CHEMISTRY LETTERS, pp. 1377-1380, 1981.

EFFECT OF OXYGEN ON THE PHOTOSTATIONARY STATE COMPOSITION IN TRIPLET SENSITIZED CIS-TRANS ISOMERIZATION OF 1-ARYL-3,3-DIMETHYL-1-BUTENES.
A CLASSIFICATION OF TRIPLET ENERGY SURFACES OF AROMATIC OLEFINS

Tatsuo ARAI, Takashi KARATSU, Hirochika SAKURAGI, and Katsumi TOKUMARU*
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

The trans-isomer ratio of 1-p-biphenylyl-3,3-dimethyl-1-butene (BDMB) at the photostationary state in triplet sensitized isomerization increases with increasing concentration of oxygen and azulene. It is proposed to classify triplet energy surfaces of some aromatic olefins containing BDMB based on the variation of their photostationary isomer ratios with oxygen and/or azulene as triplet quenchers in their photoisomerization.

In a previous communication on the triplet sensitized photoisomerization of 3,3-dimethyl-1-(2-naphthyl)-1-butene (2-NpCH=CH^{t}Bu, DMNB),$^{1)}$ we demonstrated that its twisted triplets, ^{3}p, and transoid triplets, ^{3}t, have comparable probability to be alive through the mutual interconversion, on the basis of the observation that oxygen altered the photostationary isomer ratios combined with the effects of azulene, a selective quencher of ^{3}t. In this case oxygen can quench both of ^{3}t and ^{3}p in contrast with the isomerization of stilbene$^{2)}$ and 1-(2-naphthyl)-2-phenylethylene (2-NPE),$^{3)}$ where oxygen can quench only ^{3}p.

Here, we have found a new system, 1-(p-biphenylyl)-3,3-dimethyl-1-butene (p-BpCH=CH^{t}Bu, BDMB), similar to DMNB in triplet-state behavior in the sensitized isomerization and wish to propose a classification of the triplet energy surfaces of some 1-aryl-3,3-dimethyl-1-butenes and 1,2-diarylethylenes with regard to the effects of oxygen and azulene on the photostationary isomer ratio.

On benzophenone-sensitized isomerization of BDMB in benzene at 26°C, the photostationary trans-to-cis isomer ratio, $([t]/[c])_s$, was found to increase with increasing oxygen concentration as shown in Figure 1.$^{4)}$ Figure 1 also depicts the $([t]/[c])_s$ values for 1-phenyl-3,3-dimethyl-1-butene (t-BuSt), DMNB,$^{1)}$ and stilbene$^{2)}$ in the benzophenone-sensitized isomerization. Among these olefins, BDMB and DMNB triplets suffer the oxygen effects; the $([t]/[c])_s$ values for t-BuSt, stilbene,$^{2)}$ and 2-NPE$^{3)}$ are independent of the oxygen concentration. These results show that in the isomerization of BDMB both of ^{3}t and ^{3}p are quenched by oxygen as in the case of DMNB, whereas t-BuSt triplets are quenched by oxygen only at the twisted geometry, as reported on stilbene$^{2)}$ and 2-NPE triplets,$^{3)}$ to give the same ratio of the isomers as in the absence of oxygen.$^{5)}$

Figure 2 compares the effect of azulene (Az), a selective quencher of ^{3}t leading to trans-isomers. Increase of azulene concentration, [Az], increases the trans-isomer ratios of DMNB and BDMB, but does not affect at all the isomer ratio of t-BuSt. Stilbene$^{2)}$ and 2-NPE$^{3)}$ were reported to suffer the azulene effect. Accordingly, the triplets of these olefins except for t-BuSt are shown to have population in the transoid geometry as well as in the twisted one.

As discussed in the previous communication,$^{1)}$ the isomerization mechanism of the olefins in the presence of Az and O_2 can generally be expressed by Scheme 1, where S stands for a sensitizer and α is the fraction of ^{3}p decaying to the ground-state trans-isomer. According to this scheme,

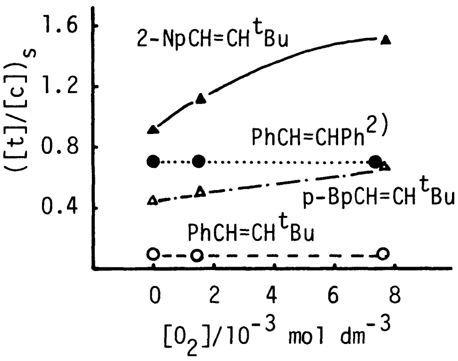


Figure 1. Oxygen Effect on Photostationary Isomer Ratio of Benzophenone-Sensitized Isomerization of Aromatic Olefins.

