THE REACTIVITY OF LIQUID PHOSGENE[1]

MODERN inorganic chemistry has developed around the so-called "universal solvent," water, and most of our chemical ideas have been formed with reference to the more common aquo-acids, bases and salts, and their behavior towards water. That this particular chemistry is, however, only a special case of a broader universal chemistry has been shown by E. C. Franklin in his brilliant conception and demonstration of the existence of an entire series of ammono-acids, bases and salts, many of which are entirely incapable of existing in the presence of water, but whose behavior towards liquid ammonia, solubility, conductivity of their solutions, formation of ammoniates, ammonolysis, etc., parallels the behavior of aquo-compounds towards water in a truly remarkable manner; in fact, ammonia enjoys the distinction of being an even more perfect solvent than water, in that it forms conducting solutions of numerous metals (alkali and alkaline earth metals) in which the anion is the electron itself, associated with ammonia, and in that it dissolves a host of organic compounds insoluble in water.

One naturally inquires why this sort of thing should be restricted to water and ammonia, and why other liquids—or liquid gases or even melted solids—should not also form the basis of a hitherto unknown chemistry. Liquid silicon dioxide, while a derivative of water, may nevertheless be looked upon as such a substance, and we may expect as one of the results of the recent success in the preparation of large amounts of liquid silica a large increase in our knowledge of the chemistry of the silicates; the laboratory of geochemistry and the workers in the glass industry have of course already made notable contributions in this field. Among the liquid gases that have been investigated along this line, such as hydrogen sulfide, hydrogen fluoride, hydrogen chloride, etc., more or less insurmountable obstacles oppose themselves—hydrogen fluoride attacks our customary apparatus, though there is no reason why the optically clear Bakelite developed some years ago should not be used in the pursuit of this subject; hydrogen sulfide, hydrogen chloride and many others, on the other hand, refuse to dissolve anything, and so prevent us from continuing the study.

Among these other substances, one that is important commercially because of its use in the preparation of certain organic compounds and in the synthesis of anhydrous chlorides from minerals, and is therefore readily obtainable, is phosgene, or carbonyl chloride, $COCl_2$, known since 1811, when it was discovered by John Davy, brother of the illustrious Sir Humphry. Phosgene may be looked upon as the acid chloride of carbonic acid, and in its reactions it behaves in this way. It is an excellent solvent for organic compounds; as an acid chloride it is very reactive in this field, and being an easily condensible gas (it boils at 8° C.) and very soluble in benzene and toluene, it may be used as a pure liquid, as a gas or as a solution in any one of a variety of solvents. At high temperatures it is likewise very reactive—probably because it dissociates, giving carbon monoxide and chlorine, and it has been found possible to open up difficult minerals by its use, to prepare anhydrous chlorides from the oxides, etc. But liquid phosgene is practically inert towards inorganic compounds and the metals. Sodium, potassium, calcium, magnesium, even mercury, remain perfectly bright in liquid phosgene, even after prolonged exposure, except as already mentioned at elevated temperatures. Among inorganic compounds, the chlorides of the non-metals and of the metalloids and aluminium chloride are soluble in liquid phosgene.

The solution of aluminium chloride in phosgene has important properties: metals are corroded or dissolved by this solution, with liberation of carbon monoxide; metallic oxides, carbonates and sulfides are attacked, with liberation of carbon dioxide or carbon oxysulfide, as the case may be, and in certain cases the solid product of the reaction is soluble, so that the reaction goes on vigorously. The solution contains a more or less soluble chloraluminate of the metal used, which may be more or less dissociated into aluminium chloride and the chloride of the other metal; on evaporation of the solvent, or on cooling the solution, crystals of a chloraluminate containing phosgene of crystallization are deposited; for example, the calcium salt has the formula $CaAl_2Cl_8 \cdot 2COCl_2$.

The explanation is simple, and entirely analogous to the mechanism of the solution of aluminium or zinc by a water solution of sodium hydroxide; *phosgene is fundamentally reactive,* but the chlorides of most metals are entirely insoluble; the double chlorides with aluminium, the chloraluminates, on the other hand, are much more soluble, and the protective film of chloride which forms on the surface of the metal, oxide, carbonate or sulfide is dissolved in the presence of aluminium chloride as chloraluminate, and the reaction proceeds.

There is no *a priori* reason why other types of soluble complex salts should not exist, not only in the case of phosgene, but for other solvents. And the chemistry of these systems simply awaits the discovery of the type of compound peculiar to the system which is soluble enough to permit the inherent reactivity of the solvent to manifest itself.

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