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EFFECT OF OXYGEN ON THE PHOTOSTATIONARY STATE COMPOSITION IN TRIPLET SENSITIZED ISOMERIZATION OF 3,3-DIMETHYL-1-(2-NAPHTHYL)-1-BUTENE

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Photostationary state compositions and quantum yields were determined for triplet sensitized isomerization of 3,3-dimethyl-1-(2-naphthyl)-1-butene in benzene. The ratio of the trans isomer at the photostationary state increased with increasing concentration of oxygen, which, combined with the azulene effect, indicates that both of transoid and twisted triplets are quenched by oxygen.

In triplet sensitized cis-trans isomerization of olefins such as stilbene and 1-(2-naphthyl)-2-phenylethylene, oxygen does not alter the ratio of cis to trans isomers at the photostationary state.[1-3] It has been proposed that the isomerization proceeds through deactivation of twisted triplets of the olefins into ground-state cis and trans isomers and oxygen quenches the twisted triplets to give the same ratios of the olefin isomers as in the absence of oxygen.[1-3]

We now wish to report that in the triplet sensitized isomerization of 3,3-dimethyl-1-(2-naphthyl)-1-butene ($2\text{-}C_{10}H_7CH{=}CH^tBu$, DMNB) oxygen increases the ratio of the trans isomer at the photostationary state, and to show that in the isomerization process transoid triplets and twisted triplets are comparably populated and both triplets are deactivated by oxygen. To our knowledge, this seems to be the first observation of the effect of oxygen altering the photostationary ratio.

The photostationary state compositions of DMNB were determined as a function of triplet energy of sensitizers as described previously.[4,5] Plots of the trans/cis compositions vs. the triplet energies gave the profile which is quite similar to those for 1-phenylpropene[4] and stilbene[6] but quite different from that for 3,3-dimethyl-1-phenyl-1-butene.[4] From the profile the triplet energies of DMNB are estimated to be about 60 and 52 kcal/mol for cis and trans isomers, respectively, according to the well-known method.[6]

Table 1 lists the quantum yields for the isomerization from cis to trans ($\Phi_{c\rightarrow t}$) and trans to cis isomers ($\Phi_{t\rightarrow c}$) determined at low conversion (<15%) in the presence of benzophenone (E_T=68.6 kcal/mol)[7] and 2-acetylnaphthalene (E_T=59.4 kcal/mol)[7] as sensitizers using benzophenone-benzhydrol actinometry.[7] When benzophenone (Φ_{isc}=1)[7] was used as a sensitizer, $\Phi_{c\rightarrow t}+\Phi_{t\rightarrow c}=0.9$, and $\Phi_{c\rightarrow t}$ is somewhat larger than $\Phi_{t\rightarrow c}$ and slightly depends on the olefin concentration. This trend is more striking in the 2-acetylnaphthalene sensitization (Φ_{isc}=0.83),[7] where $\Phi_{t\rightarrow c}/\Phi_{isc}=0.48$; however, $\Phi_{c\rightarrow t}/\Phi_{isc}$ is as large as 0.99 when extrapolated to infinite olefin concentration, i.e., $(\Phi_{c\rightarrow t}+\Phi_{t\rightarrow c})/\Phi_{isc}=1.47$. This indicates that the isomerization from cis to trans isomer is accompanied by regeneration of the triplet state of the sensitizer through a quantum chain process.[8]

The simplest mechanism to explain the observed results is given by eq. 1-6, where S stands for a sensitizer, t, c, and p mean transoid, cisoid, and twisted geometries of the olefin, respectively, and α is the fraction of the twisted triplets decaying to the ground-state trans isomer. In this scheme, the essential features lie in (a) reversible energy transfer between the triplet sensitizer and the trans isomer, particularly in the case of the reverse reaction being not so endothermic, and (b) interconversion between the transoid and twisted triplets.

