as has been postulated.[4,5,7] Instead, the ring σ molecular orbital is extensively delocalized and has large proton coefficients. Overlap of the metal orbitals with this extensively delocalized molecular orbital is the mechanism which distributes unpaired spin over the protons. The spin is placed on the atoms in the benzene in proportion to the atomic orbital coefficients in the molecular orbitals *which contain the unpaired spin.* We are extending our calculations to consideration of delocalization in other complexes of transition metals with aromatic ligands.

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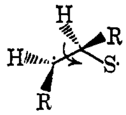
The Nature of the Intermediates in the Sensitized *cis–trans* Photoisomerization of Alkenes

Sir:

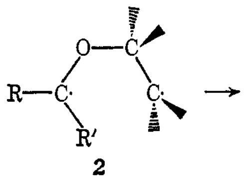
Two mechanisms have been proposed to account for *cis–trans* photoisomerization which results when simple olefins interact with triplet states of sensitizers: the Schenck mechanism involving formation of an adduct diradical, **1**, in which rotation about the central bond



$$\longrightarrow S + \alpha^0t + (1-\alpha)^0c \qquad (1)$$

1

is rapid relative to bond breaking (eq 1),[1] and the triplet mechanism in which olefin triplets are formed by excitation transfer from the sensitizer.[2,3] The triplet mechanism is favored when the excitation transfer steps are exothermic. To account for isomerization in cases where the sensitizer triplet excitation energy is not sufficient to excite the olefins to planar (spectroscopic) triplet states, nonvertical excitation transfer leading directly to twisted olefin triplet has been suggested.[4-6] For the case of carbonyl sensitizers with lowest n–π* triplet states formation of the Schenck intermediate has been proposed as a discrete step in the excitation transfer process (eq 2).[7] The following observations provide an experimental criterion for choosing between the Schenck and the triplet mechanisms.



$$\longrightarrow RR'C{=}O + {}^3[\text{olefin}] \qquad (2)$$

2

The simplest general scheme for sensitized *cis–trans* photoisomerization is given by eq 3–7, where *X represents an unspecified common intermediate, and other symbols have their usual meanings.[2] Steady-state approximations for ^{3}S and *X lead to eq 8–10.[2] Equation 8 represents the photostationary *trans/cis* ratio,

$$^0S \xrightarrow{h\nu} {}^1S \longrightarrow {}^3S \qquad (3)$$

$$^3S \xrightarrow{k_4} {}^0S \qquad (4)$$

$$^3S + {}^0t \xrightarrow{k_5} {}^*X \qquad (5)$$

$$^3S + {}^0c \xrightarrow{k_6} {}^*X \qquad (6)$$

$$^*X \xrightarrow{k_7} \alpha^0t + (1-\alpha)^0c \qquad (7)$$

$$([t]/[c])_s = (k_6/k_5)[\alpha/(1-\alpha)] \qquad (8)$$

$$\frac{1}{\phi_{t\rightarrow c}} = \frac{1}{1-\alpha}\left(1 + \frac{k_4}{k_5[t]}\right) \qquad (9)$$

$$\frac{1}{\phi_{c\rightarrow t}} = \frac{1}{\alpha}\left(1 + \frac{k_4}{k_6[c]}\right) \qquad (10)$$

and eq 9 and 10 give the dependence of *trans* → *cis* and *cis* → *trans* quantum yields on initial concentrations of *cis* and *trans* isomers.[8]

The dependence of *trans/cis* photostationary ratios for several olefins on the triplet energies of sensitizers has been attributed entirely to changes in the excitation ratio k_6/k_5.[2,11,12] Direct measurements of rate constants k_6 and k_5 have confirmed this interpretation for the stilbenes and the 1,2-diphenylpropenes.[5] For these olefin pairs photostationary state ratios could be predicted using a *single decay ratio*, $\alpha/(1-\alpha)$, in each case.[5]

Benzene-sensitized photoisomerization of alkenes has been studied in the vapor phase[3] and in solution.[12,13] Stationary states for several alkene pairs are close to unity. Since triplet excitation transfer should be, in all cases, at least 2–3 kcal/mole exothermic, k_6/k_5 is expected to be close to unity;[2] hence, for *X = ^{3}[alkene], $\alpha/(1-\alpha) = 1.0$.[14]

We have studied the *cis–trans* photoisomerization of the 2-pentenes using acetone and acetophenone as sensitizers.[15] The results are in accord with eq 9–10

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[1] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, 71, 781 (1962).

