Spectroscopic Investigations

ESR Evidence for Tight Ion-Pairs and Solvent Effects in Electron Transfer Reduction of Nitroso Compounds by Copper(0)–Isonitrile Complexes

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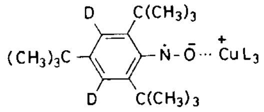
Persistent radicals are observed by ESR in electron transfer reduction of nitroso compounds by copper-(0)–isonitrile complexes. ESR spectra exhibit hyperfine splitting to one nitrogen nucleus, one copper nucleus and eventually hydrogen nucleus. The results obtained from different aromatic nitroso are consistent with the formation of nitroxide-like or anilino-like radicals. But the ESR study of solvent and temperature effects on these species, agree with the formation of nitroso radical anion–complexed copper cation tight pairs.

For example



The interaction between nitroso radical anion and copper counterion is very sensitive to solvent effect and sometimes in an unexpected manner which will be discussed.

Kinetics for Ligand exchange in paramagnetic complexes of Ni(DPM)$_2$ with Nitrogen, Oxygen and Sulfur Ligands. A Carbon-13 NMR Relaxation Study

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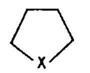
The carbon-13 paramagnetic line widths (T_{2p}^{-1}) and shifts ($\Delta\omega_p$) of 1*M* solutions of pyrrolidine (I), tetrahydrofuran (II), and tetrahydrothiophen (III) in the presence of 10^{-2} *M* Ni(dpm)$_2$ have been studied over a temperature range from 193 to 328 K.



(I), X = NH; (II), X = 0; (III), X = S.

The experimental shift and line width at each temperature depends on the isotropic shift of the complex-bound ligand ($\Delta\omega_M$), lifetime of the ligand in the complex (τ_M), and the nuclear spin–spin relaxation time in the complex (T_{2M}) in the manner described by Swift and Connick [1].

Some different models for the temperature dependence of $\Delta\omega_M$, τ_M and T_{2M} are set up and tested by simultaneous fitting of the experimental shift and line width data to the Swift and Connick expressions. The paramagnetic shifts show (especially for tetrahydrofuran) a clear non-Curie behaviour in the high temperature range. It was found that a fit to the experimental data could be obtained with an expression for $\Delta\omega_M$ which, apart from the usal Curie $1/T$ term due to the contact shift, also included a $1/T^2$ term. The temperature dependence of τ_M is given by the usual transition state theory expression. For T_{2M} we adopt a model using the modified Solomon–Bloembergen equations [2] with an assumption that the electronic relaxation is caused by the modulation of the static zero field splitting (ZFS) by molecular reorientation [3]. An advantage of this model is that it also allows calculation of the paramagnetic contribution to the nuclear spin-lattice relaxation time. Using also some ^{13}C T_1 experiments, some of the parameters of the model may therefore be calibrated.

With the above model for the temperature dependence, T_{2p} and $\Delta\omega_p$ have been simultaneously fitted to the Swift and Connick expressions, using a seven parameter non linear least squares procedure. The activation parameters and the exchange rates for the ligand exchange process in the three different complexes have been obtained. Furthermore, from the data analysis, the zero field splitting parameters, the carbon-13–electron hyperfine coupling constants, the molecular reorientation correlation times and the electronic relaxation times in the complexes have been estimated.

References

1 T. J. Swift and R. E. Connick, *J. Chem. Phys.*, *37*, 307 (1962).

2 R. E. Dwek, 'Nuclear Magnetic Resonance in Biochemistry', Clarendon Press, Oxford (1973).

3 A Carrington and C. R. Luckhurst, *Mol. Phys.*, *8,* 125 (1964).

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).

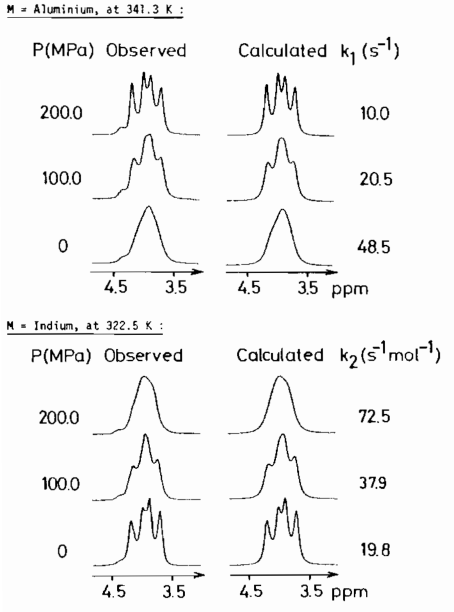

Fig. 1. Observed and calculated ^{1}H-NMR spectra in CD_3NO_2 for $[M(TMPA)_6]^{3+}$ + TMPA* ⇌ $[M(TMPA)_5(TMPA^*)]^{3+}$ + TMPA.

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.

Reference

1 K. E. Newman, F. K. Meyer and A. E. Merbach, *J. Am. Chem. Soc.*, *101,* 5588 (1979); Y. Ducommun, K. E. Newman and A. E. Merbach, *Helv. Chim. Acta*, *62,* 2511 (1979).

Bridged Bis-Cyclooctatetraenes; Synthesis and Electron Transfer Studies

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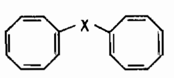
The following new compounds have been synthesized and reduced both chemical and electrochemically to their corresponding anionic species. In all cases, chemical reduction with alkali metals in hexamethylphosphoramide (HMPA) or liquid ammonia has afforded the electron spin resonance (esr) observation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