Charge-transfer Interactions of the Highest Valency Halides, Oxyhalides, and Oxides with Aromatic Hydrocarbons and Fluorocarbons: Ball–Plane Interactions

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THE acceptor tetranitromethane shows only weak or contact interactions with the aromatic hydrocarbons even though its electron-deficient centres are on the surface of the molecule and must come into direct contact with the π-donor. Titanium tetrachloride exhibits near-zero equilibrium constants in heptane with the methylbenzenes;[2] phase diagrams of systems with naphthalene[3] and the methylbenzenes[4] are simple eutectics; moreover the yellow, orange, and red colours of the benzene, *m*-xylene, and naphthalene mixtures vanish when frozen. The stable, red solution of tungsten hexafluoride in benzene freezes to white crystals and the colour intensity is directly proportional to the tungsten hexafluoride or benzene concentration in carbon tetrachloride.[5] The titanium tetrachloride tetrahedron and the tungsten hexafluoride octahedron cannot be conducive to stable complex formation with the hydrocarbons, and weakness of these interactions appears to be due to the shape rather than the bulk of the donor–acceptor partners. Moreover, high molecular electron affinities must occur where many electronegative atoms are attached to a central one.[6]

We have examined a number of possible acceptor materials for the appearance of charge-transfer absorptions with the strictly π-donors—the aromatic hydrocarbons and fluorocarbons. Observations of colour, phase and colour change properties, equilibria in the solvents carbon tetrachloride and aliphatic perhydro- and perfluoro-carbons, and the effect of temperature on solution absorption intensities have been used to investigate interactions of the tetra- and higher co-ordinate halides (fluorides and chlorides), oxyhalides, and oxides of the elements. We conclude that (a) the covalent, highest valency halides, oxyhalides, and oxides are molecules of high electron affinity and demonstrate charge-transfer absorptions with π-donors; (b) as such donors produce stable complexes only in close, plane–plane combinations, and since the interactions are mostly of the "ball–plane" type, all associations are very weak or just contact.

Among forty-six materials examined, charge-transfer absorptions have been demonstrated with certainty for the following:

Group IV Elements. Subgroup A. $SnCl_4$ and $PbCl_4$. Freezing with colour-loss was demonstrated for tin tetrachloride with mesitylene, durene, hexamethylbenzene, naphthalene, and anthracene, and for lead tetrachloride with benzene and octafluoronaphthalene.

Subgroup B. $TiCl_4$. Freezing with colour-loss was demonstrated for titanium tetrachloride.

Group V Elements. Subgroup A. PCl_5 and $SbCl_5$. Freezing with colour-loss was demonstrated for phosphorus pentachloride with hexamethylbenzene and naphthalene.

Subgroup B. $VOCl_3$, $NbCl_5$, and $TaCl_5$. Freezing with colour-loss was demonstrated only for vanadyl trichloride with octafluoronaphthalene.

Group VI Elements. Subgroup A. SO_2Cl_2, SeF_6, and TeF_6. Freezing with colour-loss was demonstrated for sulphuryl chloride with hexamethylbenzene and naphthalene, and for both selenium and tellurium hexafluorides with *m*- and *p*-xylenes and mesitylene.

Subgroup B. MoF_6 and WF_6. Freezing with colour-loss was demonstrated for tungsten hexafluoride with hexafluorobenzene, benzene, *m*-xylene, and naphthalene, and for molybdenum hexafluoride with hexafluorobenzene and octafluorotoluene, and also for uranium hexafluoride with octafluorotoluene.

Group VII Elements. ClO_2F, IF_7, and IOF_5. Freezing with colour-loss was demonstrated for iodosyl pentafluoride with hexafluorobenzene.

Group VIII Elements. RuO_4 and OsO_4. Freezing with colour-loss was demonstrated for osmium tetroxide with benzene, octafluoronaphthalene, and naphthalene.

For all of these systems the interactions are weak and are of 1 : 1 stoicheiometry for the species in solution. Although there are limitations to the assessment of acceptor electron affinities from spectral measurements, the present studies afford the first relative values for the series. We consider such values the most fundamental criteria possible of electron-acceptor or Lewis-acid strength. For the A subgroup elements, strongest acceptor properties within a series of related compounds appear for the heavier members of the Periodic Table, whereas for the transition metal, B subgroups, they appear for the lighter members. Chlorine acceptors are stronger than fluorine acceptors.

Chemical reaction, including radical formation, is typical for many of the systems of this study, indeed some of the acceptors are among the classical oxidizing agents for aromatics and olefins. An earlier proposal[7] that complex formation should lower the activation barriers for chemical reactions between acceptors and donors and hence promote reactivity would apply here to only a minor extent, for such depressions would be very small.

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