

On the Role of the Triplet State in the Photoisomerization of Retinal Isomers

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The photoisomerization of 11-*cis*- and *all-trans*-retinals is investigated in aerated and deaerated solutions using direct singlet excitation as well as *via* sensitization from the triplet states of biacetyl and biphenyl. Triplet quantum yields are established for *all-trans*- and 11-*cis*-retinal using N₂-laser photolysis and pulse radiolysis. It is concluded that triplet energy transfer to 11-*cis*-retinal leads to isomerization with an efficiency of 15–17%, while no detectable isomerization can be induced by triplet transfer to the *all-trans* isomer. An analysis of the oxygen effects indicates that photosensitized isomerization precedes the formation of the fully thermalized retinal triplet. A mechanism in which isomerization is taking place from nonrelaxed vibronic triplet levels in competition with thermal deactivation is proposed. The new data are compared with available theoretical calculations and their relevance to the mechanism of isomerization induced by direct excitation is discussed.

Introduction

Vision is associated with light absorption by pigments such as rhodopsin in which a polyene aldehyde (retinal) is bound to a protein (opsin), most probably through a Schiff base with a lysine residue.¹ It also appears to be well established that the primary photochemical event involves isomerization of the 11-*cis* polyene chromophore to its *all-trans* configuration.² It is therefore likely that a clarification of the primary processes in the excited states of molecules such as retinal, its corresponding Schiff bases and alcohol (retinol or Vitamin A), retinyl acetate, etc., may be of primary importance in understanding the early photochemical events in vision. In this respect, the question has been repeatedly asked as to the role of the lowest triplet state in photoisomerization.^{1b,3,4} This point has recently gained importance in view of evidence suggesting that the retinyllysine chromophore may actually exist as a charge-transfer complex with an appropriate protein residue,⁵ and that charge-transfer interactions may strongly enhance intersystem crossing.⁶

The feasibility of triplet-state isomerization pathways in retinals has been considered theoretically.⁷ Experimentally, the photoisomerization of retinal isomers has been studied by direct singlet excitation⁸ as well as by triplet sensitization.⁴ The latter experiments provided the first evidence indicating that isomerization can actually be induced by selective population of the triplet state. However, using the new value of $\phi_T = 0.6 \pm 0.1$ recently obtained³ for the yield of intersystem crossing in retinal, the photosensitization data of Raubach and Guzzo⁴ predict, in the case of direct excitation of the 11-*cis* isomer, a triplet contribution of ~ 0.5 to the photoisomerization yield, which is well above the overall value of 0.2 reported by Kropf and Hubbard.^{8b} Thus, with the purpose of obtaining a better understanding of the role played by the triplet state in the photoisomerization of 11-*cis*- and *all-trans*-retinals, we have carried out a set of comparative experiments recording triplet and isomerization yields in systems excited directly and *via* triplet-triplet energy transfer. Seeking a direct experimental evidence for the occurrence of triplet energy transfer, we have carried out the experiments in a system where we could directly observe by laser photolysis the decay of the donor triplet as well as the matching growing-in of the acceptor triplet.

Special precautions were taken to discriminate between isomerization due to triplet energy transfer and that due to other photochemical pathways in the excited sensitizer such as radical formation.

Experimental Section

all-trans-Retinal (Sigma Chemicals or Eastman Kodak) and 11-*cis*-retinal (a gift of Hoffman LaRoche) were used without further purification. *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and biphenyl, both Eastman Kodak, were zone refined. Biacetyl (BDH), *cis*-piperylene (Fluka), and spectrograde CCl₄ and *n*-hexane (Fluka) were used without further purification.

Absorption and emission spectra were recorded using a Cary-14 spectrophotometer and a Turner Model 210 fluorimeter. Continuous irradiations around 313 nm were carried out using the emission of a medium-pressure Hg arc filtered by a NiSO₄, CoSO₄, and potassium biphthalate solution and a 7-54 Corning glass filter. The 438-nm line was isolated combining a GG-15 Jena glass with a 7-59 Corning glass filter. Actinometry was carried out using uranyl oxalate solutions.

The pulsed photolysis technique using the 337.1-nm (10 nsec, 0.5 mJ) pulse of an Avco-Everett laser,⁹ and the pulse-radiolysis apparatus,¹⁰ have both been previously described. Solutions were deaerated by bubbling with nitrogen or argon and were oxygen saturated by bubbling with oxygen. All experiments were carried out under deep red light using freshly prepared solutions.

