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–NC)$_6$Mn^{+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–NC)$_6$Mn^{+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).
(12) Alfred P. Sloan Foundation Research Fellow.
(13) National Science Foundation Cooperative Fellow, 1965–1967.

Donald S. Matteson,[12] Rodney A. Bailey[13]
Department of Chemistry, Washington State University
Pullman, Washington 99163
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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 equilib-

(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**,

rium 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.
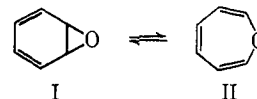
The irradiation of I–II in ether solution using a soft glass filter ($\lambda > 310$ mμ) and a broad spectrum lamp permitted the excitation of just II which has a very long tail absorption extending into the visible. The product (100%) proved to be the recently reported[2] 2-oxabicyclo[3.2.0]hepta-3,6-diene (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]

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).

$\phi_{ST} = 0.4^9$) was chosen as a sensitizer,[10] probably capable of transferring its triplet energy to both I and II. Irradiation of the I–II–naphthalene system (26°) with 2537-Å light gave only phenol and at a rate *at least 30 times faster than that of an identical but unsensitized run*. It is important to note that this enormous rate enhancement was observed under conditions where the II:I ratio is *ca.* 70:30[1] and must be a consequence of energy transfer to both species. Phenol is thus the product of triplet II as well as I and possibly also of singlet I. It follows that III, shown earlier to come from II, is the product of a singlet process and that intersystem crossing of singlet II must be extremely inefficient. Data obtained with other sensitizers are not quite as decisive as those described but are in complete accord with conclusions drawn.

Dewar benzene oxide (IV) is known to give phenol and I–II thermally as well as photochemically[11] and therefore warrants consideration as a possible intermediate in transformations of I–II. Repeated attempts

(9) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(10) Photosensitization experiments were performed in matched quartz cells. The two were identical in *all* respects, except for the deletion of sensitizer from the reference cell. Comparisons are drawn only between the two sets of data from such a pair. Except where noted, solutions (pentane) were 0.1 *M* in substrate and 1.0 *M* in sensitizer.
(11) E. E. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, **89**, 3922 (1967).

to detect intermediates such as IV have not been successful. Until direct evidence for the involvement of IV is in hand, we will assume that the photoconversion of IV to phenol proceeds *via* I–II.
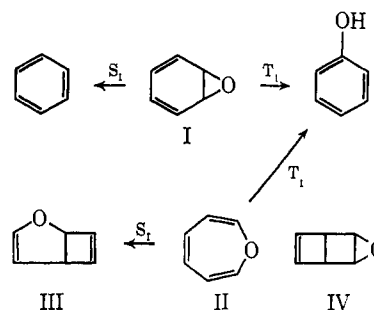
Corroborative data from quantum yield measurements are presently being obtained, and it is expected that we will be able to refine the scheme outlined above and comment in the full paper on the likelihood of hot ground-state reactions.[5,12]

(12) This is considered unlikely, because collisonal deactivation of vibrationally excited molecules is normally very fast in solution. The possibility cannot be dismissed in this case, however, because the thermal formation of phenol is quite facile.

J. M. Holovka, P. D. Gardner
*Department of Chemistry, University of Utah
Salt Lake City, Utah*

Additions and Corrections

Alkylcobaloximes and Their Relation to Alkylcobalamins [*J. Am. Chem. Soc.*, **88**, 3738 (1966)]. By G. N. SCHRAUZER and R. J. WINDGASSEN. Department of Chemistry, University of California, San Diego, California.

In Table II the values for the O–H···O signals in the ^{1}H nmr spectra of several methylcobaloximes were erroneously quoted 500 cps too far upfield. The last column of Table II should read:

Axial component	O–H··O
H₂O	−8.93
py	−8.93
P(OCH₃)₃	−8.83
P(n-C₄H₉)₃	−8.18
P(C₆H₅)₃	−8.20

On page 3741, column 1, the third line from the bottom should read: O–H···O protons at −0.6.

Aromatic Azapentalenes. III. 1,3a,6,6a-Tetraazapentalenes [*J. Am. Chem. Soc.*, **89**, 2633 (1967)]. By J. C. KAUER and R. A. CARBONI. Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

On page 2633, in the last line of the second column, "ferric" should be corrected to "ferrous."

Nucleophilic Displacements at Sulfur. III. The Exchange of Oxygen-18 between Sodium Thiosulfate-^{18}O and Water [*J. Am. Chem. Soc.*, **89**, 3379 (1967)]. By WILLIAM A. PRYOR and UMBERTO TONELLATO. Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

The mechanism postulated for this exchange, eq 7 and 9, predicts a negative slope when log k is plotted *vs.* $\mu^{1/2}$. The data of Table II and Figure 2 show that the slope is near zero. Two possible explanations can be suggested for this discrepancy. First, these data are all at ionic strengths greater than 0.1, and the Debye–Hückel limiting law may well not apply here. Second, these data of necessity were determined in unbuffered solutions, and the effect of ionic strength on the dissociation of water should be taken into account. If this is done, the data can be recalculated to show a slight negative slope. The exact value of the slope cannot be determined without a knowledge of α and K_w at 80°, but it is doubtful if these data in unbuffered solutions are accurate enough to justify a detailed treatment. In either case, the mechanistic arguments of the paper stand unchanged.