[2] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[3] E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968), and references cited therein.

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[6] *Cf.*, however, A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968).

[7] N. C. Yang, J. L. Cohen, and A. Shani, *J. Am. Chem. Soc.*, **90**, 3264 (1968); *cf.*, also, R. A. Caldwell and G. W. Sovocool, *ibid.*, **90**, 7138 (1968), and S. M. Japar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **2**, 137 (1968).

[8] Side reactions, *e.g.*, oxetane formation, have been neglected. The efficiency of intersystem crossing for the sensitizer was taken as unity. The latter is a valid assumption for acetophenone[9] and acetone.[10] Oxetane formation is a minor reaction in the case of acetophenone, and its quantum yield does not depend on the pentene isomer used. Step 4 includes reactions with solvent.

[9] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[10] (a) R. A. Borkman and D. R. Kearns, *ibid.*, **44**, 945 (1966); (b) *J. Am. Chem. Soc.*, **88**, 3467 (1966).

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[12] M. A. Golub and C. L. Stephens, *ibid.*, **70**, 3576 (1966).

[13] M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966).

[14] The best experimentally determined value seems to be $\alpha/(1-\alpha) = 1.00 \pm 0.10$ for the 2-butenes.[3]

[15] Benzophenone-sensitized *trans* → *cis* photoisomerization of the piperylenes was used for actinometry.[9] Irradiations were carried out at 30° in a merry-go-round apparatus using the 3130-Å Hg line. In the case of acetone, the sensitizer was used as solvent; in the case of acetophenone solutions were 0.057 *M* in sensitizer, and cyclohexane was used as solvent. In calculating quantum yields the results were corrected for back reaction.[9] Analyses were by glpc using a 50 ft × $^1/_8$ in. column packed with 20% AgNO$_3$ in ethylene glycol on Firebrick.

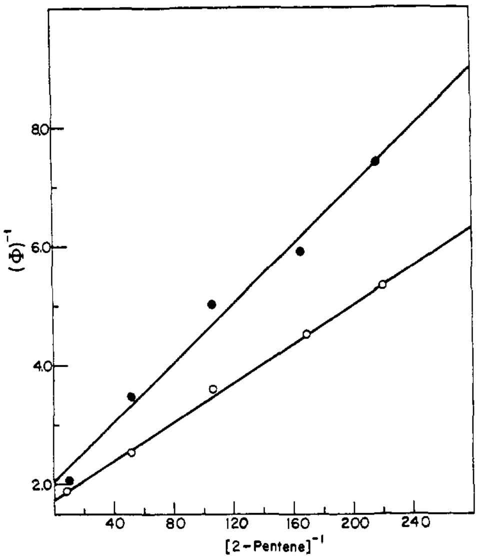

Figure 1. Acetone-photosensitized isomerization of *cis*- and *trans*-2-pentene, open and full circles, respectively.

(Figures 1 and 2). Decay ratios for intermediates produced with each sensitizer were obtained from the ratios of the intercepts in Figures 1 and 2. Excitation ratios were calculated from the decay ratios and the *trans*/*cis* photostationary state ratios. The results are shown in Table I. An independent check of the proposed general mechanism is available in that the ratios of the slopes in the plots predict closely the observed photostationary states as required by eq 8–10. Limiting quantum yields at high pentene concentrations are $\phi_{t\rightarrow c} = 0.49, 0.26$, and $\phi_{c\rightarrow t} = 0.58, 0.50$, for acetone and acetophenone, respectively.[16]

Table I. Sensitized Photoisomerization of the 2-Pentenes

Sensitizer	E_T, kcal/mole[a]	$\alpha/(1-\alpha)$	k_6/k_5	$(t/c)_s$ Obsd	$(t/c)_s$ Predicted[c]
Benzene	84	1.0_0[b]	0.92[b]	0.92[b]	
Acetone	80	1.1_7	1.3_0	1.5_2	1.5_2
Acetophenone	74	1.9_0	2.8_5	5.4	4.7

[a] Triplet excitation energies: benzene, ref 3; acetone, ref 10; acetophenone, ref 2. [b] Values for the butenes from ref 3. [c] From the ratios of the slopes in Figures 1 and 2.

