(12) $H_3Re_3(CO)_{12}$ is, however, also known to be produced by thermal decomposition of $HRe_3(CO)_{14}$.[8]

(13) J. K. Hoyano and W. A. G. Graham, *Inorg. Chem.*, 11, 1265 (1972).

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Solvation Energies of Aliphatic Ammonium Ions in Water and Fluorosulfuric Acid

Sir:

We wish to report the heats of ionization (ΔH_i) of ammonia and 12 aliphatic amines in HSO_3F and the heats of solvation of the corresponding ammonium ions ΔH_S (BH^+) in this medium. The results allow an informative comparison with those for the same amines and their ions in water. HSO_3F is 21–22 powers of ten stronger than H_2O as a Brönsted acid toward amines;[1] nonetheless the *relative* values, $\delta\Delta H_i$ and $\delta\Delta H_S$ (BH^+), for these bases and their ions are of similar magnitude in both media. Thus the dramatic leveling of amine base strengths in water relative to those in the gas phase[2–4] is not peculiar to aqueous systems.

The heat of ionization in HSO_3F has been suggested as a useful criterion of Brönsted basicity which may be applied to most types of organic bases.[5,6] At present the amines are the only class of neutral organic base for which we also have a large collection of basicity data referred unequivocally to a standard state in water. They are therefore a natural choice for initiating studies of the solvation energies of onium ions in different media.[7]

Presented in Table I are the data necessary for determining the relative heats of solvation of ammonium ions into HSO_3F from the gas phase, $\delta\Delta H_S$ (BH^+) HSO_3F, using gas phase ionization enthalpies, ΔH_i (g), and heats of vaporization, ΔH_v, with heats of ionization in HSO_3F, ΔH_i, and the use of a Born–Haber cycle described previously.[2–4,8,9]

What we call heats of ionization are in fact heats of transfer from an "inert" solvent to HSO_3F. This device is required by the fact that in this medium the heat of solution of the neutral amine cannot be measured without ionizing it. No such difficulty arises in water where ΔH_i is obtained readily as the difference between heats of solution at low pH, where ionization is complete, and at high pH, where ionization is negligible. It is crucial for comparing ΔH_i values in HSO_3F that no specific interactions occur between the "inert" solvent and the different amines as a result of structural variation in the latter. Results presented in Table II demonstrate that for several of the smaller amines the variation in heat of solution from one solvent to another is not systematic and is on the average about ±0.5 kcal/mol.[10] Heats of solution of gaseous amines employed apparatus similar to that used by Jones[2]—liquid amines were treated as before.[5,6] We note regretfully that there is no means at present for estimating relative free energies of ionization in HSO_3F.

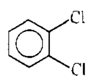
Figure 1 presents a comparison of the heats of solvation of ammonium ions in HSO_3F and in water. Despite the enormous difference in basicity of these media and the complete absence (by definition) of hydrophobic contributions in HSO_3F, there is a remarkably close parallel in trend *and in magnitude* between the two sets of data although the slope (0.83) shows that HSO_3F is a less discriminating solvent for these ions than is water. The points in Figure 1 are differentiated primarily in terms of the number of protons

Table I. Enthalpies of Ionization (ΔH_i), Solution (ΔH_S), and Vaporization (ΔH_{vap}) for Aliphatic Amines and Their Ammonium Ions

