Although the homogeneity of the synthetic product has not yet been completely established, it exhibits to a significant degree those biological activities associated with HGH. These data provide evidence that the hormone does possess intrinsic[3] lactogenic activity.

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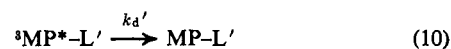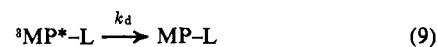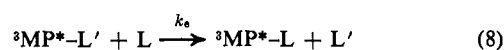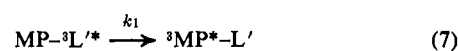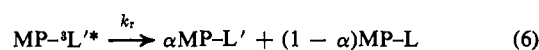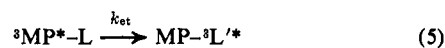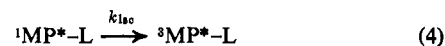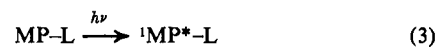## Reversible Energy Transfer in Metalloporphyrin Complexes. A Mechanism for Photocatalysis

*Sir:*

Previously we reported the unusually efficient cis–trans photoisomerization of stilbene-like olefins such as 1-(1-naphthyl)-2-(4-pyridyl)ethylene (NPE) and 4-stilbazole attached as ligands to zinc and magnesium etioporphyrin I.[1] For example, irradiation of degassed benzene solutions $5 \times 10^{-5}$ $M$ in zinc etioporphyrin I and $5 \times 10^{-3}$ $M$ in cis-NPE at 25–30° with light absorbed only by the near-ultraviolet or visible bands of the metalloporphyrin caused cis-to-trans isomerization of NPE with $\varphi_{c \to t} = 7$. The isomerization was efficient only in the thermodynamically favored cis-to-trans process; stationary states contained ca. 96% trans. Flash experiments revealed no transients other than the porphyrin triplet; the porphyrin triplet lifetime and absorption spectrum were unchanged by addition of NPE. The results were consistent with a photocatalysis described by eq 1 and 2, where MP = metalloporphyrin, L = cis-olefin, and L' = trans-olefin.

$$MP L \xrightarrow{h\nu} MPL^* \rightleftarrows MPL'^* \tag{1}$$

$$MPL'^* + L \rightleftarrows MPL^* + L' \tag{2}$$
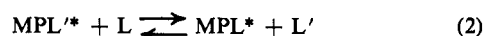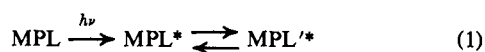
In the present communication we describe results of experiments which allow determination of the mechanism of the photocatalysis. While the observed results cannot be explained by porphyrin-to-ligand energy transfer and decay of a ligand excited state with isomerization, we suggest that reversible energy transfer with isomerization is a likely path.

Stilbene triplets can be quenched selectively to the trans ground state by substances having lower triplet energies, such as azulene;[2,3] we have observed similar phenomena with the stilbazoles.[4] The "azulene effect" has been interpreted in terms of a triplet surface having energy minima near both twisted and trans geometries. The metalloporphyrin has $E_T = 40–42$ kcal/mol;[1] the spectroscopic triplet of trans-NPE is estimated as

~50 kcal/mol from the onset of weak singlet–triplet absorption in o-iodotoluene. $E_T$ for cis-NPE is probably somewhat higher, based on analogy with similar systems.[2,4-6] Triplet energy transfer from the metalloporphyrin to cis-NPE should therefore require some thermal activation,[7] but the possibility of excitation to a distorted NPE triplet may well make the barrier easily surmountable at the temperatures studied (25–30°).[2,5,12,13] Triplet energy transfer to the ligand olefin, followed by rapid equilibration of the olefin triplet between trans and twisted forms, and subsequent energy transfer from trans triplet back to the porphyrin provide a path for isomerization without excited-state deactivation. The proposed sequence is described by