Results

I. Triplet Spectra and Quantum Yields. Figure 1 shows transient spectra attributable to the triplet intermediates¹¹ produced by N₂ laser excitation of 11-*cis*- and *all-trans*-retinal in *n*-hexane. The spectra of the two intermediates are very similar, exhibiting also the same $(1.2 \pm 0.1 \times 10^5 \text{ sec}^{-1})$ decay rate constant. In aerated solutions the triplet lifetime is shortened to 100 nsec. However, aeration is not associated with any detectable change in either spectrum or yield (in contrast with the case of retinol¹²) of the triplet intermediate. The last observation is consistent with our failure to observe optically any form of ground-state interaction between retinal and oxygen as

well as with the lack of fluorescence^{7c} or excited singlet-singlet absorption¹² in retinal solutions.

The triplet extinction coefficient and quantum yield were redetermined by the method recently described by Bensasson, *et al.*,³ involving energy transfer to *all-trans*-retinal (R) from the triplet of biphenyl (³B*). To assure total quenching of ³B* by R, we determined the reaction rate constant by analyzing the effect of [R] on the lifetime of ³B* produced by laser photolysis in a TMPD-biphenyl system,¹² in which we observed the retinal triplet growing-in (450 nm) at a rate matching the decay of ³B* (at 370 nm). The essentially diffusion-controlled value obtained ($k_q = 3 \pm 1 \times 10^{10} \text{ sec}^{-1} M^{-1}$) guarantees complete triplet energy transfer in the 0.1 M biphenyl, $10^{-3} M$ *trans*-retinal solution in argon-saturated *n*-hexane which was submitted to pulse radiolysis excitation.¹³ Using $4.28 \times 10^4 M^{-1} \text{ cm}^{-1}$ for the molar extinction coefficient of ³B* at 365 nm,³ we obtained the value $\epsilon_{\text{T}}^{\text{R}} = 7.5 \times 10^4 M^{-1} \text{ cm}^{-1}$ for the extinction of retinal triplet at 450 nm, which is very close to the values reported by Dawson and Abrahamson^{11b} and by Bensasson, *et al.*^{3a,c}

In these two cases, the [TMPD] + [B] + [R] submitted to the laser photolysis and the [B] + [R] system irradiated by pulse radiolysis, we have recorded similar T-T absorption spectra (λ_{max} 450 nm) as compared with that obtained previously in the direct N₂-laser photolysis experiment of a system containing [R] alone. Moreover in all the three systems described above the decay rate constant of the triplet state of [R] measured at 450 nm is $(1.2 \pm 0.1) \times 10^5 \text{ sec}^{-1}$. This procedure for the determination of $\epsilon_{\text{T}}^{\text{R}}$ assumes that triplet energy transfer from ³B* is the only route leading to ³R*. The fact that the value obtained for $\epsilon_{\text{T}}^{\text{R}}$ is independent (within 5%) of the retinal concentration (varied from 10^{-3} to $5 \times 10^{-4} M$ in the present work, and from 10^{-6} to 10^{-4} in the work of Bensasson, *et al.*^{3a,c}) indicates that energy transfer from excited biphenyl singlets^{3d} is not important in the present system. Other arguments, ruling out any substantial contribution of singlet energy transfer, have been discussed by Bensasson, *et al.*^{3b}

The above value of $\epsilon_{\text{T}}^{\text{R}}$ was used for the evaluation of the yield of intersystem (ϕ_{ISC}) in *all-trans*-retinal by comparing the triplet absorbance formed by direct N₂-laser excitation of $\sim 5 \times 10^{-5} M$ retinal in *n*-hexane with those of the triplets of pyrene and anthracene produced under identical experimental conditions. Using the known anthracene^{3a,b} and pyrene¹⁴ triplet yields and extinction coefficients we obtained the value of $\phi_{\text{ISC}} = 0.7 \pm 0.1$ which is very close to that of Bensasson, *et al.*,³ ($\phi_{\text{ISC}} = 0.6 \pm 0.1$) correcting the early estimate ($\phi_{\text{ISC}} = 0.11$) of Dawson and Abrahamson.^{11b}

Using the pulse-radiolysis method we have also determined the extinction coefficient of the 11-*cis* triplet state, finding it identical with that of the *all-trans* isomer. From the laser photolysis data of Figure 1 we thus obtain for the yield of ISC in the *cis* isomer the value $\phi_{\text{ISC}} = 0.6 \pm 0.1$. We should finally point out that the above values of ϕ_{ISC} are derived assuming that in the pulse radiolysis experiments the observed triplets are those corresponding to the original ground-state isomers. The photosensitized isomerization data presented below show that this assumption is probably strictly valid in the case of the *all-trans* isomer and accurate to a degree of $\sim 15\%$ in the case of 11-*cis*-retinal.