	$-\Delta H_S$ (HSO_3F)	ΔH_{inert}	$-\Delta H_i$ (HSO_3F)	ΔH_{vap}	ΔH_S (B)	ΔH_i(g)	$-\delta\Delta H_i$(g)	$-\delta\Delta H_i$ (HSO_3F)	$-\delta\Delta H_S$ (B)	$\delta\Delta H_S$ (BH^+)HSO_3F	$\delta\Delta H_S$ (BH^+)H_2O
1. NH_3	47.3 ± 0.7[a]	−4.0 ± 0.2[a]	43.3 ± 0.9[a]		−4.0	207[a,d]	0	0	0	0	0[d]
2. $MeNH_2$	51.7 ± 0.3[a]	−5.4 ± 0.2[a]	46.3 ± 0.5[a]		−5.4	216[a,d]	9.3	3.0	1.4	4.9	6.0[d]
3. Me_2NH	53.8 ± 0.5[a]	−6.0 ± 0.2[a]	47.8 ± 0.7[a]		−6.0	222.4[a,d]	15.4	4.5	2.0	8.9	11.2[d]
4. Me_3N	53.5 ± 0.7[a]	−6.0 ± 0.2[a]	47.5 ± 0.9[a]		−6.0	226.6[a,d]	19.6	4.2	2.0	13.4	18.6[d]
5. $EtNH_2$	52.9 ± 0.6	−6.1 ± 0.2	46.8 ± 0.8		−6.1	218.8[a,d]	11.8	3.5	2.1	6.2	6.1[d]
6. Et_2N	48.1 ± 0.3[c]	−0.42 ± 0.06	47.7 ± 0.3[c]	7.45	−7.9	227.2[a,d]	20.2	4.4	3.9	11.9	13.1[d]
7. Et_3N	49.8 ± 0.3[c]	−0.64 ± 0.08	49.2 ± 0.3[c]	8.35	−9.0	233.3[a,d]	26.3	5.9	5.0	15.4	20.3[d]
8. $PrNH_2$	45.7 ± 0.5	0.43 ± 0.05	46.2 ± 0.5	7.5	−7.0	(219.9)[e]	12.9	2.9	3.0	(7.0)[f]	(6.7)[f]
9. Pr_2NH	48.4 ± 1.0	0.19 ± 0.02	48.6 ± 1.0	9.57	−9.4	(229.5)[e]	22.5	5.3	5.4	(11.8)[f]	(13.1)[f]
10. $BuNH_2$	45.0 ± 0.4	1.15 ± 0.07	46.2 ± 0.7	8.55	−7.4	(220.4)[e]	13.4	2.9	3.4	(7.1)[f]	(6.3)[f]
11. Bu_2NH	46.7 ± 0.5[c]	−0.30 ± 0.05	46.4 ± 0.6[c]	11.8	−12.1	(230.3)[e]	23.3	3.1	8.1	(12.1)[f]	(11.7)[f]
12. *i*-$PrNH_2$	48.8 ± 0.8	0.46 ± 0.4	49.3 ± 0.8	6.60	−6.1	221.2[d]	14.2	6.0	2.1	6.1	7.9[d]
13. *t*-$BuNH_2$	48.4 ± 0.5	0.44 ± 0.06	48.8 ± 0.5	7.08	−6.6	223.3[d]	16.3	5.5	2.6	8.2	8.8[d]

[a] From E. M. Arnett and J. F. Wolf, *J. Am. Chem. Soc.*, 95, 978 (1973). [b] From E. M. Arnett and J. V. Carter, *ibid*, 93, 1516 (1971). [c] From ref 5. [d] From ref 2. [e] From ref 4; 2.4 kcal/mol has been subtracted from values in ref 2 to normalize them to same scale as those from ref *a*. [f] Calculated from adjusted values, see footnote *e*.

Table II. Heats of Solution (ΔH_S) and of Condensation (ΔH_{cond}) for Gaseous Amines into Various Inert Liquids

	ΔH_S (kcal/mol) at 25°			
Compound	C_6H_6	CCl_4		ΔH_{cond}[a]
NH_3	−3.5 ± 0.20	*b*	−4.45 ± 0.18	−4.90[d]
CH_3NH_2	−5.72 ± 0.18	−5.36 ± 0.4	−5.18 ± 0.10	−5.996
$CH_3CH_2NH_2$	−5.84 ± 0.21	−6.08 ± 0.12	−6.29 ± 0.21	−6.580
$(CH_3)_3CCH_2NH_2$	0.66 ± 0.09[c]		0.37 ± 0.06[c]	*c*
$(CH_3)_2NH$	−5.84 ± 0.14	−6.63 ± 0.19	−5.66 ± 0.12	−5.779
$(CH_3)_3N$	−5.69 ± 0.16	−6.47 ± 0.16	−5.87 ± 0.14	−5.243

[a] From tabulation in F. M. Jones, III, and E. M. Arnett, *Prog. Phys. Org. Chem.*, 11, 264 (1974). [b] Ammonia reacts rapidly with CCl_4 so the value for ΔH_S in Table I is the average of ΔH_S in benzene and *o*-dichlorobenzene. [c] This amine in contrast to the others is a liquid at room temperature. [d] "Lange's Handbook for Chemistry", 10th ed, McGraw-Hill, New York, N.Y., 1961.

