

organic chemists, but its application to complicated biological transformations is obvious.

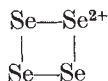
NON-AQUEOUS SOLVENTS

Strong and Unusual Interactions

by a Correspondent

Two themes dominated the second international conference on non-aqueous solvents organized by the Chemical Society at Manchester from July 28 to 30. The first was the behaviour of some very unusual solvent systems and the second was the nature and predictability of strong solvent-solute interactions and the effect these had on ion-pairing. Introducing the first topic, Professor C. C. Addison (University of Nottingham) discussed the variation in the products of reactions carried out in liquid N_2O_3 , N_2O_4 and N_2O_5 , and mixtures of these. Quite startling differences in product could be obtained by varying the composition of the nitrogen oxide solvent when reactions with transition metals and their salts were carried out. Taking mixtures of N_2O_4 and $NOCl$ as solvent and reacting them with uranium metal, one can obtain products ranging in composition from $UO_2(NO_3)_2$ (0-40 per cent $NOCl$) through UO_2Cl_2 (below 98 per cent $NOCl$) to UCl_4 (98-100 per cent $NOCl$). Anhydrous nitrites can conveniently be prepared in N_2O_3 , rather in the same way that N_2O_4 can be used for the preparation of anhydrous nitrates. This latter point was emphasized by Dr B. O. Field (City University, London), who reported the preparation of anhydrous $Cu(NO_2)_2$ from metallic copper and N_2O_3 . The compound reacts, both in the solid state and in organic solvents, with molecular oxygen to give $Cu(NO_3)_2$.

Extremely acidic protonic solvents also received a good deal of attention. Work in disulphuric acid ($H_2S_2O_7$) was discussed by Professor R. C. Paul (Panjab University, Chandigarh, India), who presented evidence based on conductivity and cryoscopic measurements that confirmed the protonation of such weak bases as $POCl_3$ to give $P(OH)Cl_3^+$ in the solvent, a result hitherto only suspected. Dr R. J. Gillespie (McMaster University, Ontario) gave a fascinating account of work in the so-called "super-acid systems". These are mixtures of HSO_3F and SbF_5 or HSO_3F , SO_3 and SbF_5 . They are certainly the most acidic systems yet discovered, with Hammett acidity functions as high as 16.6 in HSO_3F/SbF_5 mixtures. $HSO_3F/SO_3/SbF_5$ mixtures are even stronger acids. In these solvents simple aliphatic carbonium ions such as $(CH_3)_3C^+$ can be stabilized. Using peroxydisulphuryl difluoride, $S_2F_2O_6$, as an oxidizing agent, species such as I_2^+ and Se_4^{2+} can be produced and identified by Raman spectroscopy. The Se_4^{2+} has an unusual square planar structure



Both new theories and experimental results were forthcoming about solvent-solute interactions. Dr V. Gutmann (Technische Hochschule, Vienna, Austria) gave an account of the concept of donor number or donicity, defined as the enthalpy of interaction of a solvent species with SbF_5 in a neutral medium. He also reported correlations between this and other properties of donor solvents. The observation by

infrared spectroscopy of vibrational frequencies of ions in solvent cages was reported by Dr A. I. Popov (Michigan State University, East Lansing) and Dr G. J. Janz (Rensselaer Polytechnic Institute, New York) attributed the removal of degeneracies in vibrations of the nitrate ion in concentrated acetonitrile solutions of silver nitrate to the formation of contact ion-pairs. Other evidence on the detection of contact ion-pairs, reported by Popov, came from a study of the concentrated dependence of the ^{23}Na nuclear magnetic resonance chemical shift in solutions of sodium iodide in various solvents. Ion-pairing obviously plays an important part in determining the course of reactions in solution as Dr M. L. Tobe (University College, London) pointed out when discussing the mechanism of octahedral substitution in non-aqueous solvents. Their existence is postulated to explain the difference between D mechanisms (that is, S_N1 limiting) and I_a mechanisms (in which the reaction rate is sensitive to the nature of both the entering and leaving groups).

Professor T. C. Waddington (University of Durham) in a summarizing lecture expressed the view that it would be difficult to subsume all solvents under one head and that a single scale of "solvent-power" was probably not feasible. He pointed out that it was necessary to distinguish between the coordinating role of the solvent, perhaps best measured by the dissociative equilibrium constant of a dative covalent complex in the solvent, for example,



and the solvating power of the solvent, perhaps best measured by the free energy of solution, ΔG_s , of a salt such as $\phi_4As^+B\phi_4^-$ in the solvent.

THE EARTH

Sulphur in the Core?

from our Geomagnetism Correspondent

THE Earth's core is generally thought to consist chiefly of iron with a small proportion of nickel. But that cannot be the whole story. For one thing, the density of the core seems to be about 10 per cent lower than that of iron-nickel in the appropriate conditions of temperature and pressure. If this is really so, the core must contain quite large amounts (about 10 to 20 per cent) of another, lighter element, in addition to the iron and nickel.

What, then, can this element be? An obvious choice would be silicon—a view supported strongly by Ringwood (see, for example, *Geochim. Cosmochim. Acta*, **30**, 41; 1966). But the presence of silicon in the core requires large scale high temperature reduction in the Earth. If, as Ringwood has suggested, the reducing agent was carbon, large quantities of carbon monoxide would have entered the atmosphere of the early Earth and then subsequently been lost. By the same token, the Earth would also have lost much of its sulphur as well as several other volatile elements. According to Rama Murthy and Hall (*Phys. Earth Planet. Interiors*, **2**, 276; 1970), on the other hand, if the other core element is sulphur an altogether less catastrophic event is required.

By comparing the combined crust-mantle abundances of various volatile elements with the abundances from different types of meteorites, Rama Murthy and Hall show that sulphur in the Earth's crust and mantle