$$MP{-}L \xrightarrow{h\nu} {}^1MP^*{-}L \tag{3}$$

$$^1MP^*{-}L \xrightarrow{k_{\mathrm{isc}}} {}^3MP^*{-}L \tag{4}$$

$$^3MP^*{-}L \xrightarrow{k_{\mathrm{et}}} MP{-}^3L'^* \tag{5}$$

$$MP{-}^3L'^* \xrightarrow{k_r} \alpha MP{-}L' + (1 - \alpha)MP{-}L \tag{6}$$

$$MP{-}^3L'^* \xrightarrow{k_1} {}^3MP^*{-}L' \tag{7}$$

$$^3MP^*{-}L' + L \xrightarrow{k_e} {}^3MP^*{-}L + L' \tag{8}$$

$$^3MP^*{-}L \xrightarrow{k_d} MP{-}L \tag{9}$$

$$^3MP^*{-}L' \xrightarrow{k_d'} MP{-}L' \tag{10}$$

Making the usual steady-state approximations for intermediates and assuming $k_d = k_{d'}$, we obtain the following expression for $\varphi_{c \to t}$.

$$\varphi_{c \to t} = \frac{k_{\mathrm{et}}(k_d + k_e[L])(k_i + \alpha k_r)\varphi_{\mathrm{isc}}}{(k_d + k_e[L])(k_i + k_r)(k_{\mathrm{et}} + k_d) - k_e[L]k_ik_{\mathrm{et}}} \tag{11}$$

If we assume $k_e[L] \gg k_d$[14] and $k_1 \gg k_r$, the expression reduces to[16]

$$\varphi_{c \to t} = \frac{k_{\mathrm{et}}\varphi_{\mathrm{isc}}}{k_d} \tag{12}$$

We have previously reported[1] $k_d \approx 2 \times 10^3$ sec$^{-1}$ for zinc etioporphyrin I–NPE in benzene solution at 25°.[17]

(5) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).
(6) The triplet energy of porphyrin-bound NPE is unknown; implicit in this discussion is the assumption that $E_T$ of the bound ligand is nearly unchanged.
(7) Several cases[8-11] of activated energy transfer to higher energy excited states have recently been reported.
(8) J. Saltiel, *et al., J. Amer. Chem. Soc.*, **92**, 410 (1970).
(9) A. A. Lamola, *ibid.*, **92**, 5045 (1970).
(10) P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *ibid.*, **92**, 5269 (1970).
(11) M. Wrighton, L. Metts, and J. Saltiel, Abstracts, Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, Canada, 1970, ORGN 48.
(12) A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968); A. Bylina and Z. R. Grabowski, *Trans. Faraday Soc.*, **65**, 458 (1969).
(13) A. A. Lamola, *Tech. Org. Chem.*, **14**, 17 (1969).
(14) Results of earlier experiments[15] indicate that both ground and excited states of zinc etioporphyrin undergo very rapid ligand exchange.
(15) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Amer. Chem. Soc.*, **90**, 7196 (1968).
(16) At very low ligand concentrations, $\varphi_{c \to t}$ increases with increasing (NPE), but if the concentration is high enough to ensure complete coordination in the ground state, further increase in (NPE) has no effect on $\varphi_{c \to t}$.
(17) Although metalloporphyrin triplets have been shown to decay according to the equation $-dT/dt = k_1(T) + k_2(T)^2 + k_3(T)$ (G), where $T$ = triplet concentration and G = ground-state concentration,[18] the relatively weak exciting light used in our flash experiments and the much weaker light used for steady irradiation result in such low concentra-

(1) D. G. Whitten, P. D. Wildes, and I. G. Lopp, *J. Amer. Chem. Soc.*, **91**, 3393 (1969).
(2) G. S. Hammond, *et al., ibid.*, **86**, 3197 (1964).
(3) J. Saltiel and E. D. Megarity, *ibid.*, **91**, 1265 (1969); J. Saltiel, *ibid.*, **90**, 6394 (1968); **89**, 1036 (1967).
(4) D. G. Whitten and M. T. McCall, *ibid.*, **91**, 5097 (1969).