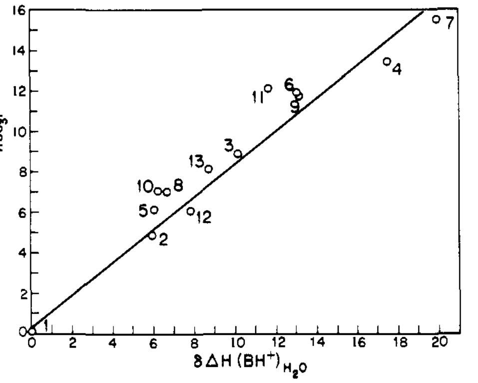


Figure 1. Correlation of relative heats of solvation of ammonium ions in water, $\delta\Delta H_S$ $(BH^+)H_2O$ vs. those in fluorosulfuric acid, $\delta\Delta H_S$ $(BH^+)HSO_3F$. Data points refer to Table I.

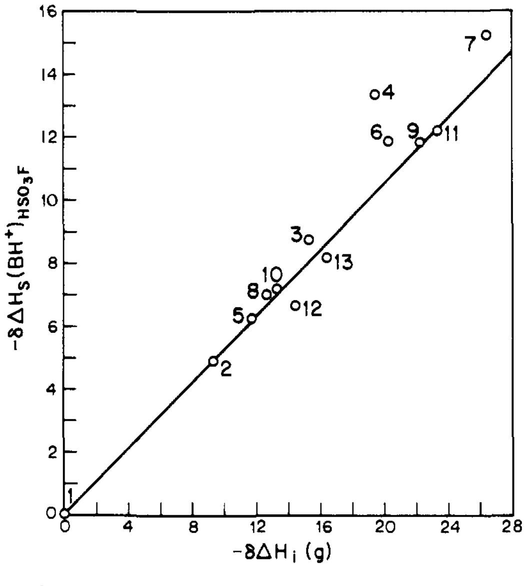


Figure 2. Correlation of relative heats of ionization in gas phase $\delta\Delta H_i$ (g) for aliphatic amines with heats of solvation of the corresponding ammonium ions in fluorosulfuric acid, $\delta\Delta H_S$ (BH^+) HSO_3F. Correlation coefficients are: 0.9696 (all 13 points), 0.9832 (excluding points 4 and 7). A corresponding correlation for heats of solvation into water (ref 2) is 0.8947.

attached to the ammonium nitrogen—those carrying the most protons being solvated most exothermically in both media. This is consistent with hydrogen bonding to solvent or counterion being the chief differentiating factor as was suggested previously.[2,8,9,12-14] Increments of about 6 kcal/mol differentiate primary from secondary from tertiary ions of similar carbon number in both solvents.

Within each group (primary, secondary, tertiary) there is a general tendency for larger ions to be less exothermically solvated in both media. This trend is qualitatively consistent with the varying requirements for cavity formation against the internal pressure in either solvent (note, for example, the trend in ΔH_{inert} for the neutral amines). It is also consistent with the gradually decreasing electrostatic solvation energy as ionic volume is increased. We are unaware of rigorous methods for resolving these factors.

Figure 2 compares the effect of structural change on the heat of ionization in the gas phase with the heat of solvation of the onium ion in HSO_3F. The good correlation (r – 0.9696) of these seemingly unrelated properties suggests that they both reflect the influence of the alkyl group on charge distribution in the ion. In the gas phase the alkyl group delocalizes charge internally; in solution it affects solvation by the mechanisms referred to above.[15] No significant correlation was found between $\delta\Delta H_i$ (g) and $\delta\Delta H_i$ (HSO_3F).

Acknowledgment. This work was supported by National Science Foundation Grant GP-6550-X for which we are most appreciative.

