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

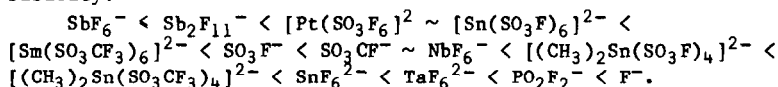
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Strong protonic acids and super acid media are limited in their ability to allow generation and stabilisation of highly electrophilic cations by two inter-related factors: (I) the 'acidity' or proton donor ability, a solvent system dependent quantity, experimentally determined and expressed in terms of the Hammett parameter $-H_0$; and (II) the 'basicity' 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, HSO₃F and HSO₃CF₃ 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 (CH₃)₂Sn moiety. The principal ¹¹⁹Sn Mössbauer parameter, the isomer shift δ and quadrupole splitting ΔE_q 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 ΔE_q for these systems and an empirical ranking in order of increasing basicity:



This list is currently being expanded further.

The presentation will emphasize the following aspects:

- (i) Synthetic procedures in superacids with general implications,
- (ii) ¹¹⁹Mössbauer parameter of the (CH₃)₂Sn²⁺ electronic structure probe with ΔE_q 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 nucleophilicity parameter for highly fluorinated, weakly basic anions.