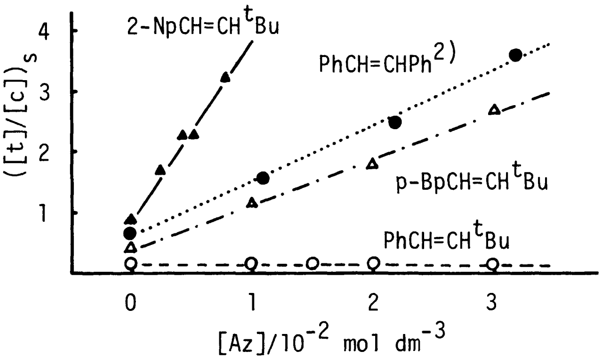


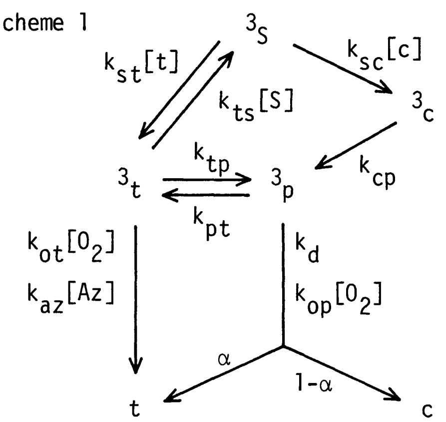
Figure 2. Azulene Effect on Photostationary Isomer Ratio of Benzophenone-Sensitized Isomerization of Aromatic Olefins under Degassed Condition.

the isomer ratio in the presence of Az and/or O_2 is expressed by eq. 1. The $([t]/[c])_s$ values were determined for benzophenone-sensitized isomerization of BDMB in benzene as a function of [Az] under degassed, air-saturated, and O_2-saturated conditions. The plot of $([t]/[c])_s$ is linear against [Az] in each case, and the results are summarized in Table 1. Increase of oxygen concentration in solution effected a noticeable attenuation in slope and an increase in intercept.

The decay rate constant, k_d, for ^3p of BDMB can be estimated from the slopes in Table 1 using eq. 2, where r and r' are the slopes under two different experimental conditions with respect to oxygen concentration, and $[O_2]$ and $[O_2]'$ represent the oxygen concentrations of the corresponding conditions. If k_{op} is taken to be 5×10^9 dm^3/mol·s, nearly diffusion-controlled, k_d can be estimated as $(2.8\text{-}4.4)\times10^7$ s^{-1}. Furthermore, when k_{ot} and k_{az} are assumed to be the same as k_{op} and 7×10^9 dm^3/mol·s, respectively, as estimated for DMNB,[1)] the equilibrium constant, K_{tp} $(=k_{tp}/k_{pt})$, can be evaluated as 1.9-3.0. From the values for k_d and K_{tp} the lifetime of the olefin triplets, τ_T, can be estimated as 35-48 ns (eq. 3). The similarly estimated values for DMNB are $(2.5\text{-}3.5)\times10^7$ s^{-1} for k_d, 1.5-2.0 for K_{tp}, and 40-70 ns for τ_T.[1)]

On the basis of the above and previously reported effects of the triplet quenchers on the isomer ratio, we now postulate a classification of the triplet energy surfaces of the aromatic olefins into three classes as summarized in Table 2. Thus, in class A as represented by t-BuSt, the isomer ratio is not affected at all with Az and O_2. According to eq. 1, for class A olefins with τ_T=30 ns,[6)] $K_{tp}\geq10^2$ is required to result in no detectable variation in the isomer ratio with both of the quenchers.[7)] In class B olefins, stilbene and 2-NPE, the isomer ratio is altered with

