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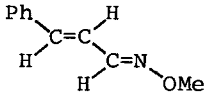
TRIPLET SENSITIZED ISOMERIZATION OF A C=C-C=N SYSTEM. ENERGY SURFACE OF THE TRIPLET STATE AND EFFECTS OF AZULENE, OXYGEN, AND DI-tert-BUTYL NITROXIDE

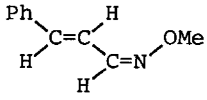
Keiko IKOMA, Akiko OKAMI, Tatsuo ARAI, Hirochika SAKURAGI,*
and Katsumi TOKUMARU
Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

The photostationary isomer ratios and quantum yields for triplet sensitized isomerization of the four isomers of a conjugated imine, 1-methoxyimino-3-phenyl-2-propene, were determined to explore the reaction mechanism.

Photochemical isomerization of simple conjugated imines is of great importance as a model for higher homologues and of much interest in connection with the mechanism of vision.1) In a previous communication2) we reported photochemical behavior of a conjugated imine, 1-methoxyimino-3-phenyl-2-propene (MIPP), on direct excitation, which led to cis-trans, syn-anti, and their concurrent isomerizations. We now wish to report triplet sensitized isomerization of MIPP which exhibits similar three types of isomerizations and to discuss the triplet energy surface on the basis of the effects of quenchers on the photostationary isomer ratios.

The quantum yields for the initial stages of the isomerization of the four MIPP isomers, trans-anti (ta), trans-syn (ts), cis-anti (ca), and cis-syn (cs), were measured in benzene in the presence of 2-acetylnaphthalene (2-AcN) as triplet sensitizer,3,4) and summarized in Fig. 1. Inspection of Fig. 1 shows that cis-trans, syn-anti, and synchronous cis-trans/syn-anti isomerizations take place, and that the quantum yields for production of a given isomer are very similar irrespective of starting isomers. Moreover, the quantum yields of each isomer is in good agreement with its photostationary isomer ratio (Fig. 1). These results show that the isomerization proceeds through a common triplet intermediate $(^{3}p^{*})$.


ta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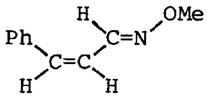
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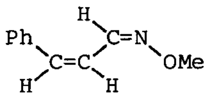
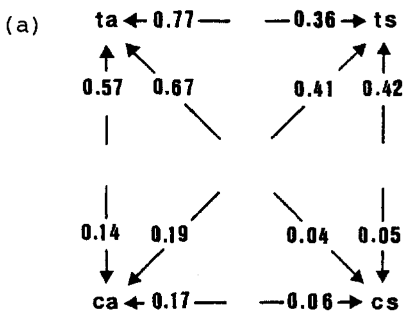

cs

Azulene is a well-known quencher of trans triplets.5) Fig. 2 shows the effect of azulene on the photostationary isomer ratios in 2-AcN sensitized isomerization of MIPP. The ratios of the isomers aroung the C=C double bond,



(b)

ca	cs	ta	ts
13	4	52	31

Fig. 1. Quantum Yields (a) and Photostationary Isomer Ratio (b) in 2-AcN Sensitized Isomerization of MIPP in Benzene.

