Ionisation of Acid Halides

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WE report a simple method to determine if acid halides, which have been extensively studied as non-aqueous solvents, have sufficient basic oxygen to form donor–acceptor complexes; this method is based on whether the halide is sufficiently ionisable to form halogenosulphuric acid in disulphuric acid.

Disulphuric acid is a dissociated and self-ionised solvent, and an equilibrium which exists between various species[1] may be represented as

$$2H_2S_2O_7 \rightarrow H_2SO_4 + H_2S_3O_{10} \rightleftharpoons H_3SO_4^+ + HS_3O_{10}^-$$

Because of its very high acidity, weak bases are fully protonated:[2]

$$B + 2H_2S_2O_7 \rightarrow BH^+ + HS_3O_{10}^- + H_2SO_4 \quad \text{(i)}$$

and ionic chloride is quantitatively converted into chlorosulphuric acid:

$$KCl + 3H_2S_2O_7 \rightarrow K^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4 \quad \text{(ii)}$$

Chlorosulphuric acid thus formed behaves as a non-electrolyte.

Phosphoryl chloride[3] and bromide,[4] thiophosphoryl chloride,[5] and selenyl chloride,[6] which are supposed to have ionisable halide ions, form stable and highly conducting solutions in disulphuric acid. Cryoscopic and conductimetric studies in disulphuric acid indicate that they behave as simple bases. There is no indication of any ionisable halide in these compounds. Their reactions may be represented as follows:

$$POCl_3 + 2H_2S_2O_7 \rightarrow [P(OH)Cl_3]^+ + HS_3O_{10}^- + H_2SO_4$$

Carbonyl chloride, thionyl chloride and bromide, and sulphuryl chloride form nonconducting solutions in disulphuric acid. Conductance measurements and cyroscopic studies indicate that these compounds behave as nonelectrolytes, suggesting that these halides have neither sufficiently basic oxygen to be protonated by strong protonic acids nor sufficiently ionisable halide to form chlorosulphuric acid.

However, conductance and cyroscopic studies on the solutions of nitryl chloride, nitrosyl chloride, and acetyl chloride and bromide show that these compounds contain ionisable halide and their behaviour in disulphuric acid can be represented by the following equations.

$$CH_3COCl + 3H_2S_2O_7 \rightarrow CH_3CO^+ + HS_3O_{10}^- + HSO_3Cl + 2H_2SO_4$$

$$2CH_3COBr + 6H_2S_2O_7 \rightarrow 2CH_3CO^+ + Br_2 + SO_2 + 2HS_3O_{10}^- + 5H_2SO_4$$

$$NOCl + 3H_2S_2O_7 \rightarrow NO^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4$$

$$NO_2Cl + 3H_2S_2O_7 \rightarrow NO_2^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4$$

The i.r. spectra of these solutions confirm the presence of acetylium ($\nu[R\text{–}C{\equiv}O^+]$ 2300 cm.$^{-1}$) and nitrosyl ions ($\nu[R\text{–}N{\equiv}O^+]$ 2160 cm.$^{-1}$). The Raman spectrum of nitryl chloride in disulphuric acid shows a sharp abosrption band at 1398 cm.$^{-1}$ which is characteristic for NO_2^+ ion in strongly acidic media.[7] These cations are strong electrophiles and have been stabilised in weakly nucleophilic medium. These observations agree well with spectroscopic investigations of solid complexes of these halides with Lewis acid.[8,9]

Furthermore, the validity of this method has been verified by the behaviour of phosphorus pentachloride, selenium tetrachloride, and tellurium tetrachloride in disulphuric acid. Cryoscopic and conductimetric studies of these solutions show that the compounds are ionic in nature.

$$PCl_5 + 3H_2S_2O_7 \rightarrow PCl_4^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4$$

$$TeCl_4 + 3H_2S_2O_7 \rightarrow TeCl_3^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4$$

$$SeCl_4 + 3H_2S_2O_7 \rightarrow SeCl_3^+ + HSO_3Cl + HS_3O_{10}^- + 2H_2SO_4$$

These observations agree well with spectroscopic results reported recently for these compounds in the solid state.[10,11]

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