$$S \xrightarrow{h\nu} {}^1S^* \xrightarrow{\Phi_{isc}} {}^3S^* \tag{1}$$

$${}^3S^* + t \underset{k_{ts}}{\overset{k_{st}}{\rightleftarrows}} S + {}^3t^* \tag{2}$$

$${}^3S^* + c \xrightarrow{k_{sc}} S + {}^3c^* \tag{3}$$

$${}^3c^* \xrightarrow{k_{cp}} {}^3p^* \tag{4}$$

$${}^3t^* \underset{k_{pt}}{\overset{k_{tp}}{\rightleftarrows}} {}^3p^* \tag{5}$$

$${}^3p^* \xrightarrow{k_d} \alpha t + (1-\alpha)c \tag{6}$$

Using the usual steady-state approximations for all species, the following expressions can be derived for initial quantum yields (under conditions where all the sensitizer triplets are captured by the olefin) and photostationary state compositions. The quantum yield expressions, eq. 7 and 8, predict a normal quantum

$$\Phi_{c\to t} = \Phi_{isc}(\alpha + k_{ts}[S]/K_{tp}k_d) \tag{7}$$

$$\Phi_{t\to c} = \Phi_{isc}(1 - \alpha) \tag{8}$$

$$([t]/[c])_{pss} = \frac{k_{sc}}{k_{st}} \frac{\alpha + k_{ts}[S]/K_{tp}k_d}{1 - \alpha}, \text{ where } K_{tp} = k_{tp}/k_{pt} \tag{9}$$

yield for the trans-to-cis process and, for the reverse process, dependence of the quantum yield on the sensitizer concentration through the relative magnitude of the quantum chain propagation step ($k_{ts}[S]$) and termination step ($K_{tp}k_d$).

For 2-acetylnaphthalene sensitization, using the data in Table 1 and assuming Φ_{isc}=0.83 and α=0.48 as obtained from the photostationary ratio in benzophenone-sensitized isomerization, one obtains the ratio, (i) $k_{ts}/K_{tp}k_d$=1.5 M^{-1}.

The effect of oxygen supports the above proposition on the interconversion between the transoid and twisted triplets. As Table 2 indicates, when benzophenone-sensitized isomerization of DMNB was conducted in degassed benzene solutions and in the presence of air and oxygen, the ratio of the trans isomer at the photostationary state was increased with increasing concentration of oxygen. As for the quantum yields, $\Phi_{c\to t}$ was only slightly increased with the concentration of oxygen, but $\Phi_{t\to c}$ was noticeably decreased. If oxygen would interact only with the twisted triplets of DMNB as in stilbene,[1] the ratio of the quantum yields, $\Phi_{c\to t}/\Phi_{t\to c}$, and, consequently, $([t]/[c])_{pss}$ should be equal independent of oxygen concentration. Hence, these results suggest that oxygen acts not only on the twisted triplets decaying to the cis and trans isomers but also on the transoid triplets giving the trans isomer, thus resulting in the higher ratio of the trans isomer.

This postulation is further supported by the effect of azulene, a selective quencher of transoid triplets of olefins to trans isomers.[3] The photostationary state compositions of DMNB were determined for benzophenone-sensitized isomerization

Table 1. Quantum Yields for Isomerization of 3,3-Dimethyl-1-(2-naphthyl)-1-butene

Sensitizer	Concentration/M		$\Phi_{t \to c}/\Phi_{isc}$	$\Phi_{c \to t}/\Phi_{isc}$
	Sensitizer	Olefin		
Benzophenone	0.10	0.02	0.42	0.46
	0.10	0.05	0.42	0.51
2-Acetylnaphthalene	0.35	0.02	0.49	0.64
	0.35	0.05	0.47	0.81
		∞		0.99[a]

a) Quantum yield extrapolated to infinite olefin concentration.