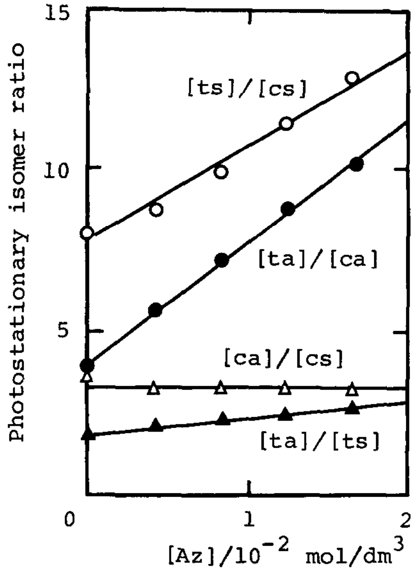


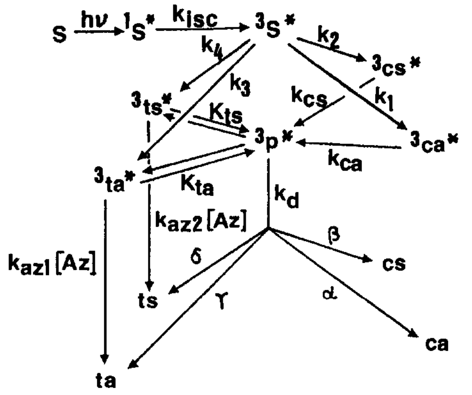
Fig. 2. Effect of Azulene in 2-AcN Sensitized Isomerization of MIPP in Benzene.

$([ta]/[ca])_s$ and $([ts]/[cs])_s$, increase linearly with increasing azulene concentration, whereas the ratios of the isomers around the C=N double bond, $([ta]/[ts])_s$ and $([ca]/[cs])_s$, remain almost unchanged in spite of increase of the azulene concentration. From these results it can be reasonably assumed that azulene quenches only the trans triplets, $^3ta^*$ and $^3ts^*$, among the triplets. Consequently, the energy surface around the C=C double bond is very similar to that of stilbene triplets,[5)] and thus $^3ta^*$ and $^3ts^*$ are higher in energy than the corresponding cis triplets, $^3ca^*$ and $^3cs^*$, respectively. The isomerization mechanism can be illustrated by Scheme 1, where the triplets, $^3ta^*$, $^3ts^*$, $^3ca^*$, and $^3cs^*$, generated by energy transfer from the sensitizer to the corresponding four isomers afford the common triplet, $^3p^*$, and this triplet, in equilibium with $^3ta^*$ and $^3ts^*$, decays to the ground state surface leading to the four isomers with certain decay ratios (α, β, γ, and δ). According to this mechanism, the isomer ratios at the photostationary state can be expressed by the following equations:

$$([ta]/[ca])_s = (k_1/k_3)(\gamma/\alpha + k_{az1}[Az]/\alpha k_d K_{ta}) \quad (1)$$
$$([ts]/[cs])_s = (k_2/k_4)(\delta/\beta + k_{az2}[Az]/\beta k_d K_{ts}) \quad (2)$$
$$([ca]/[cs])_s = (k_2/k_1)(\alpha/\beta) \quad (3)$$
$$([ta]/[ts])_s = (k_4/k_3)(\gamma k_d + k_{az1}[Az]/K_{ta})/(\delta k_d + k_{az2}[Az]/K_{ts}) \quad (4)$$

From the isomer ratio in the absence of any quencher the decay ratios can be determined as follows: $\alpha = 0.13$, $\beta = 0.04$, $\gamma = 0.52$, and $\delta = 0.31$.
Rate constants for energy transfer from the sensitizer triplets to each isomer are assumed to be equally diffusion controlled ($k_1 = k_2 = k_3 = k_4$) since these

Scheme 1



processes are amply exothermic.6,7) If rate constants for quenching of the trans triplets by azulene, k_{az1} and k_{az2}, are assumed to be diffusion controlled, $9 \times 10^9\ dm^3 mol^{-1} s^{-1}$,10) the ratio K_{ts}/K_{ta}, which means the ratio of populations of the trans triplets $[^3ta^*]/[^3ts^*]$, can be estimated as 4.2 and the triplet lifetime, $\tau = 1/k_d$, as 1.1×10^{-7} s from slopes of the plots of $([ta]/[ca])_s$ and $([ts]/[cs])_s$ in Fig. 2.

The photostationary isomer ratios in the triplet sensitized isomerization of MIPP was found to be affected by paramagnetic quenchers. The effects of oxygen and di-tert-butyl nitroxide (DTBN) were shown in Figs. 3 and 4, where the percentages of the four isomers are plotted against quencher concentrations.

Oxygen can quench both of trans and twisted triplets of olefins, and the quenching of the trans triplets is recognized as increase of the trans isomer composition at the photostationary state for the olefins, of which the triplet states are comprised of almost equal populations of the triplets of trans and twisted geometries.11) In the present case, however, oxygen increases the composition of the ca isomer and decreases that of the ts isomer.