Differences in total porphyrin concentration and in light intensity make it difficult to draw a comparison between the flash experiments and the steady-illumination experiments; however, $k_d = 10^3$ sec$^{-1}$ is probably a reasonable estimate of the triplet decay rate in the latter. $\varphi_{isc}$ is estimated at 0.3–0.7;[19,20,20a] using these values and our measured value of $\varphi_{c\rightarrow t} = 7$ we obtain $k_{et} = 1 - 2.3 \times 10^4$ sec$^{-1}$. The former value corresponds to $\Delta G^{\ddagger} = 12.3$ kcal/mol from absolute rate theory.

As a test of the proposed scheme we prepared cis- and trans-1-phenyl-2-(4-pyridyl)propene (PPP) and cis- and trans-1-(1-naphthyl)-2-(4-pyridyl)propene (NPP), methylated derivatives of 4-stilbazole and NPE which are not expected to have energy minima near the transoid triplet.[2,4,13] Addition of azulene has no effect on the benzophenone-sensitized photoisomerization of 1,2-diphenylpropene,[2,4] and we find similar behavior for PPP.[21,22] For PPP and NPP we would anticipate that selective quenching of the olefin triplet to trans with regeneration of the porphyrin triplet could not occur; consequently $\varphi_{c\rightarrow t}$ should not exceed unity and the stationary state should be richer in cis-olefin.

As predicted, the zinc etioporphyrin I sensitized photoisomerization of NPP and PPP is markedly different from that of NPE and 4-stilbazole. Photostationary states measured from both directions give 30% cis for PPP and 31% cis for NPP in contrast to <1% cis for 4-stilbazole and ~4% for NPE. For NPP, $\varphi_{c\rightarrow t} = 0.4$ and $\varphi_{t\rightarrow c} = 0.2$; for PPP, $\varphi_{c\rightarrow t} = 0.1$ and $\varphi_{t\rightarrow c} = 0.05$. Since triplet energy transfer from zinc etioporphyrin I to PPP or NPP should be irreversible, the difference in $k_d$ for a zinc etioporphyrin I–NPP solution and a zinc etioporphyrin I–NPE or zinc etioporphyrin I–pyridine (benzene) solution should provide an estimate of $k_{et}$ for triplet energy transfer to NPP. The value of $k_{et}$ thus determined is $1 \times 10^4$ sec$^{-1}$, in excellent agreement with the value of $k_{et}$ calculated for NPE using eq 12.

Studies on the temperature dependence of isomerization and energy transfer reveal that reaction 5 requires a surprisingly low activation energy.[6] Isomerization yields for zinc etioporphyrin I–cis-NPE show very little increase with temperature ($\varphi_{c\rightarrow t}^{50°}/\varphi_{c\rightarrow t}^{30°} = 1.14$); an Arrhenius plot for $k_{et}$ can be obtained from eq 12 after correcting for the measured small increases of $k_d$ with temperature. The Arrhenius plot (correlation coefficient 0.99) so obtained gives $E_a = 3.2$ kcal/mol; using $\Delta G^{\ddagger} = 12.3$ kcal/mol, we obtain $\Delta S^{\ddagger} = -32$ eu. From $k_{et}$ for zinc etioporphyrin I–cis-NPP we obtain an Arrhenius activation energy of 2.5 kcal/mol, and from the preexponential term, $\Delta S^{\ddagger} = -34$ eu. The

low $E_a$ values indicate that energy transfer to a >50-kcal/mol "cis"-olefin triplet[6] is not important. The high negative entropy of activation appears to be in accord with an interpretation involving energy transfer to yield a distorted olefin triplet.[12,13] Little is known concerning the temperature dependence of $k_{et}$ and the magnitude of $\Delta S^{\ddagger}$ for related intermolecular processes.[5,13] It is not clear whether the observed large negative $\Delta S^{\ddagger}$ will prove to be a general phenomenon or one specific to this system. These points will be more fully discussed in the full paper.[23]

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## Stable Thiophene Sulfoxides

*Sir:*

Substituted thiophene sulfones are reasonably well-characterized substances,[1] although the parent, thiophene 1,1-dioxide, may be obtained only in solution.[2] We have isolated two disubstituted thiophene 1-oxides, and here report upon their structure and comment upon the nature of cyclic delocalization in the heterocyclic ring.