II. Photoisomerization. a. 11-*cis*-Retinal. Photoisomerizations of 11-*cis*-retinal were carried out using both direct

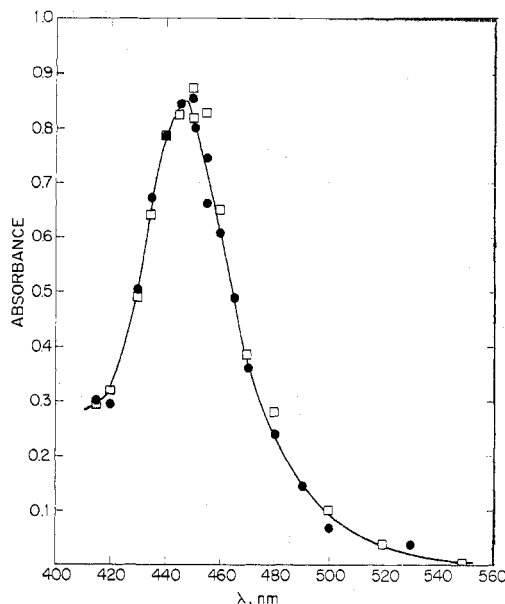


Figure 1. Transient triplet spectra obtained (100 nsec after pulsing) in the N₂-laser photolysis of $\sim 2 \times 10^{-4} M$ 11-*cis*- (□) and $1 \times 10^{-4} M$ *all-trans*- (●) retinal in deaerated *n*-hexane at room temperature. With the purpose of matching the two spectra the 11-*cis* absorbance values have been normalized by a factor of 1.16.

and photosensitized excitation. In the direct-excitation experiments (irradiation at 313 nm) the 11-*cis* → *all-trans* conversion was monitored in $8 \times 10^{-5} M$ hexane solutions by following the absorbance drops at 254 and 280 nm, as well as the accompanying rise at 365 nm.⁸ The quantum yield obtained for this process (0.12) was found to be identical in both aerated and deaerated solutions.

Photosensitized isomerization experiments were carried out for 11-*cis*-retinal using as sensitizer ³B* produced in a TMPD-biphenyl (B) system excited at 313 nm. The present technique produces ³B* indirectly, *via* $^1(\text{TMPD})^* + \text{B} \rightarrow ^1(\text{TMPD} \cdot \text{B})^* \rightarrow \text{TMPD} + ^3\text{B}^*$, where $^1(\text{TMPD} \cdot \text{B})^*$ denotes a fluorescent charge-transfer exciplex.^{6,12} This indirect method was preferred to direct excitation of either TMPD or biphenyl (followed by ISC and triple energy transfer) since it avoids reabsorption of the donor's fluorescence by retinal. We have also established that the lifetime of the exciplex fluorescence is unaffected by the presence of ($5 \times 10^{-5} M$) retinal, thus ruling out any exciplex quenching by R which could contribute to the generation of ³R* *via* singlet energy transfer. The decay rate of the retinal triplet (³R*) as measured on the laser apparatus in the TMPD-biphenyl solution was found identical with that recorded in pure retinal solutions. This excludes any interaction between ³R* and TMPD or biphenyl. The rates of isomerization determined from the initial absorbance increments at 365 nm^{4,8} in aerated and deaerated solutions are shown in Figure 2A. In such photosensitized experiments the presence of biphenyl prevented measurements at 254 and 280 nm where, in the case of direct excitation of 11-*cis*-retinal, isomerization (to *all-trans*) is associated with a drop in absorbance accompanying the growth at 365 nm.⁸ However, the initial change in the band shape around 365 nm was identical for both biphenyl-sensitized and direct excitation, indicating that the same photoprocess (*i.e.*, isomerization to the *all-trans* isomer) takes place.

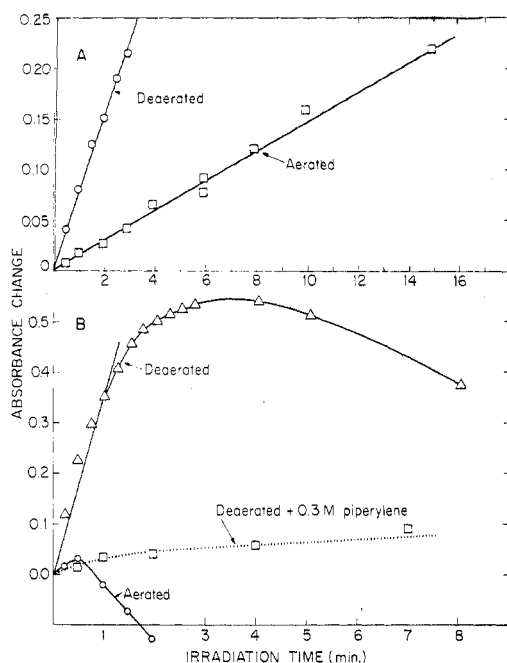


Figure 2. Absorbance changes induced by photosensitization at the maximum of the α (365 nm) band of 11-*cis*-retinal: (A) biphenyl sensitization, [TMPD] = 5×10^{-3} M, [biphenyl] = 0.1 M, [retinal] = 5.5×10^{-5} M in *n*-hexane, excitation at 313 nm; (B) biacetyl sensitization, [biacetyl] = 7×10^{-2} M, [retinal] = 5.5×10^{-5} M in CCl_4 ; excitation at 438 nm.

