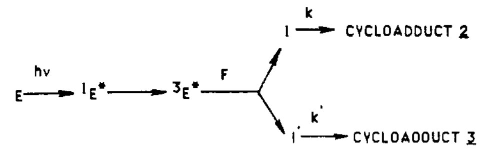
Scheme II



follows: **2**, $a = 7.701$ (2), $b = 16.593$ (3), $c = 12.041$ (3) A; **3**, $a = 7.722$ (2), $b = 16.631$ (4), $c = 11.741$ (3) A. Final agreement factors were $r = 0.0479$ for **2** and 0.0485 for **3**.[6] Although these results appear to confirm the photochemical generation of *trans*-PK,[1] subsequent results indicate this is probably not the case. No reaction between PK and furan occurs on heating at 150–155 °C for up to 48 h.

Laser flash photolysis of PK at 308 nm in acetonitrile using pulses from an excimer laser leads to the formation of an intermediate with a lifetime of ca. 15 ns with absorption centered at 270–277 nm.[7] This very short lifetime, at the limit of the time resolution of this flash system, precluded quenching studies to fully characterize this transient species. However, by analogy with previous laser flash studies of cyclohexenones[8] and other cyclic enones,[9] we assign this absorption to a highly twisted triplet excited state of PK; a general correlation of triplet lifetimes of cyclohexenones with structure has been observed, in which the lifetime is inversely correlated with the ability to twist around the C═C bond.[8-10] Consistent with these findings is that methylnaphthalene (MN) (E_T 61 kcal/mol) in concentrations up to 0.86 M (PK 0.013 M, furan 0.05 M) does not quench the formation of **2** and **3**. However, the free radical tetramethyl-1-piperidinyloxy (TEMPO) quenches formation of **2** and **3**, with Stern–Volmer quenching constants $k_q\tau$ of 12.5 ± 0.6 and 6.6 ± 0.3 M^{-1}, respectively, where k_q is the quenching rate constant and τ is the lifetime of the intercepted intermediate. Quenching by oxygen was also observed, with $k_q\tau = 438 \pm 8$ and 132 ± 5 M^{-1}, respectively.

Differential quenching by TEMPO and O_2 is consistent only with a nonconcerted photocycloaddition mechanism, as shown in Scheme II, in which the highly twisted triplet of PK reacts with furan (F) to give two distinct quenchable intermediates, I and I′, which are direct precursors of **2** and **3**, respectively. Since the adducts have lost conjugation, the possibility that I and I′ could be adduct triplet states can be eliminated on energetic grounds. It seems more likely that I and I′ are short-lived triplet biradicals, interceptable by TEMPO and O_2 but not by MN. The quantum efficiency for formation of **2** and **3**, 0.062 ± 0.005 and 0.065 ± 0.005, suggests that reversion to ground states of PK and F may occur from I and I′ as well as PK*. The observed stereochemistry suggests that reaction occurs on only one face of the twisted triplet of PK but indiscriminately exo and endo to the oxy bridge of furan. Since Diels–Alder addition of ground state *trans*-PK to furan should be concerted mechanistically even if nonsynchronous,[11] quenching of this process by TEMPO or O_2 is not expected.[12]

Mechanistic examination of [4 + 2] photocycloaddition reactions of dienes to cyclic enones[13] and to other systems in which strained trans ground state intermediates have been proposed[14] appear warranted.

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Supplementary Material Available: Tables consisting of 300-MHz ^1H NMR spectral data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, details of the structure determination, and a computer-generated plot with atom labels for **2** and **3** (9 pages); tables of observed and calculated structure factors for **2** and **3** (18 pages). Ordering information is given on any current masthead page.

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(6) The full NMR and X-ray data are provided as Supplementary Material.

(7) These data were kindly obtained by Dr. J. C. Scaiano at the National Research Council, Ottawa, Canada.

(8) Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706. Dunn, D. A. Ph.D. Dissertation, New York University, 1985.

(9) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816.

(10) Schuster, D. I.; Dunn, D. A.; Brown, P. B.; Bonneau, R., unpublished data.

(11) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771.