References and Notes

(1) Based on the H_0 value of −16: (a) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Am. Chem. Soc.*, **93**, 5083 (1971); (b) R. J. Gillespie, *Acc. Chem. Res.*, **1**, 202 (1968); (c) E. M. Arnett, J. J. Burke, J. V. Carter, and C. F. Douty, *ibid.*, **94**, 7837 (1972).
(2) E. M. Arnett, F. M. Jones, III, M. Taagapera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972).
(3) M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332 (1965).
(4) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972).
(5) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Am. Chem. Soc.*, **92**, 1260 (1970).
(6) E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974).
(7) A few comparable data for oxonium ions will be presented soon (Arnett and Scorrano, in preparation).
(8) E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973).
(9) F. M. Jones, III, and E. M. Arnett, *Prog. Phys. Org. Chem.*, **11**, 263 (1974).
(10) Note the close similarity between the heats of solution for each amine in itself as represented by the heat of condensation ($-\Delta H_{vap}$) and its heat of solution in the inert solvents.
(11) Similar comparisons for the enthalpy of transfer of neutral molecules from one solvent to another by R. Fuchs, T. M. Young, and R. F. Rodewald, *Can. J. Chem.*, **51**, 4122 (1973), and R. Fuchs, personal communication; M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **94**, 6877 (1972); E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2365 (1970), support our assumption that no large error will result from using the heat of solution in a nonpolar, nonassociating solvent as the reference state $(\Delta H)_{inert}$ for a series of structurally similar homologs.
(12) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).
(13) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958).
(14) Although HSO_3F is probably a poor hydrogen-bond acceptor, the SO_3F^- should be a good one by analogy to SO_4^{2-} and HSO_4^-, see I. M. Kolthoff and M. K. Chantooni, *J. Am. Chem. Soc.*, **91**, 25 (1969); R. P. Taylor and I. D. Kuntz, Jr., *ibid.*, **94**, 7963 (1972).

(15) See E. M. Arnett, L. E. Small, R. T. McIver, Jr; J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974), for a similar correlation for alkoxide ions in DMSO.

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An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt

Sir:

We wish to report on the first use of a room temperature, high Lewis acid molten salt system to study the electrochemistry of organometallics and an alkylaromatic compound. The redox behavior of two aliphatic diimine complexes of iron(II), ferrocene, and hexamethylbenzene are shown here to be accessible in a 2:1 aluminum chloride: ethylpyridinium bromide melt.[1]

The chemical[2,3] and electrochemical[4] one-electron reversible oxidation of either tris(glyoxalbis(methylimine))iron(II), Fe(GMI)$_3^{2+}$,[5] or tris(biacetylbis(methylimine))iron(II), Fe(BMI)$_3^{2+}$,[5] can only be observed at very high acid concentrations, e.g., $\geq$ 10 *M* H_2SO_4. At lower acid concentrations using cerium(IV) as the oxidant, ligand oxidation takes place with the consumption of several equivalents of cerium(IV) accompanied by the formation of several new ligand-oxidized complexes.[6] The electrochemical oxidation of these complexes at lower acidities results in nondestructive ligand oxidation with the transfer of several electrons.[4]

In the 2:1 aluminum chloride:ethylpyridinium bromide melt (potential range: -0.2 to $+$ 1.8 V vs. Al reference electrode) the electrochemical oxidation of Fe(GMI)$_3^{2+}$ and Fe(BMI)$_3^{2+}$ at a disc vitreous carbon working electrode at 25° can be described as a simple one-electron reversible process as shown by the cyclic voltammograms of Figure 1, and by the pulse voltammograms of Figure 2. The corresponding log $(i/(i_d - i))$ vs. E plots for the pulse voltammograms yielded slopes of 59 ± 5 mV, and half-wave potentials of 1.59 and 1.12 V vs. Al wire reference electrode for Fe(GMI)$_3^{2+}$ and Fe(BMI)$_3^{2+}$, respectively. The difference of 0.47 V in the half-wave potentials of the two complexes indicates that in the molten salt the replacement of hydrogen by methyl groups at the diimine group stabilizes the ferric form more than the ferrous form due to an increase σ bonding ability of the ligand. A similar effect was found in 11 *M* H_2SO_4, where a difference of 0.36 V was observed.

