also appear to be protonated in FSO_3H-SO_2 at −45°. However, no high-field signals are observed in these cases. Experiments aimed at deduction of the structures of these compounds in strong acid media are in progress.

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Rates of Electron Exchange between Manganese(I) and -(II) Isonitrile Complexes

Sir:

Manganese–isonitrile complex ions $(R-NC)_6Mn^+$ and $(R-NC)_6Mn^{+2}$ exchange an electron at rates measurable by ^{55}Mn nmr line broadening. We have found that when the group R is saturated alkyl and therefore an electrical insulator, the mechanism of exchange is simple electron transfer, and the rate is slowed by bulky R groups. When R is unsaturated or aromatic, more complicated phenomena are observed, but these are consistent with the idea that the unsaturated group acts as an electron conductor.

Previously studied simple electron exchange systems, such as manganate–permanganate[1] and cuprous–cupric[2] ions, offered no opportunity for variation of the ligands. Taube and coworkers[3] and Gould[4] have found acceleration of reduction of cobalt(III) by chromium(II) when electron conduction through a ligand is possible, but these reactions involve a transfer of a ligand as well as an electron.

We prepared the diamagnetic, "krypton-configuration" manganese(I) complexes $(R-NC)_6Mn^+$ from the isocyanide and manganese(II) iodide in ethyl or *t*-butyl alcohol[5] and made the nitrate salts by ion exchange. These were obtained with R = ethyl, *t*-butyl, vinyl,[6] and phenyl.[7] Oxidation with nitric acid[8] yielded the corresponding $(R-NC)_6Mn^{+2}$ complexes, isolated as the hexafluorophosphates when R was alkyl and the tetrabromocadmiates when R was vinyl or phenyl.[7]

The ^{55}Mn nmr signal of a solution of 0.3 *M* hexa(ethyl isocyanide)manganese(I) nitrate in Spectro Grade acetonitrile was broadened in direct proportion to increments of hexa(ethyl isocyanide)manganese(II) hexafluorophosphate added, up to a concentration of about 10^{-3} *M*. The rate constant for electron exchange calculated from the broadening[9] is 6.4 × 10^5 at 7°. The proper Arrhenius temperature dependence was observed, as illustrated in Figure 1; ΔH^* is 1.74 × 0.2 kcal/mole and ΔS^* is −25 eu. The rate constant for electron exchange between the *t*-butyl isocyanide complexes of Mn(I) and Mn(II) is significantly lower, 4.0 × 10^4 at 7°, ΔH^* is higher, 4.56 kcal, and ΔS^* is about the same, −21 eu. Solvent effects are slight, the rate for the ethyl isocyanide complexes being unchanged in ethanol and about doubled in dimethyl sulfoxide.

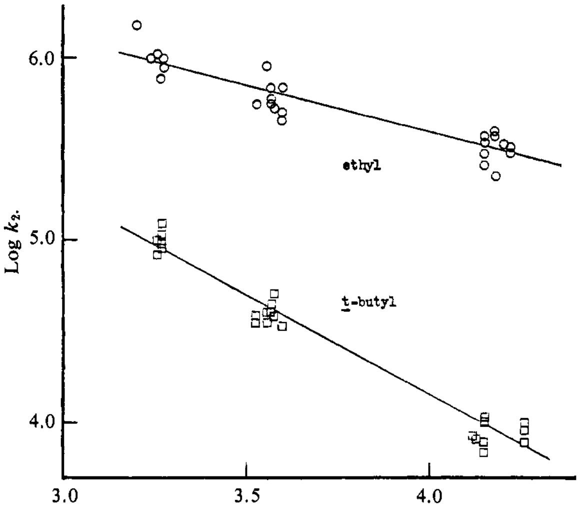

Figure 1. Plot of log k_2 *vs.* 1000/*T* for Mn(I)–Mn(II) electron exchange: ○, ethyl isocyanide complex; □, *t*-butyl isocyanide complex.

