Chem. Lett. 5 (1969) 999.
[38] H.A. Carter, A.M. Qureshi, F. Aubke, Chem. Commun. (1968) 1461.
[39] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 4th edn., Wiley, New York, 1980.
[40] H. Heubes, Dipl. Thesis, Heinrich Heine Universität, Düsseldorf, Germany, 1994.
[41] D. Zhang, S.J. Rettig, J. Trotter, F. Aubke, Inorg. Chem. 35 (1996) 6113.
[42] G.A. Olah, A. Commeyras, J. Am. Chem. Soc. 91 (1969) 2929.
[43] D. Brunet, A. Germain, A. Commeyras, Nowo. J. Chim. 2 (1978) 275.