Scheme 1



$$([t]/[c])_s = \left(\frac{k_{sc}}{k_{st}}\right)\left(\frac{\alpha}{1-\alpha} + \frac{(k_{ot}/K_{tp})[O_2] + (k_{az}/K_{tp})[Az]}{(1-\alpha)(k_d + k_{op}[O_2])}\right) \quad (1)$$

$$k_d = \frac{k_{op}(r'[O_2]' - r[O_2])}{r - r'} \quad (2)$$

$$\tau_T = \frac{1 + K_{tp}}{K_{tp}k_d} \quad (3)$$

Table 1. Attenuation of Azulene Effect by Oxygen in Benzophenone-Sensitized Isomerization of 1-(p-Biphenylyl)-3,3-dimethyl-1-butene (0.01 mol/dm^3)

Condition	Slope/dm^{3}mol^{-1}	Intercept	[O_2]/10^{-3} mol·dm^{-3} a)
Degassed	71	0.47	0
Air	60	0.54	1.62
Oxygen	30	0.72	7.74

a) J. E. Jolly and J. H. Hildebrand, J. Am. Chem. Soc., 80, 1050 (1958).

Az, but not with O_2. The reported data[2,3b] for the isomer ratio with Az and/or O_2 are analyzed according to eq. 1, and K_{tp}'s are estimated as ca. 25 and 5 for stilbene and 2-NPE, respectively. For class C olefins, DMNB and BDMB, their isomer ratios are altered with both of Az and O_2, and $K_{tp} \cong 2$ as estimated above. Therefore, K_{tp} increases from nearly unity for class C to 5-25 for class B, and supposedly to 10^2 or more for class A. In Table 2, the free energy changes, ΔG, from ^3t to ^3p are listed as evaluated from these K_{tp} values at 26°C. In the sequence of classes A, B, and C, the free energy change becomes smaller and the population of the transoid triplet will increase. Thus, the transoid triplets will be populated in class B sufficiently to be quenched with Az but not with O_2, and further highly populated in class C to be quenched with both Az and O_2.

The difference in the triplet energy surfaces between these classes of the olefins could be interpreted in terms of avoided crossing of curves of the potential energy. The first excited triplet state, ψ_1 (=T_1), of styrenes lying, in the planar geometry, ca. 61 kcal/mol above the ground state[8] has been shown to be correlated to the second excited singlet state, S_2, an

Table 2. Classification of Triplet-State Energy Surface of Aromatic Olefin through the Effect of Azulene and Oxygen on the Photostationary Isomer Ratio

Class	Example	Azulene	Oxygen	K_{tp} a)	-ΔG/kcal·mol^{-1} a)
A	PhCH=CH^{t}Bu	ineffective	ineffective	10^2-10^3	3-4
B	PhCH=CHPh 2-NpCH=CHPh	effective	ineffective	$5^{b)}$-$25^{c)}$	1-2
C	2-NpCH=CH^{t}Bu p-BpCH=CH^{t}Bu	effective	effective	~2	0.5

a) At 26°C. b) At 25°C (ref. 3b). c) At 30°C (ref. 2).

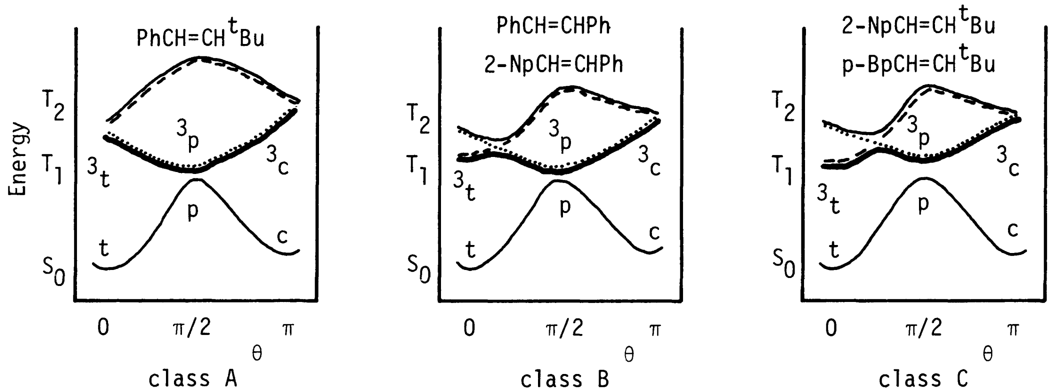


Figure 3. Triplet Energy Surfaces of Aromatic Olefins: θ denotes the angle of twist; ψ_1 ··················· , ψ_2 – – – – – .

