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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.

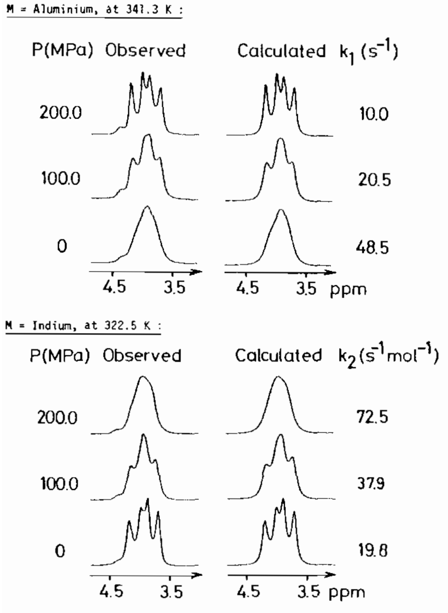

Fig. 1. Observed and calculated ^{1}H-NMR spectra in CD_3NO_2 for $[M(TMPA)_6]^{3+}$ + TMPA* $\rightleftharpoons$ $[M(TMPA)_5(TMPA^*)]^{3+}$ + TMPA.

Reference

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Bridged Bis-Cyclooctatetraenes; Synthesis and Electron Transfer Studies

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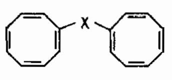
The following new compounds have been synthesized and reduced both chemical and electrochemically to their corresponding anionic species. In all cases, chemical reduction with alkali metals in hexamethylphosphoramide (HMPA) or liquid ammonia has afforded the electron spin resonance (esr) observation 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 = $-C_6H_4-$