The effect of DTBN was very similar to that of oxygen. As Fig. 4 shows,

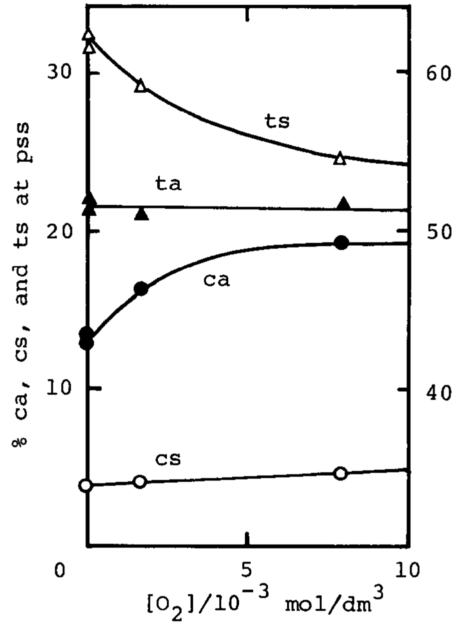


Fig. 3. Effect of Oxygen in 2-AcN Sensitized Isomerization of MIPP in Benzene.

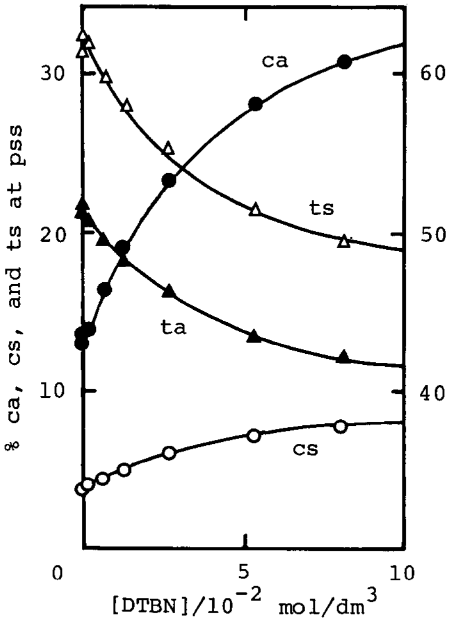


Fig. 4. Effect of DTBN in 2-AcN Sensitized Isomerization of MIPP in Benzene.

the cis isomers, ca and cs, increase and the trans isomers, ta and ts, decrease in composition at the photostationary state. A similar DTBN effect increasing cis composition was reported in stilbene isomerization by Caldwell,[12] and for type II reaction Scaiano[13,14] reported that DTBN and oxygen changed the mode of biradical partition. Caldwell and Creed[15] also showed a DTBN effect in photocycloaddition. These authors proposed formation of some complex intermediates between DTBN and triplet species (biradicaloids and 1,4-biradicals).

The present result can be classified into the same category. The imine triplets, which deactivate to some point of the ground state surface affording the four isomers with the decay ratios of α, β, γ, and δ in the absence of any quencher, interact with the paramagnetic quenchers to adopt some different geometries from the free triplets, and thus deactivate to the point of the ground state leading to the isomer ratios different from the normal ones.

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3) Each isomer [$(4-5)\times10^{-3}$ mol/dm^3] was irradiated in benzene under argon atmosphere in the presence of 2-AcN (0.16 mol/dm^3) with 366 nm light isolated from a 100 W high pressure mercury lamp through a Toshiba UVD36B glass filter. The quantum yields were determined at conversion as low as 7-9% with respect to potassium tris(oxalato)ferrate(III) actinometry.[4]

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6) Triplet excitation energy of 2-AcN: 59.4 kcal/mol (Ref. 4, p 5).

7) Triplet excitation energies of MIPP were estimated as ca. 55 kcal/mol for the cis isomers, ca and cs, and ca. 48 kcal/mol for the trans isomers, ta and ts, from the Hammond-Saltiel plots.[8,9]

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