In contrast to the alkyl compounds, the vinyl and phenyl isocyanide manganese(II) complexes are not "well behaved." Magnetic susceptibilities were measured in acetonitrile solution by the proton nmr shift method.[10] The magnetic moments of the ethyl and *t*-butyl compounds are 1.95–2.1 BM, as expected for the strong-field d^5 Mn^{+2} ion with one unpaired electron. However, the magnetic moments of the vinyl and phenyl isocyanide complexes were found to be zero. The expected epr signal, six lines due to ^{55}Mn splitting, was found for both alkyl compounds, but no epr signal could be detected in freshly prepared acetonitrile solutions of $(C_6H_5NC)_6Mn^{+2}$. The alkyl compounds are pale pink solids and yield pale yellow solutions, in accord with the forbidden character of the Mn(II) t_{2g} to e_g transition, but the vinyl compound is a deep orange-red (λ_{max} 450 mμ) and the phenyl is purple-red (λ_{max} 490 mμ), comparable to previously reported $(Ar-NC)_6Mn^{+2}$ ions.[8]

Thus, the phenyl and vinyl isocyanide–manganese(II) complexes must exist as diamagnetic dimers. We postulate that these are π complexes involving face-to-face interaction of one or two of the phenyl (or vinyl) groups from each unit, as illustrated below. These resemble donor–acceptor π complexes of the usual variety in structure, but owe their stability to electron exchange and spin pairing.

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(3) F. R. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **88**, 4295 (1966); R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961); R. T. M. Fraser, D. K. Sebera, and H. Taube, *ibid.*, **81**, 2906 (1959).

(4) E. S. Gould, *ibid.*, **88**, 2983 (1966).

(5) A. Sacco, *Gazz. Chim. Ital.*, **86**, 201 (1956); *Ann. Chim.*, **48**, 225 (1958); *Chem. Abstr.*, **53**, 204*g* (1959).

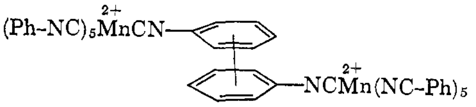
(6) Vinyl isocyanide: D. S. Matteson and R. A. Bailey, *Chem. Ind.* (London), 191 (1967).

(7) Satisfactory analyses for all elements (except oxygen) in each compound were obtained, except that the tetrabromocadmiate salts contained some cadmium bromide.

(8) L. Naldini, *Gazz. Chim. Ital.*, 90, 971 (1960).

(9) M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963).

(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).



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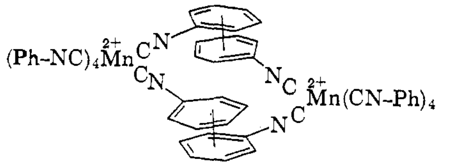

Hexa(phenyl isocyanide)manganese(II) dimer is in rapid equilibrium with a paramagnetic species (perhaps so short-lived that its epr signal is too broad to be observed) and also equilibrates with the manganese(I) complex, as shown by paramagnetic isotropic contact shifts[11] in the 60-MHz proton nmr spectrum. Addition of some Mn(II) complex to the Mn(I) in acetonitrile splits the phenyl proton peak into two parts, with the *meta* protons shifted downfield and the *ortho* and *para* protons shifted about twice as far upfield. With nearly pure 10^{-2} *M* $(Ph\text{-}NC)_6Mn^{+2}$ at −20° the downfield shift reaches 269 Hz and the line width is increased roughly six times. The qualitative behavior of the vinyl isocyanide complex is similar, with the terminal protons shifted upfield and the other proton shifted downfield. The shifts in the phenyl compound are approximately proportional to [Mn(II)]/[Mn(I) + Mn(II)], suggesting that the paramagnetic state is a triplet of the dimer. However, solutions of $(Ph\text{-}NC)_6Mn^{+2}$ are unstable, decomposing readily to the Mn(I) complex as well as high-spin Mn^{+2}, limiting the accuracy of these observations. We made a rough measurement of the Mn(I)–Mn(II) exchange rate at −20° by ^{55}Mn nmr line broadening and found k_2 to be about 5×10^4. This is obviously not a measure of the electron exchange rate between the Mn(I) and Mn(II) monomers, though it sets a lower limit.

