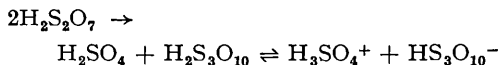


Ionisation of Acid Halides

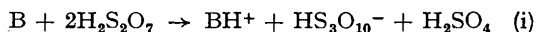
By RAM CHAND PAUL,* V. P. KAPILA, and K. C. MALHOTRA
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WE report a simple method to determine if acid halides, which have been extensively studied as non-aqueous solvents, have sufficient basic oxygen to form donor-acceptor complexes; this method is based on whether the halide is sufficiently ionisable to form halogenosulphuric acid in disulphuric acid.

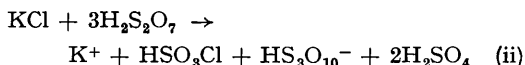
Disulphuric acid is a dissociated and self-ionised solvent, and an equilibrium which exists between various species¹ may be represented as



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

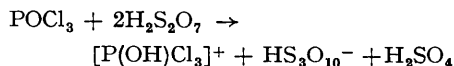


and ionic chloride is quantitatively converted into chlorosulphuric acid:



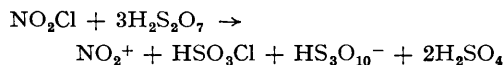
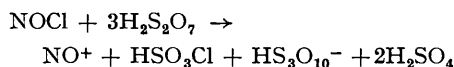
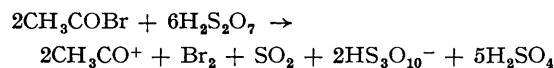
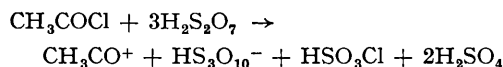
Chlorosulphuric acid thus formed behaves as a non-electrolyte.

Phosphoryl chloride³ 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:



Carbonyl chloride, thionyl chloride and bromide, and sulphuryl chloride form nonconducting solutions in disulphuric acid. Conductance measurements and cryoscopic 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.

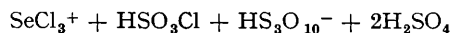
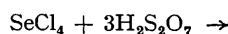
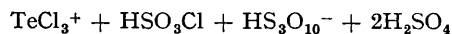
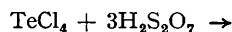
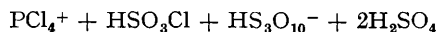
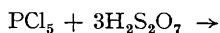
However, conductance and cryoscopic studies on the solutions of nitryl chloride, nitrosyl chloride, and acetyl chloride and bromide show that these compounds contain ionisable halide and their behaviour in disulphuric acid can be represented by the following equations.



The i.r. spectra of these solutions confirm the presence of acetylium ($\nu[\text{R}-\text{C}\equiv\text{O}^+]$ 2300 cm^{-1}) and nitrosyl ions ($\nu[\text{R}-\text{N}\equiv\text{O}^+]$ 2160 cm^{-1}). The Raman spectrum of nitryl chloride in disulphuric acid shows a sharp absorption 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.



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

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