In order to determine the isomerization yield associated with energy transfer from $^3\text{B}^*$ ($\phi_{\text{isom}}^{\text{T}}$) we had to account for (a) the small light fraction absorbed directly by retinal, and (b) the fact that the quenching of $^3\text{B}^*$ was incomplete. (Higher [R] values required for total quenching lead to an excessively high optical density around 365 nm preventing reasonably accurate measurements of absorbance changes.)

The contribution of some direct excitation of retinal to isomerization in the deaerated photosensitized experiments of Figure 2A was estimated using the direct-excitation yield measured in the absence of TMPD and biphenyl, accounting for the relative amounts of light absorbed by retinal and TMPD in the mixed systems. It was found that $\sim 10\%$ of the isomerization rate is due to direct excitation of 11-*cis*-retinal.

The retinal triplet yield ($\phi_{\text{T}}^{\text{R}}$) formed by photosensitization was determined by measuring on the laser apparatus the retinal triplet absorbance in the TMPD-biphenyl-retinal system, relatively to the value obtained in pure retinal solutions (where $\phi_{\text{ISC}} = 0.6 \pm 0.1$). The value obtained (0.4 ± 0.04) is consistent with that calculated using the expression

$$\phi_{\text{T}}^{\text{R}} = \phi_{\text{T}}^{\text{B}} \phi_{\text{ET}}$$

where $\phi_{\text{T}}^{\text{B}}$ is the biphenyl quantum yield in the TMPD-biphenyl system and ϕ_{ET} is the yield of energy transfer. For $\phi_{\text{T}}^{\text{B}}$ a value of 0.5 was obtained by comparing the $^3\text{B}^*$ absorbance with that of the pyrene triplet produced on the laser apparatus in hexane solutions.^{14b} ϕ_{ET} is given by $\phi_{\text{ET}} = k_{\text{q}}[\text{R}]/[k_{\text{q}}[\text{R}] + k_{\text{d}}]$ where k_{d} is the decay rate constant of $^3\text{B}^*$ in the absence of retinal. Using $k_{\text{q}} = 3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, $k_{\text{d}} = 3 \times 10^5 \text{ sec}^{-1}$, and $[\text{R}] = 6 \times 10^{-5} \text{ M}$, we obtain $\phi_{\text{ET}} = 0.86$, so that $\phi_{\text{T}}^{\text{R}} = 0.43$. The photoisomerization yield obtained using the above corrections is presented in Table I along with the direct-excitation value.

TABLE I: Photoisomerization Yields Obtained for 11-*cis*- and all-*trans*-Retinal by Photosensitized and Direct Excitation^a

	11- <i>cis</i> -Retinal	all- <i>trans</i> -Retinal
Biphenyl photosensitized ^b	0.17 ± 0.02	<0.002
Biacetyl photosensitized ^c	0.15 ± 0.02	<0.002
Direct excitation (313 nm) ^d	0.12 ± 0.01	0.10 ± 0.01

^a Quantum yields were estimated from the initial changes in the absorbance at the α (370 nm) band using the known extinction coefficients of the retinal isomers.^{4,8} The corresponding processes assumed were 11-*cis* \rightarrow all-*trans* and (for an upper limit estimate^{4,8}) all-*trans* \rightarrow 13-*cis*. ^b 313-nm excitation. [TMPD] $\approx 5 \times 10^{-3} \text{ M}$, [biphenyl] = 0.1 M, and [retinal] $\approx 6 \times 10^{-5} \text{ M}$ in deaerated *n*-hexane. The quantum yield represents the fraction of photoisomerized molecules produced for each triplet of retinal formed by energy transfer. The values have been corrected for some direct light absorption by retinal and for incomplete quenching of $^3\text{B}^*$ as described in the text. ^c 438-nm excitation. [Biacetyl] = $7.5 \times 10^{-2} \text{ M}$, [retinal] $\approx 6 \times 10^{-5} \text{ M}$ in deaerated CCl_4 . Assuming $\phi_{\text{ISC}} = 0.9$ for ($^3\text{Ba}^*$).⁴ ^d $\sim 6 \times 10^{-5} \text{ M}$ retinal in deaerated or aerated *n*-hexane.

