

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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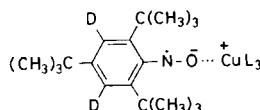
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Persistent radicals are observed by ESR in electron transfer reduction of nitroso compounds by copper(0)–isonitrile complexes. ESR spectra exhibit hyperfine splitting to one nitrogen nucleus, one copper nucleus and eventually hydrogen nucleus. The 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 1M solutions of pyrrolidine (I), tetra-

hydrofuran (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 = O; (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 usual 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 ¹³C 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).