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High-Pressure NMR Kinetic Evidence for a Dissociative–Associative Changeover for the Trimethylphosphate Exchange with Hexasolvates along the Series Aluminium(III), Gallium(III) and Indium(III)

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On the basis of ΔV^* we have shown that for the first row labile octahedral divalent transition-metal ions, only the later members show dissociative I_d behaviour, while the earlier members show an associative I_a behaviour, with the changeover occurring around iron(II) [1]. This changeover was discussed in terms of two possible effects: the first is a simple ion size argument and the second is based on the availability of suitable low-lying orbitals (t_{2g}) capable of accepting a lone pair of electrons from the incoming solvent molecule. From the change in ionic size alone one expects a mechanistic changeover for substitution along the series from Al^{3+}(0.53 Å), to Ga^{3+}(0.62 Å) and In^{3+}(0.80 Å).

For the trimethylphosphate exchange on the hexasolvates in nitromethane we conclude to a dissociative *d* activation mode for Al^{3+} and Ga^{3+} (ΔV^* = +22.5 and +20.7 cm^3 mol^{-1}) and to an associative *a* activation mode for In^{3+} (ΔV^* = –22.8 cm^3 mol^{-1}). The corresponding retardation and acceleration of the exchange reactions with pressure, at constant temperature, are shown in the Fig. 1.

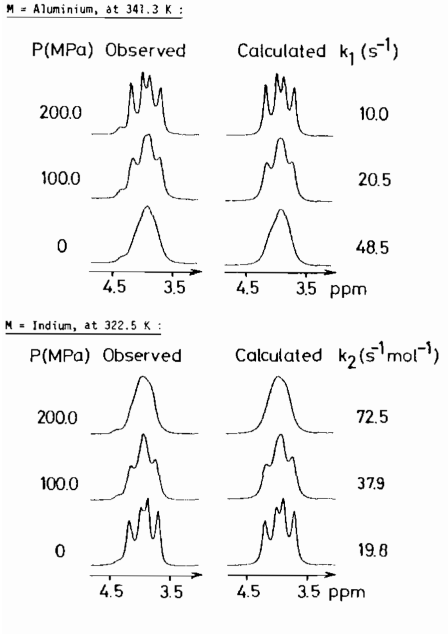

Fig. 1. Observed and calculated ^{1}H-NMR spectra in CD_3NO_2 for $[M(TMPA)_6]^{3+}$ + TMPA* ⇌ $[M(TMPA)_5(TMPA^*)]^{3+}$ + TMPA.

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Bridged Bis-Cyclooctatetraenes; Synthesis and Electron Transfer Studies

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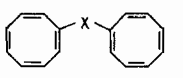
The following new compounds have been synthesized and reduced both chemically and electrochemically to their corresponding anionic species. In all cases, chemical reduction with alkali metals in hexamethylphosphoramide (HMPA) or liquid ammonia has afforded the electron spin resonance (esr) observation of the anion radicals of these systems at different temperatures. n-Butylcyclooctatetraene (nbCOT) has been used as reference for comparison with the results obtained for (I$^{\cdot}$). Both radical anions show almost identical esr spectra as well as identical linewidths at all temperatures investigated. This indicates that the unpaired electron is probably not exchanging between the two COT moieties in (I). Attempts are currently underway to form the trianionic radical species of (I) to see if the electron transfer is facilitated between the COT groups. Since COT dianion and COT anion radical have essential planar geometries, intramolecular electron transfer should be easier for the trianion than for the monoanion. Addition of salts to the trianion should



(I) X = $-CH_2CH_2CH_2CH_2-$
(II) X = $-Si(CH_3)_2-$
(III) X = $-C_6H_4-$

promote ion pairing with the dianionic COT moiety of the trianion thus slowing the intramolecular electron transfer process. These parameters are currently under study.