(12) No one has ever observed quenching by radical traps of a thermally induced Diels–Alder reaction, to the best of our knowledge. Dewer (ref 11) goes to great pains to distinguish between a concerted, nonsynchronous, two-stage mechanism in which the two bonds are formed to different extents at the transition state and two-step nonconcerted addition via biradical *intermediates*. In the absence of experimental and theoretical evidence for a two-step mechanism in *any* ground-state Diels–Alder process, we cannot accept the possibility raised by a referee that Diels–Alder reactions of a ground-state *trans*-cyclohexenone might be uniquely quenchable. See, also: Tolbert, L. M.; Mahfuza, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 3806.

(13) For examples of photocycloaddition of dienes to cyclohexenone and cyclopentenone, see: Cantrell, T. S. *J. Org. Chem.* **1974**, *39*, 3063.

(14) Dauben, W. G.; van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *J. Am. Chem. Soc.* **1979**, *101*, 1901.

Ionic Strength Dependence of Intervalence Transition Bands in Electron Tunnelling Processes

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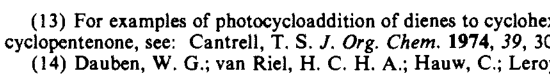
We wish to report the first study of the effect of ionic strength on an intervalence transition band (IT band). It is apparent that not only is the nature of the anion present important in determining the position of the IT band[1] but also the present work shows that there can be a strong ionic strength dependence of the band so that the concentration of the binuclear itself contributes to the band position as does the concentration of the oxidant or reductant used to generate the mixed-valence species. The ruthenium binuclear used in this investigation was the μ-2,6-dithiaspiro-[3.3]heptanedecaamminediruthenium(II,III) species studied earlier (complex I);[2] electron transfer in this molecule is known to be



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significantly nonadiabatic.[3,4] The oxidant employed was $[Fe(bpy)_3](PF_6)_3$. The ionic strength was controlled to the desired values by the addition of tetra-*n*-butylammonium hexafluorophosphate (TBAH). For ion-pairing in optical electron transfers, the Guntelberg[5] modification of the Debye–Huckel equation may be expressed as

$$E_{op} = E_{op}^{\circ} + \frac{2z_1z_2A\sqrt{\mu}}{1 + \sqrt{\mu}}$$

where z_1 and z_2 are the charges of the ions, μ is the ionic strength, A is a Debye–Huckel constant, E_{op} is the energy of the IT band, and E_{op}° is the energy of the IT band at infinite dilution. The ionic strength dependence of complex I was studied in two solvents, dimethyl sulfoxide and *N*-methylformamide; the results are graphically displayed in the figure, where the lines shown are

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(1) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

(2) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693.

(3) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596.

(4) Stein, C. A.; Lewis, N. A.; Seitz, G.; Baker, A. D. *Inorg. Chem.* **1983**, *22*, 1124.

(5) Guntelberg, E. *Z. Phys. Chem.* **1926**, *123*, 199.

0002-7863/88/1510-2306$01.50/0

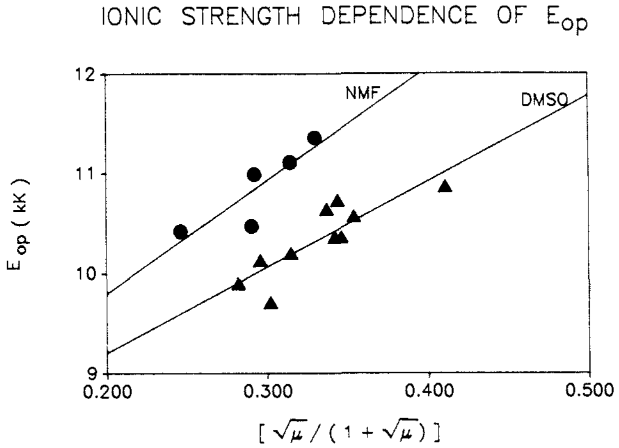

Figure 1. Modified Debye–Huckel plot for intervalence transition band energies of complex I in dimethyl sulfoxide (triangles) and *N*-methylformamide (circles).

computer-generated least-squares fits to the data. It is apparent that the energies of the IT bands in these solvents extrapolated to zero ionic strength (7.49 in dimethyl sulfoxide and 7.54 kK in *N*-methylformamide, a difference of only 0.7%) were essentially identical within experimental error, whereas the energies at any other value of the ionic strength differed by a measureable amount. For example, without any added salts, a common way of performing these experiments, the corresponding values were 9.90 and 10.4 kK, a difference of 5.1%. There was no systematic change in the peak shape or width as a function of ionic strength. The average value of the full-width at half-height was 7.6 ± 0.2 kK in *N*-methylformamide, whereas it was 6.2 ± 0.8 kK in dimethylformamide.