"ethylenic" state,[8] and a "benzenic" triplet state, ψ_2 (=T_2), was supposed to correspond to the "benzenic" S_1 state and to lie at ca. 72 kcal/mol above the ground state.[9] The above rather large energy difference between the triplet states suggests that there is no crossing of these triplet surfaces in styrenes.[9] The present observation for t-BuSt is in accord with this assumption (Figure 3, class A).

Introduction of a 2-naphthyl or a p-biphenylyl group instead of the phenyl group at the 1-position of 3,3-dimethyl-1-butene will stabilize the "arenic" ψ_2 state of the olefins, DMNB or BDMB,[10] resulting in avoided crossing between the two triplet potential curves, ψ_1 and ψ_2. The resulting lowest triplet state, T_1, must have the energy minima at twisted and transoid geometries (Figure 3, class C).[11] This is also the case for the triplet surfaces of stilbene (Figure 3, class B).[12] In these classes of the olefins the energy minima, as indicated by the K_{tp} or ΔG values, are located at almost the same level at the twisted and transoid geometries. However, the difference between the class B and class C olefins can arise from a different stabilization of the "ethylenic" ψ_1 state at the twisted geometry. The extent of the stabilization of ψ_1 at the twisted geometry can be affected by substituents at the olefinic carbon atoms since the twisted triplet states can be assumed to have a biradical character with the two chromophores twisted each other. Thus, the twisted triplet states of 1,2-diarylethylenes like stilbene and 2-NPE (class B) will be more stabilized than those of monoarylethylenes like DMNB and BDMB (class C) since for the former with a bis-benzyl biradical character electronic repulsion between the two chromophores will be removed to a more extent by virtue of conjugation of each benzyl chromophore than for latter with an alkyl-benzyl biradical character.

We believe that the present postulation can provide the basis to understand the behavior of the triplet olefins which has hitherto seemed complicated. The work is now in progress to extend the scope and to elucidate the energetics through examining various olefins.

References

1) T. Arai, H. Sakuragi, and K. Tokumaru, Chem. Lett., 1980, 1335.
2) J. Saltiel, A. Marinari, C. W.-L. Chang, J. C. Mitchener, and E. D. Megarity, J. Am. Chem. Soc., 101, 2982 (1979).
3) a) G. Gennari, G. Cauzzo, and G. Gallazzo, J. Phys. Chem., 81, 1551 (1977).
   b) J. Saltiel and D. W. Eaker, Chem. Phys. Lett., 75, 209 (1980).
4) Irradiations were performed with 366-nm light isolated from a 1-kW high pressure mercury lamp equipped with Toshiba UVD36B filters and the resulting isomers were analyzed by GLPC.
5) For stilbene and 2-NPE oxygen can vary the isomer ratio in the presence of azulene.[2,3]
6) R. A. Caldwell and C. Pac, Chem. Phys. Lett., 64, 303 (1979).
7) 1-Phenylpropene is reported to suffer no detectable azulene effect on the photostationary state composition: R. E. Schwerzel and R. A. Caldwell, J. Am. Chem. Soc., 95, 1382 (1973).
8) P. M. Crosby, J. M. Dyke, J. Metcalfe, A. J. Rest, K. Salisbury, and J. R. Sodeau, J. Chem. Soc., Perkin Trans. 2, 1977, 182.
9) R. Bonneau, J. Photochem., 10, 439 (1979).
10) Triplet energies of naphthalene and biphenyl are reported to be 61 and 66 kcal/mol, respectively: S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, N.Y. (1973).
11) Phosphorescence observed for DMNB and BDMB in 3-methylpentane at 77K could be attributed to their transoid triplets. The transoid triplet energies are estimated from the phosphorescence spectra to be 58 and 62 kcal/mol for DMNB and BDMB, respectively.
12) J. B. Birks, Chem. Phys. Lett., 38, 437 (1976).

(Received June 1, 1981)