The anion radical of (II) at 10 °C in HMPA–THF solution again indicates that the unpaired electron resides exclusively in one of the COT moieties. Esr spectral data clearly indicates that –Si(CH_3)COT acts as an electron withdrawing group. This is probably the reason why the electron does not exchange between the COT's, since the unpaired electron resides primarily in a COT molecular orbital which has a node in the substituted position. Interestingly, an esr signal for COT$^{\cdot-}$ is observed simultaneously with that of the compound. This signal grows as a function of time, suggesting that there is slow decomposition of one of the C–Si bonds. Experiments are underway to generate the trianion radical of (II) at low temperatures to see if electron transfer can be detected. Ion pairing perturbations will be also investigated.

Compound (III) has been recently synthesized. Electron transfer between COT moieties in (III$^{\cdot-}$) is definitely expected. The transfer rate will be investigated as a function of both temperature and ion pairing parameters.

Electron Spin Relaxation in the Study of Boundary Layers at the Liquid–Solid Interphase

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The electron spin relaxation of transition metal ions is largely sensitive towards structural changes of the complex and towards mobility alterations of the solvent. In the case of Cu(II) ($S = 1/2$), structural changes influence both the magnetic parameters (g and A tensors) and the line width as a consequence of the relaxation mechanisms dominating in solution (spin-rotation and A and g anisotropies modulation). Solvent mobility variations also alter the line width, at low and high temperature, in opposite ways. In the case of Mn(II) ($S = 5/2$), structural changes influence the zero-field splitting term, thus effecting the line width, without appreciably modifying the line position (static term in the spin Hamiltonian). Decreased solvent mobility increases the correlation time for the motion and therefore the line width (dynamic term in the spin Hamiltonian).

The liquid mobility at the solid–liquid interface is expected to be decreased and to induce large effect on the line width of paramagnetic probes in the boundary layers. From a line width analysis, the correlation times for the motion can be calculated as a function of the distance from the surface.

The above procedure is applied to liquid–solid interphases in which SiO_2, Al_2O_3, TiO_2, and carbon were the porous solid supports, and water, NaOH water solution, and organic fluids were the liquids. The probes used were $Mn(H_2O)_6^{2+}$, $Cu(H_2O)_2^{2+}$, $Cu(OH)_4^{2-}$, and $Cu(acac)_2$.

Diastereomeric Electron-Donor–Acceptor Complexes

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An electron–donor acceptor (EDA) interaction has been assumed to contribute, besides hydrogen bonding, to the formation of certain diastereomeric complexes [1]. We have now shown, for different molecular systems, the existence of diastereomeric complexes which seem to be held together by EDTA attraction *exclusively*.

Among others, carbazole derivatives were chosen as π-donors and fluorenone derivatives as π-acceptors [2] (*e.g.* Fig. 1). The ^1H NMR signals of racemic

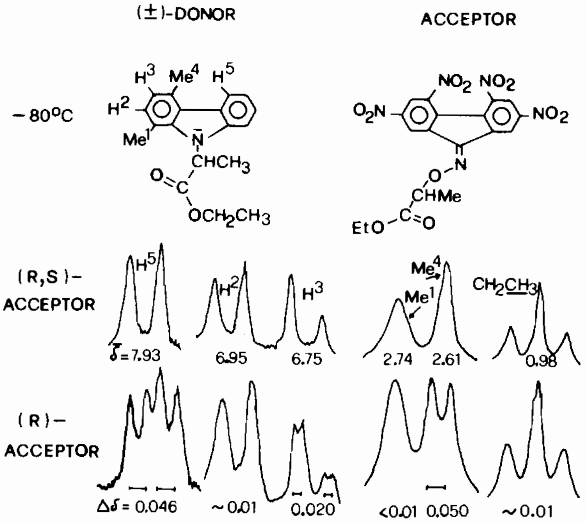

Fig. 1. ^1H NMR in [D_6]acetone of a racemic donor in the presence of 1.10 equivalents of (R,S)- or (R)-acceptor, respectively. Δδ: Shift difference between protons of (+)- and (–)-donor, determined from splittings or estimated from linewidths.