We stress here that, in contrast to the stilbenes and the 1,2-diphenylpropenes, a *single decay ratio does not account for observations with different sensitizers in the case of the 2-pentenes.* The variation of photostationary ratios of 2-octenes and 2-pentenes with the triplet energy of sensitizers was incorrectly attributed solely to changes in excitation ratios for alkene triplet formation.[12] Since a common decay ratio does not obtain, it is clear that *different intermediates are produced with different sensitizers.*

The triplet mechanism should be important with sensitizers whose triplet excitation energy is close to that of ethylene, ~82 kcal/mole.[17] With lower energy sensitizers the triplet mechanism should diminish in importance except in cases where nonvertical excitation transfer can occur.[4,7] We propose that *for alkenes* deviation of the decay ratio from unity is a measure of the

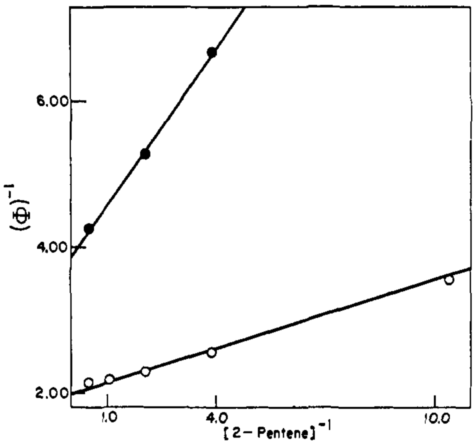

Figure 2. Acetophenone-photosensitized isomerization of *cis*- and *trans*-2-pentene, open and full circles, respectively.

involvement of Schenck intermediates, **2**, in the photoisomerization. Thus, the small increase of the decay ratio obtained with acetone as sensitizer indicates that at 30° the Schenck intermediate is involved to a minor extent, and that triplet excitation transfer represents the major path for the isomerization.[18] On the other hand, the large decay ratio increase obtained with acetophenone as sensitizer suggests that the Schenck mechanism predominates in this case. It may be more than a coincidence that for acetophenone and other n–π^* sensitizers with even lower triplet-state energies the photostationary ratios are very close to the thermodynamic ratio.[12,19] The mechanism accounts for the observations that triphenylene[7] and some carbonyl compounds with π–π^* lowest triplet states[12] are ineffective as sensitizers of the *cis–trans* isomerization of alkenes. The possibility that the abnormally *trans*-rich photostationary states obtained for the stilbenes with a few sensitizers[2,5,20] were due to competing decay from Schenck intermediates is under investigation.[20a]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(16) The acetone results are in qualitative agreement with those in ref 10b. The maximum limits of error on our results are: $(t)/(c) = 1.52 \pm 0.12$; sum of limiting quantum yields = 1.06 ± 0.10.

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(18) This interpretation agrees with that proposed in ref 10b, where two competing mechanisms were suggested on the basis of variation of photostationary state ratios with temperature.

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(20) R. Searle, J. L. R. Williams, D. E. De Meyer, and J. C. Doty, *Chem. Commun.*, 1165 (1967).

(20a) NOTE ADDED IN PROOF. Similar conclusions have been reached by Professor N. C. Yang and Dr. J. I. Cohen for the sensitized photoisomerization of the 3-methyl-2-pentenes. We thank Professor N. C. Yang for communicating their results to us.

(21) National Institutes of Health Postdoctoral Fellow, 1968–1969.

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The Thermal Rearrangement of 6,6-Dichloro-3,3-dimethyl-2-oxabicyclo[3.1.0]hexane. A Novel Case of Steric Hindrance to Ionization

Sir:

The recent literature[1] contains a number of reports of attempts to observe steric hindrance to ionization.

(1) (a) Reviewed by H. C. Brown, I. Rothberg, P. von R. Schleyer,