I_{13}

SYNTHESIS IN SUPER ACID MEDIA – DERIVATION OF A NUCLEOPHILICITY SCALE FOR WEAKLY BASIC FLUORO ANIONS

S. P. Mallela, J. R. Sams and F. Aubke*
Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Y6 (Canada)

Strong protonic acids and super acid media are limited in their ability to allow generation and stabilisation of highly electrophilic cations by two inter-related factors: (I) the '<u>acidity</u>' or proton donor ability, a solvent system dependent quantity, experimentally determined and expressed in terms of the Hammet parameter $-H_0$; and (II) the '<u>basicity</u>' or nucleophilicity of the solvent system - or the superacid anion. This quantity has not been experimentally determined and quantitized before for extremely weakly basic fluoro anions.

Recent synthetic work in HF, HSO_3F and HSO_3CF_3 derived super acid systems, which will be briefly alluded to, has afforded a wide range of complexes with dipositive metallic and organo-metallic cations, all stabilized by coordination to acid and super acid anions.

Among these, cationic dimethyl tin (IV) salts have a common structural feature: a linear C-Sn-C grouping in an octahedral coordination environment. Interaction with F or O atoms from fluoro or oxyfluoro anions in the plane, perpendicular to the dimethyltin cations, affects the electronic structure within the $(CH_3)_2Sn$ moiety. The principal ^{119}Sn Mössbauer parameter, the isomer shift δ and quadrupole splitting ΔEq are both found to be very sensitive to counteranion basicity. Both Mössbauer parameters based on 15 relevant, mostly novel derivatives, provide a linear relationship between δ and ΔEq for these systems and an empirical ranking in order of increasing basicity:

$SbF_6^- < Sb_2F_{11}^- < [Pt(SO_3F_6]^2 \sim [Sn(SO_3F)_6]^{2-} < [Sm(SO_3CF_3)_6]^{2-} < SO_3F^- < SO_3CF^- \sim NbF_6^- < [(CH_3)_2Sn(SO_3F)_4]^{2-} < [(CH_3)_2Sn(SO_3CF_3)_4]^{2-} < SnF_6^{2-} < TaF_6^{2-} < PO_2F_2^- < F^-$.

This list is currently being expanded further.

The presentation will emphasize the following aspects:

(i) Synthetic procedures in superacids with general implications,

(ii) ^{119}Mössbauer parameter of the $(CH_3)_2Sn^{2+}$ electronic structure probe with ΔEq values in excess of 6.00 mm s^{-1}, well beyond the highest previously reported values;

(iii) a relationship to the Hammett $-H_0$ scale and ramifications regarding relative acidities in various superacid systems; and finally

(iv) development of a nucleoplinicity parameter for highly fluorinated, weakly basic anions.