Table 2. The Effect of Oxygen on the Benzophenone-Sensitized Isomerization of 3,3-Dimethyl-1-(2-naphthyl)-1-butene (0.02 M)

Condition	$\Phi_{c \to t}/\Phi_{isc}$	$\Phi_{t \to c}/\Phi_{isc}$	$\Phi_{c \to t}/\Phi_{t \to c}$	$([t]/[c])_{pss}$
Degassed	0.46	0.42	1.10	0.93
Air	0.49	0.36	1.36	1.12
Oxygen	0.49	0.27	1.81	1.60

Table 3. Attenuation of the Azulene Effect by Oxygen in the Benzophenone-Sensitized Isomerization of 3,3-Dimethyl-1-(2-naphthyl)-1-butene (0.01 M)

Condition	Slope/M^{-1}	Intercept	$[O_2]/10^{-3}$ M[a]
Degassed	282	0.94	0
Air	211	1.19	1.62
Oxygen	121	1.63	7.74

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

in benzene as a function of azulene concentration in degassed solutions and in the presence of air and oxygen. Plots of $([t]/[c])_{pss}$ vs. azulene concentration are linear in each case; however, as shown in Table 3, increase of oxygen in solution effected a noticeable attenuation in slopes and an increase in intercepts. The present result indicates competitive deactivation of the transoid triplets by azulene and oxygen leading to the trans isomer.

These ideas can be expressed in eq. 10-12, which lead to an expression 13, where Az stands for azulene.

$$^{3}t^{*} + Az \xrightarrow{k_{az}} t + {}^{3}Az^{*} \quad (10) \qquad {}^{3}t^{*} + O_2 \xrightarrow{k_{ot}} t + O_2 \quad (11)$$

$$^{3}p^{*} + O_2 \xrightarrow{k_{op}} \alpha t + (1-\alpha)c + O_2 \quad (12)$$

$$([t]/[c])_{pss} = \frac{k_{sc}}{k_{st}} \frac{\alpha k_d + (\alpha k_{op} + k_{ot}/K_{tp})[O_2] + k_{az}[Az]/K_{tp}}{(1-\alpha)(k_d + k_{op}[O_2])} \quad (13)$$

This expression can explain the present findings. Using the observed values in Table 3 and adopting $k_{sc}=k_{st}$,[9] one obtains from eq. 13 (ii) $k_d/k_{op}=(5\text{-}7) \times 10^{-3}$M, (iii) $k_{ot}/K_{tp}k_{op}=0.5\text{-}0.7$, and (iv) $k_{az}/K_{tp}k_{op}=0.7\text{-}0.9$. Combination of these values with (i) gives (v) $k_{az}/k_{ot}\simeq1.5$ and (vi) $k_{ts}/k_{ot}\simeq1.5 \times 10^{-2}$.

If k_{ot} is taken to be 5×10^9 $M^{-1}s^{-1}$, nearly diffusion-controlled, then k_{ts} for 2-acetylnaphthalene can be estimated from (vi) as 7×10^7 $M^{-1}s^{-1}$. This value seems not to be so unreasonable on taking account that for distorted excited states the experimental quenching constants are generally higher than the rates expected from triplet energy difference.[10] Similarly k_{az} can be obtained from (v) as 7×10^9 $M^{-1}s^{-1}$, which is a reasonable rate constant for the effective quenching of the transoid triplets by azulene.[11] When k_{op} is assumed to be the same as k_{ot}, k_d can be estimated as $(2.5\text{-}3.5) \times 10^7$ s^{-1}. These estimates lead to $K_{tp}=1.5\text{-}2$, indicating that K_{tp} is not far from unity. From k_d and K_{tp} the lifetime of the olefin triplets can be estimated as 40-70 ns. This value seems reasonable since the triplet lifetimes of aromatic olefins have been reported to be 30-150 ns in non-polar solvents.[11,12] Therefore, the present result shows that the twisted triplets and transoid triplets are nearly the same in energy and have comparable probability to be alive through the mutual interconversion.

Investigation concerning the detailed mechanism and extending the oxygen effects is now in progress.

References and Notes

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