In summary, surrounding the isonitrile–manganese complexes with insulating *t*-butyl groups retards electron transfer from Mn(I) to Mn(II). This type of electron-transfer rate cannot be measured when the surrounding groups are electron conductors such as vinyl or phenyl, but the dimerization of the Mn(II) complexes in these cases represents the ultimate in an electron exchange rate, namely, chemical bonding.

(11) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960); D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *ibid.*, **37**, 347 (1962); D. R. Eaton, W. D. Phillips, and D. S. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

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(13) National Science Foundation Cooperative Fellow, 1965–1967.

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Photolysis and Photoisomerization of the Benzene Oxide–Oxepin System

Sir:

The benzene oxide–oxepin (I–II) system[1,2] is uniquely attractive for photochemical studies because the equilibrium constant for their interconversion varies enormously with solvent polarity and to some extent with temperature, and one is, therefore, able to work with solutions highly enriched in either I or II. The ground-state interconversion rate (*ca.* 10^7 sec^{-1}) is rapid relative to the lifetimes of most triplet excited states. However, this does not necessarily mean that the interconversion of excited states will also occur rapidly. The excited-state interconversion is in fact expected to be a "forbidden" electrocyclic process.[3] This communication presents evidence for singlet and triplet chemistry of both I and II.

I II

The irradiation of I–II in ether solution using a soft glass filter (λ >310 mμ) and a broad spectrum lamp permitted the excitation of just II which has a very long tail absorption extending into the visible. The product (100%) proved to be the recently reported[2] 2-oxabicyclo[3.2.0]hepta-3,6-diene (III).[4] By contrast, irradiation of I–II at −80° with 2537-Å light (59% conversion) gave III (11%), benzene (15%), and phenol (74%).[5] This exciting energy corresponds quite well with the maximum in the approximated absorption spectrum[1] of I but is well off the maximum in that of II. This and the fact that the ratio I:II is larger at lower temperatures[2] indicate that the observed products were derived largely from I. Under the same conditions but with acetone as a photosensitizer (solvent), the reaction rate was somewhat faster than that of the unsensitized run (75% conversion at the same irradiation time). Phenol was the sole product formed. This dramatic change in product composition suggests that benzene is derived from singlet I. The enhanced rate of formation of phenol strongly suggests that it is the product of a triplet process, although the possibility that some phenol is formed from singlet I cannot be ruled out on the basis of these data. The combination of a polar solvent and low temperature, both of which favor a high I:II ratio, indicates that much if not all of the phenol is formed from I. The significant sensitizing effect of acetone ($\phi_{ST} \sim 1$)[6] would suggest that singlet I crosses to the triplet state with only fair efficiency.

Although we are still uncertain about E_T values for I and II, it can be estimated that I will be the higher and in the range 50–55 kcal.[7] Naphthalene (E_T = 61,[8]

(1) E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Letters*, 609 (1965); H. Günther, *ibid.*, 4085 (1965).

(2) E. Vogel and H. Günther, *Angew. Chem. Intern. Ed. Engl.*, **6**, 385 (1967).

(3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(4) Analytical, hydrogenation, and nmr data support this assignment. Double-resonance nmr spectra will be presented in the full paper. Good precedent for the assignment is the photoisomerization of 2,7-dimethyloxepin to 1,3-dimethyl-2-oxabicyclo[3.2.0]hepta-3,6-diene: L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).

(5) Analytical data were obtained gas chromatographically using an aluminum column of 5% ethylene glycol succinate supported on Teflon. On-column injections were made through a port outfitted with a glass liner (110°). Under these conditions no decomposition of I–II occurred during analyses.

(6) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(7) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963), report 53.5 kcal for 1,3-cyclohexadiene.

(8) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).