In the 2:1 aluminum chloride:ethylpyridinium bromide melt the two compounds studied show a characteristic intense inverse charge transfer band at 555 and 567 nm respectively for Fe(GMI)$_3^{2+}$ and Fe(BMI)$_3^{2+}$ which is practically identical with the λ_{max} values obtained in 11 *M* H_2SO_4.[7] In the melt these complexes exhibit a higher molar absorptivity, and the characteristic diimine chromophore[8] seems to be preserved. If decomposition is allowed to occur, the presence of other species that absorb strongly around 400 nm can be detected. The rate of dissociation of the complexes in the melt proceeds ca. 10 times faster in the melt than in 11 *M* H_2SO_4.

In 11 *M* H_2SO_4 it was shown[4] that these diimine complexes have larger solvodynamic mean radii (via the Stokes-Einstein equation) as compared to the structural mean radii. The correlation of solvodynamic mean radii vs. structural mean radii was found to be linear within experimental error for a series of aliphatic diimine complexes, tris(2,2′-bipyridine)iron(II), and tris(1,10-phenanthroline)iron(II). The data obtained in water[9] were interpreted in forms of a strong solvation of the complex ions by water molecules attached firmly to the complex ions in the pockets formed by the ligands. The linear correlation obtained for the aliphatic diimine complexes could imply that in 11 *M* H_2SO_4 these ions are as strongly solvated as the aromatic ones in water. However, at such high acid concentration, where the activity of water is very low, it is more likely that the aliphatic diimine ions are strongly solvated by H_3O^+ ions due to the similarity of structural mean radii as compared to that of H_2O. This solvation could also explain the higher stability of the ferric complexes toward the internal redox reaction that leads to ligand-oxidized complexes by deterring nucleophilic attack by water molecules. (cf. ref 6).

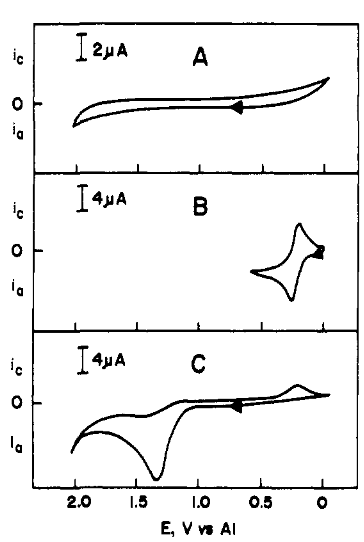

Figure 1. Cyclic voltammograms of 2.0 × 10^{-3} *M* Fe(GMI)$_3^{2+}$ (A) and 2.0 × 10^{-3} *M* Fe(BMI)$_3^{2+}$ (B), in the 2:1 aluminum chloride: ethylpyridinium bromide melt, at 25°. Scan rate = 0.4 V/sec.

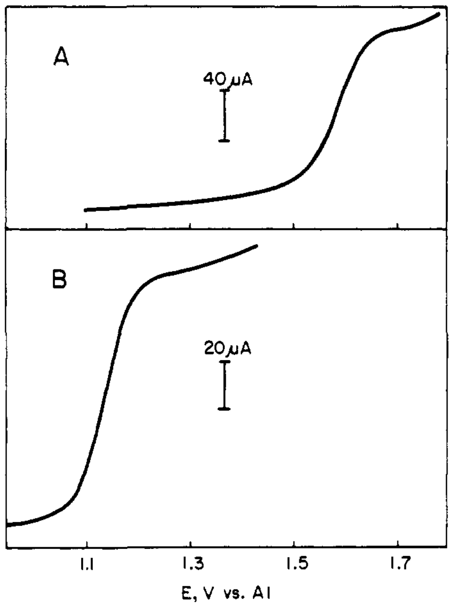

Figure 2. Pulse voltammograms; same conditions as in Figure 1.

In the melt, diffusion coefficients for the complex species obtained by the analyses of the cyclic and pulse voltammograms were found to be (2.5 ± 0.5) × 10^{-7} and (1.3 ± 0.3) × 10^{-7} cm^2/sec, respectively, for Fe(GMI)$_3^{2+}$ and Fe(BMI)$_3^{2+}$. These values are ca. two times smaller than