Oxidation of 2,5-di-tert-butylthiophene (**1**) with 1 equiv of m-chloroperbenzoic acid in methylene chloride gave, in addition to 2,5-di-tert-butylthiophene 1,1-dioxide (**2**) and some other products, approximately a 5% yield of 2,5-di-tert-butylthiophene 1-oxide[3] (**3**), mp 97–98°, isolated by column chromatography (eq 1).
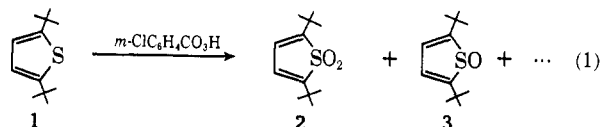


Interest in this substance centers about the sulfur atom. For optimal contribution to a conventional aromatic sextet, one might think it should be trigonally hybridized, with a formal lone pair of electrons in a 3p orbital perpendicular to the plane of the ring and with the sulfur–oxygen bond in that plane. On the other hand, sulfoxides normally exist exclusively in the pyramidal form, with a sizable barrier to inversion.

Spectroscopic evidence suggests that this sulfoxide is indeed tetrahedrally hybridized. In particular, the sulfur–oxygen stretch in the infrared occurs at $\lambda_{max}^{KBr}$ 9.5 $\mu$, a normal value. The olefinic ring protons in the nmr resonate in **3** at $\delta_{TMS}^{5\%CCl_4}$ 6.08 (cf. **1**, 6.46 **2**, 6.16).[4,5]

(1) J. L. Melles and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 72, 314 (1953); L. G. Vorontsova, *Zh. Strukt. Khim.*, 7, 240 (1966).
(2) W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 76, 1932, 1936, 1940 (1954).
(3) *Anal.* Calcd for C$_{12}$H$_{20}$SO: C, 67.89; H, 9.50. Found: C, 67.66; H, 9.54.
(4) However, the couplings between the ring protons (a possible measure of the C(3)–C(4) bond order: M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 91, 6325 (1969)) are: 1, $J = 3.6$; 2, $J = 5.0$; 3, $J = 3.5 \pm 0.1$ Hz (as seen from C-13 satellites). We have elsewhere commented on difficulties of abstracting structural information from the nmr spectra of cyclic sulfones: M. P. Williamson, W. L. Mock, and S. M. Castellano, *J. Magn. Res.*, 2, 50 (1970).

tions of triplets that bimolecular quenching is negligible and the decay of triplet absorption follows good first-order kinetics.
(18) H. Linschitz and K. Sarkanen, *J. Amer. Chem. Soc.*, 80, 4826 (1958).
(19) G. P. Gurinovich, A. I. Patsko, and A. N. Sevchenko, *Dokl. Phys. Chem.*, 174, 402 (1967).
(20) P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, 31, 1 (1969).
(20a) NOTE ADDED IN PROOF. A recent measurement of $\varphi_{isc} = 0.9$ has been reported; see B. Dzhagarov, *Opt. Spektrosk.*, 28, 66 (1970). Using $\varphi_{isc} = 0.9$, we obtain $k_{et} = 8 \times 10^3$ sec$^{-1}$.
(21) The benzophenone-sensitized photostationary state in benzene is 41% cis.
(22) The absence of an azulene effect on sensitized photoisomerization of NPP was not verified since we were unable to design an experiment in which direct excitation of NPP could be rigorously excluded.