Attention should now be paid to the oxygen effect on the photoisomerization of 11-*cis*-retinal in the sensitized experiments of Figure 2. In aerated solutions the quenching of the TMPD-biphenyl exciplex by oxygen is known to decrease the $^3\text{B}^*$ yield to 20% of the value measured in deaerated systems,^{6b} leading to a corresponding drop in $\phi_{\text{T}}^{\text{R}}$. A further decrease in $\phi_{\text{T}}^{\text{R}}$ arises from the competition between O_2 and R on $^3\text{B}^*$ leading to an energy transfer yield in aerated solutions ($\phi_{\text{ET}}(\text{O}_2)$) which is smaller than the value (ϕ_{ET}) in deaerated systems. Since $\phi_{\text{ET}}(\text{O}_2) = k_{\text{q}}[\text{R}]/[k_{\text{q}}[\text{R}] + k_{\text{d}} + k_{\text{q}}(\text{O}_2)[\text{O}_2]]$ we obtain, using $k_{\text{q}}(\text{O}_2) = 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and $[\text{O}_2] \approx 2 \times 10^{-3} \text{ M}$, $\phi_{\text{ET}}(\text{O}_2) \approx 0.3$ so that $\phi_{\text{T}}^{\text{R}}(\text{O}_2) = \phi_{\text{T}}^{\text{B}}(\text{O}_2) \phi_{\text{ET}}(\text{O}_2) = 0.03$ where $\phi_{\text{T}}^{\text{R}}(\text{O}_2)$ and $\phi_{\text{T}}^{\text{B}}(\text{O}_2) = 0.1$ are the retinal and biphenyl triplet yields in aerated solutions. Since $\phi_{\text{T}}^{\text{R}}(\text{O}_2)$ is around 10% of the value ($\phi_{\text{T}}^{\text{R}} = 0.4$) in deaerated solutions, the triplet transfer mechanism will contribute 10% to the isomerization yield in the aerated system as compared to the deaerated solution. This assumption, obviously implying that the photosensitized isomerization of retinal is not affected by the quenching of $^3\text{R}^*$ by O_2 (see further arguments in the Discussion), leads to the conclusion that the residual ($\sim 20\%$) isomerization yield observed in the aerated solution of Figure 2A can be accounted for by an approximately equal ($\sim 10\%$) contribution of both direct-excitation and triplet-transfer mechanism. This agreement between observed and estimated values contribute a further indication to the conclusion that photosensitized retinal triplet formation is the major route leading to isomerization in the TMPD-biphenyl-11-*cis*-retinal system. It is furthermore consistent with the assumption that the quenching of $^3\text{R}^*$ by O_2 does not affect the isomerization proceeding via $^3\text{R}^*$.

Photoisomerization experiments with the 11-*cis* isomer were also carried out using biacetyl (Ba) as sensitizer.⁴ The corresponding data are presented in Figure 2B and Table I, showing that $\phi_{\text{isom}}^{\text{T}}$ is essentially identical with that measured in the biphenyl system. The photosensitized isomerization yield (using $^3\text{Ba}^*$ as a sensitizer) of this work (0.15) is in variance with the value of (0.75) reported by Raubach and Guzzo.⁴ We would like to emphasize that the same value (0.17 ± 0.2 , Table I) has been obtained in the present work using two different sensitizers. As shown in Figure 2B, 0.3 M piperylene essentially eliminates the

photoisomerization. Using a Stern-Volmer analysis on the phosphorescence of biacetyl (Ba) in CCl_4 at room temperature ($\tau = 0.8 \times 10^{-8}$ sec) we have determined a rate constant of $2.5 \times 10^8 \text{ sec}^{-1} \text{ M}^{-1}$ for the reaction between the biacetyl triplet ($^3\text{Ba}^*$) and piperlyene. We have also established that $^3\text{R}^*$ (35 kcal/mol)⁴ is unreactive to 0.3 M piperlyene (triplet energy 56.9 kcal/mol). Thus, the effect of piperlyene on the biacetyl photosensitized isomerization is consistent with total quenching of $^3\text{Ba}^*$, preventing the formation of $^3\text{R}^*$. (For piperlyene $k_q^{\text{P}}[\text{P}] = 7.5 \times 10^7 \text{ sec}^{-1}$, while, for 11-*cis*-retinal $k_q^{\text{R}}[\text{R}] = 1.3 \times 10^5 \text{ sec}^{-1}$,⁴ where k_q^{P} and k_q^{R} are the corresponding $^3\text{Ba}^*$ quenching rate constants and [P] and [R] are the quenchers concentrations.) In the case of molecular oxygen as a total quencher of $^3\text{Ba}^*$ (quenching rate constant $5.1 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$ ¹⁵) the initial photoisomerization slope is similar to that with piperlyene (Figure 2B). However, at longer irradiation time the change in absorbance changes sign probably indicating irreversible destruction of the retinal.⁴

b. all-trans-Retinal. The yield of the direct photoisomerization of *all-trans*-retinal irradiated at 313 nm in *n*-hexane solution is given in Table I and it is not affected by oxygen as was found in the case of 11-*cis*-retinal. Sensitization experiments with the *all-trans* isomer using as sensitizer $^3\text{B}^*$, produced in the deaerated TMPD-biphenyl system, did not lead to a detectable drop in the absorbance around 365 nm characterizing the (*all-trans*) \rightarrow (*cis* isomers) isomerization.⁸ Since the experimental conditions (including the amount of energy transfer as determined on the laser apparatus) were similar to those previously described for the 11-*cis* isomer, we conclude that triplet energy transfer to the *all-trans* isomer does not lead to isomerization. The estimated upper limit for this process is shown in Table I along with the upper limit for the direct photoisomerization quantum yield calculated assuming an *all-trans* \rightarrow 13-*cis* process.^{4,8}