In the usual theoretical treatments[6-11] of electron-transfer reactions, no specific ion-pairing interactions are assumed. The theories also usually assume that the solvent forms a dielectric continuum around the reacting species although this is known[1,12-14] to be a poor approximation. Noncontinuum effects have recently been shown to overwhelm the dielectric continuum effects, especially in ruthenium ammine complexes.[1] In the absence of high concentrations of ions, specific solute–solvent interactions are the main sources of these noncontinuum effects, via hydrogen bonding interactions. In the presence of suitable concentrations of oppositely charged ions, under conditions typical of those employed to run IT bands, ion pairs become possible. There is thus a competition between the solvent and anions (or cations) to complex with the cationic (or anionic) binuclear species in solution. The extent of ion pairing that results depends inversely on the dielectric constant of the solvent, directly on the charges of the ions involved, and directly on the concentrations of the ions.

The effect of the ion pairing on the potential energy surface may be rationalized in terms of the polarization around the binuclear, $\vec{P}(\vec{r})$. The ground-state potential energy surface may be expressed as a functional of this polarization, $F[\vec{P}(\vec{r})]$. Thus, $F[\vec{P}(\vec{r})]_0$, the ground-state potential surface, may be defined by specific solute–solvent interactions at zero ionic strength. The surface so defined becomes perturbed in the presence of appreciable quantities of anions, as atmospheric condensation ensures.[15] The ground-state potential energy surface experiences a stabilization as a result of this perturbation, i.e.,

$$E_{op}(\mu) = E_{op}{}^{\circ} + \Delta G(\mu)$$

Although the ion pairing stabilizes the ground-state equilibrium potential energy surface, the excited state surface does not necessarily experience a corresponding stabilization. The lifetime of the excited state is relatively short compared with the time required to reorganize the ion pair into an equilibrium configuration compatible with the new electronic state. Consequently, the separation between the ground state and the excited state potential energy surfaces tends to widen as the ionic strength of the medium increases. This leads to the observed increase in E_{op} with increasing ionic strength.

In an interesting paper concerning measurements of IT bands in several frozen solvents under pressure at 25 °C, Drickamer et al.[16] determined that there was essentially no change in peak maxima in going from the liquid to the solid state although the static dielectric constant changed by almost a factor of 10 under the same conditions. From these observations, they concluded, and the conclusion is further reinforced in the present paper, that the dielectric continuum model was inadequate to account for the behavior of IT bands.

It is reasonable to expect that arguments based on the dielectric continuum theory would give better agreement between theory and experiment if values for IT bands extrapolated to zero ionic strength were used instead of values measured without regard to the ionic environment present. We are further exploring these ideas, especially with regard to the possible differences in ionic strength on electron transfers proceeding by purely adiabatic mechanisms and those, such as that which occurs in complex I, in which a significant degree of tunnelling occurs.

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Registry No. I, 76723-23-4.

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[6] Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853.
[7] Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.
[8] Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.
[9] Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1003.
[10] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.
[11] Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.
[12] Caswit, C. J.; DuBois, M. K. *Inorg. Chem.* **1986**, *25*, 74.
[13] Kjaer, A. M.; Kristjansson, I.; Ulstrup, J. J. *Electroanal. Chem.* **1986**, *204*, 45.
[14] Kjear, A. M.; Ulstrup, J. *Inorg. Chem.* **1986**, *25*, 644.
[15] Laszlo, P. *Pure Appl. Chem.* **1985**, *57*, 1051.
[16] Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Chem. Phys. Lett.* **1986**, *132*, 231.

Three-Center Binding of a Nitroxyl Free Radical to Copper(II) Bromide

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Transition-metal–nitroxyl complexes are currently of great interest since they are now used in the design of new magnetic materials.[2,3] Copper(II)–nitroxyl species exhibit remarkable magnetic properties which are strongly correlated to their coordination geometry; complexes with an equatorially bound nitroxyl ligand[4-7] exhibit strong antiferromagnetism, while those containing

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[2] Laugier, J.; Rey, P.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6931–6937.
[3] Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2191–2192.
[4] Porter, L. C.; Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 678–684, and references therein.
[5] Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1985**, *24*, 1006–1010.