The data concerning the diacetyl photosensitized isomerization are shown in Figure 3. The results in deaerated solutions show an absorbance drop around 380 nm indicating a substantial photoisomerization which apparently contradicts the previous conclusions derived for biphenyl sensitized system. However, one should note that oxygen, which quantitatively quenches $^3\text{Ba}^*$ preventing the formation of $^3\text{R}^*$, does not change the photoisomerization yield. A plausible explanation for this behavior is one attributing the photoisomerization in the presence and absence of O_2 to free radicals¹⁶ formed in the photolysis of biacetyl.¹⁷ In fact, the addition of $1.2 \times 10^{-3} \text{ M}$ piperlyene to an oxygen saturated solution ($[\text{O}_2] = 10^{-2} \text{ M}$) markedly decreases the isomerization yield although piperlyene does not efficiently compete (less than 1%) with O_2 on the quenching of $^3\text{Ba}^*$. In view of the polyene character of piperlyene this is consistent with a competition between piperlyene and retinal on free radicals. In conclusion, we believe that the overall behavior with biacetyl as sensitizer does not contradict the conclusion derived in the biphenyl sensitized system, *i.e.*, that $^3\text{R}^*$ produced by energy transfer does not play a detectable role in the photoisomerization of *all-trans*-retinal. We should finally point out that at present we cannot account for the different sensitivity of the 11-*cis* and *all-trans* isomers toward radicals formed in the biacetyl photolysis. It is known however that the various retinal isomers show a different reactivity in the I_2 -catalyzed^{8a} and dye-catalyzed^{16a} photoisomerization presumably involving free radicals.^{16b}

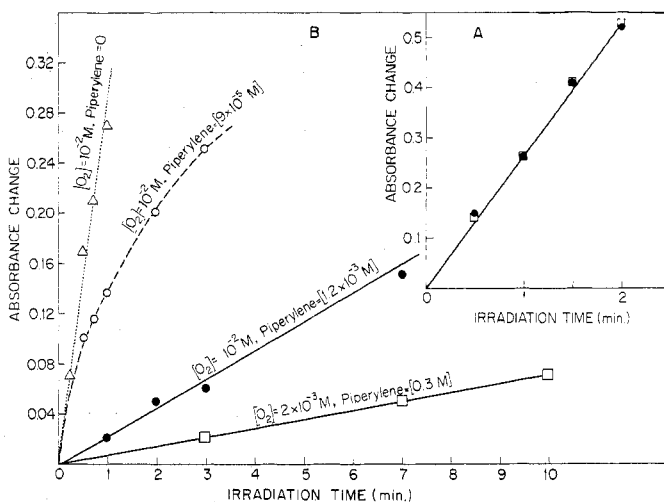


Figure 3. The effects of oxygen and piperlyene in the biacetyl photosensitized isomerization of *all-trans*-retinal. $\sim 5 \times 10^{-5} \text{ M}$ retinal and $7 \times 10^{-2} \text{ M}$ biacetyl in CCl_4 at room temperature excited at 438 nm: (A) (\square) aerated, (\bullet) deaerated; (B) (Δ) oxygen saturated, (\circ) oxygen saturated plus $9 \times 10^{-5} \text{ M}$ piperlyene, (\bullet) oxygen saturated plus $1.2 \times 10^{-3} \text{ M}$ piperlyene, (\square) aerated plus 0.3 M piperlyene.

Discussion

a. The Mechanism of the Triplet-Sensitized Isomerization. The data of the present work indicate that triplet energy transfer to 11-*cis*-retinal leads to isomerization with an efficiency of 15–17%. In the case of the *all-trans* isomer, sensitized triplet population does not lead to detectable isomerization. Such observations are obviously inconsistent with an isomerization mechanism involving the establishment of thermal equilibrium between *cis* and *trans* forms during the lifetime of the triplet state. (Such a mechanism predicts a complementary (83–85%) yield for the reverse *trans* \rightarrow *cis* triplet sensitized process which is in variance with the present data.) The experimental data are there explainable in terms of the following alternative mechanisms.

(a) Fast thermalization in the excited 11-*cis* T_1 state deactivates the system to a 0° (*cis*) T_1 trap from which a thermally activated rotation irreversibly leads to *all-trans* in competition with intersystem crossing to S_0 (11-*cis*). The reverse *trans* \rightarrow *cis* process is prevented by a deeper potential well around the *all-trans* triplet configuration.

(b) Energy transfer from the triplet donor leads, in the case of 11-*cis*, to a nonrelaxed T_1 state where thermalization traps either *cis* (83–85%) or *trans* (15–17%) configurations. No subsequent thermal interconversion between isomers occurs during the triplet lifetime, meaning that the 0° (*cis*) and 180° (*trans*) traps in T_1 are considerably deep. It is possible that the nonthermalized T_1 states are reached *via* T_2 which being predicted around 53 kcal/mol⁷ is still below the triplets of biphenyl (65 kcal/mol) and biacetyl (55 kcal/mol). However, the $\sim 2 \text{ eV}$ barrier calculated for both *cis* \rightleftharpoons *trans* rotations of T_2^{7c} rules out any isomerization pathway directly involving this state.

It should be emphasized that, from a purely phenomenological point of view, isomerization from nonthermalized triplet level is equivalent to the “nonvertical” energy transfer suggested by Hammond and coworkers,¹⁸ in which the acceptor is excited with significant change in geometry. Accordingly, triplet energy transfer to 11-*cis*-retinal may form directly the (thermalized) *all-trans* trip-

let, along with the 11-cis triplet, without requiring further interconversion between the two geometries during the lifetime of the thermalized triplet. Alternatively, a triplet of intermediate geometry ("phantom triplet") is formed following energy transfer which deactivates to either cis or trans ground states. In both cases the decisive change in geometry occurs before formation of the thermalized triplet following energy transfer and, in this respect, the "nonvertical" transfer process is analogous to the vibronic mechanism discussed above.

A discrimination between mechanisms a and b, favoring the second alternative, is provided by an analysis of the oxygen effects on both direct-excitation and photosensitized isomerization yields. Let us assume that isomerization to all-trans actually occurs according to a with 15% efficiency from the thermalized 11-cis triplet geometry. In view of the ISC yield ($\phi_{ISC} = 0.6$) obtained for 11-cis-retinal, this assumption implies that most (~80%) of the isomerization yield (0.12) observed upon direct excitation of 11-cis-retinal is due to the (thermalized) triplet state. However, partition among ground-state isomers during the lifetime of the triplet is in variance with the complete lack of any oxygen effect on the direct-excitation isomerization under conditions of total quenching of $^3R^*$ by O_2 . We therefore conclude that the thermalized 11-cis triplet state does not contribute substantially to the isomerization process. This conclusion is supported by our previous analysis of the oxygen effect on the biphenyl-sensitized isomerization of 11-cis-retinal (see above) which was found to be consistent with the assumption that the quenching of $^3R^*$ by O_2 does not affect the isomerization via $^3R^*$.

The question arises as to the inefficiency of the trans \rightarrow cis conversion in the photosensitization experiments. Assuming the vibronic triplet mechanism, there should be no energetic reasons favouring the cis \rightarrow trans over the trans \rightarrow cis process. The experimental observations can be rationalized by assuming that isomerization from a nonrelaxed triplet can efficiently compete with thermalization in the case of 11-cis but not of all-trans. It is possible that, following triplet energy transfer to 11-cis-retinal, relatively more energy is accumulated in the isomerization-active torsional modes of the 11-12 bond, than in those of either 11-12, 9-10, or 13-14 bonds, following triplet excitation of the all-trans isomer.

b. On the Direct-Excitation Isomerization. When attempting to derive, from the triplet-sensitized experiments, conclusions relevant to the direct-excitation isomerization, it should be recalled that in photosensitization (of the retinal's systems) the decisive geometrical change occurs prior to the formation of the thermal T_1 state. Since we expect the initial energy distribution, and the consecutive changes with time, to depend on the particular way of excitation, it is difficult to infer from the triplet-sensitized yields on those expected in direct singlet excitation followed by ISC to T_1 . All one can at present say is that here too no isomerization takes place from the thermalized 11-cis triplet configuration. However, a discrimination between isomerization paths proceeding via (thermalized or nonthermalized) S_1 and (nonthermalized) T_1 is still impossible. The wavelength dependence reported for the directly (singlet) excited photoisomerization of 11-cis-retinal^{18b} indicates that vibronic effects have also to be considered for the direct (singlet or triplet) mechanism. The fact that directly excited all-trans-retinal undergoes isomerization with an efficiency comparable to

that of the 11-cis isomer, while being inactive upon triplet photosensitization (Table I), may in such a case favor S_1 over T_1 as the isomerizing intermediate following direct excitation. However, as long as additional evidence is not available, the mechanism of the direct-excitation isomerization remains an open question.

c. Comparison with Theoretical Energy Curves. It is interesting to consider the above conclusions in terms of the theoretical potential energy curves for twisting around the 11-12 bond.⁷ The early calculations of Inuzaka and Becker^{7a} and those of Wiesenfeld and Abrahamson^{7b} predict essentially no barrier for the 11-cis \rightarrow all-trans rotation in the lowest excited triplet state, T_1 . A considerable energy barrier (higher than 0.5 eV) is however estimated for the reverse trans \rightarrow cis rotation of T_1 . Thus, although agreeing with the lack of thermalized triplet isomerization of all-trans to 11-cis, such estimates predict (assuming^{16b} a normal frequency factor of 10^{13} – 10^{14} sec⁻¹) a 100% cis \rightarrow trans conversion in the thermalized 11-cis T_1 state and are therefore in variance with the results of the present work. The same applies to the more recent calculations of Becker, *et al.*,^{7c} which include complete singly excited or complete singly plus partial doubly excited state configurational interaction, leading to three comparably shallow (of the order of 0.1 eV) potential energy minima around the 0 (cis), 90, and 180° (trans) configurations of T_1 . This will seem to allow thermal isomerization within a totally relaxed 11-cis T_1 predicting a complementary (83–85%) yield for the reverse trans \rightarrow cis triplet-sensitized process, which is not in keeping with the present data. In reference to the latter calculations, it should be noted that if the 90° minimum is sufficiently deep, part of the triplets observed after direct or photosensitized excitation may actually possess this partially twisted configuration. Also, the 90° triplet may be an intermediate in the 11-cis \rightarrow all-trans isomerization (see above). However, in such a case the fact that we have ruled out mechanism a in favor of b means that such an intermediate cannot be formed from the thermal 11-cis triplet state.

The results of the present work, implying relatively deep energy minima at both 11-cis and all-trans geometries, appear to be in best agreement with the theoretical energy curves of Langlet, Pullman, and Berthod,^{7d} predicting for T_1 a 1.4-eV trans \rightarrow 11-cis barrier and ~1.0-eV barrier for the reverse 11-cis \rightarrow trans rotation. Such potential wells essentially rule out any thermally activated isomerization within the lifetime (of the order of 6 μ sec) of the triplet state, in keeping with the present observations.

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Laser Photolysis Studies on the Primary Processes of Photoinduced Ionic Polymerizations

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Primary processes of photoinduced cationic polymerization of α -methylstyrene in the presence of tetracyanobenzene or pyromellitic dianhydride have been investigated by the nanosecond laser photolysis method. Ionic photodissociations in both charge-transfer singlet and triplet states are observed for the α -methylstyrene-tetracyanobenzene complex in methylene chloride. The contribution of these two states to the ion yield was found to depend on the temperature. In the case of the α -methylstyrene-pyromellitic dianhydride complex, however, ions are formed exclusively from the charge-transfer triplet state. The decay behavior of ion pairs depends on the states from which they are formed. Ions formed from the singlet state decay faster than those from the triplet state. The difference was interpreted by the concept of spin conservation in the reaction system. Initiation processes, i.e., dimerization and trimerization, were also elucidated. The ions formed from the singlet state neither give a photocurrent nor do they initiate photopolymerization, while ions formed from the triplet state give a photocurrent and react with the monomer to form a dimer radical cation of α -methylstyrene. The dimerization rate constant was estimated to be $1 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$.

Introduction

Ionic photopolymerization is one of the most attractive photochemical reactions which are brought about by light absorption of charge-transfer (CT) systems. We reported in previous papers² that cationic polymerization of α -methylstyrene or styrene are induced by light in the presence of electron acceptor molecules such as tetracyanobenzene (TCNB) or pyromellitic dianhydride (PMDA). Although the ionization process is the essentially important step of the photopolymerization, the detailed study in the polymerization system has not yet been made because of experimental difficulties to detect the very fast reactions.

However, recently it has become possible to elucidate the behavior of excited electron donor acceptor (EDA) complexes with nanosecond time resolution by the appli-

cation of the short-pulse laser excitation technique. The extensive studies in nonpolymerizable systems³⁻⁹ have revealed that the excited complexes dissociate into ion pairs in polar solvents via three routes, CT singlet, CT triplet, and excited Frank-Condon states. The PMDA-mesitylene complex in ether-isopentane glass at -156° was reported to dissociate in its CT triplet state³ while it was proved that dissociation from the CT singlet state occurs in the case of TCNB-toluene complex in acetonitrile.^{4a} Ionic dissociation in the excited Frank-Condon state was found for the TCNB-benzene complex in 1,2-dichloroethane.⁵

The phenomenological classification of the photodissociation mechanism described above is rather temporary and it has been pointed out that the mechanism markedly depends on several factors such as the combination of the donor and the acceptor, the nature of the solvent, and the