Triplet Lifetime of Conjugated Trienes. Allo-ocimine and Cholestatriene†

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Summary The triplet lifetimes of two model conjugated trienes determined by two methods (photochemical kinetics and flash photolysis) are reported.

Determinations of olefin triplet lifetimes by kinetic flash-photolysis have been limited to highly conjugated systems such as stilbene, diphenylpolyenes,[1] vitamin A, retinal, and higher carotenoids.[2] Our previous effort to study diene triplets by sensitized kinetic flash-photolysis at room temperature did not lead to detectable transients[3] even though photochemical results suggest their possible detection.[4] We now report results of our photochemical and flash-photolysis studies of two trienes, allo-ocimene (I) and cholesta-4,6,8(14)-triene (II), a rigid model triene and the measurement of triplet lifetimes at two different temperatures.

Benzophenone-sensitized irradiation of benzene solutions of the triene (I) leads to rapid geometric isomerization and establishment of photostationary states. The compositions are found to depend on triene concentration and, when added, quencher (azulene) concentration. The data have been analysed with the two stationary state equations (1) and (2) derived from the Scheme.

$$\left(\frac{100}{\%ct}\right)_{\text{pss}} = \frac{1}{k_7\tau} + \frac{k_9}{k_7}[(\text{I})] + \frac{k_q}{k_7}[\text{Q}] \quad (1)$$

$$\left(\frac{100}{\%cc}\right)_{\text{pss}} = \frac{1}{k_8\tau} + \frac{k_9}{k_8}[(\text{I})] + \frac{k_q}{k_8}[\text{Q}] \quad (2)$$

where $\tau = (k_5 + k_6 + k_7 + k_8)^{-1}$

Excitation:

$$S^* + tt \xrightarrow{k_1} S + \text{X}$$

$$S^* + tc \xrightarrow{k_2} S + \text{X}$$

$$S^* + ct \xrightarrow{k_3} S + \text{X}$$

$$S^* + cc \xrightarrow{k_4} S + \text{X}$$

Decay:

$$\text{X} \xrightarrow{k_5} tt$$

$$\text{X} \xrightarrow{k_6} tc$$

$$\text{X} \xrightarrow{k_7} ct$$

$$\text{X} \xrightarrow{k_8} cc$$

Quenching:

$$\text{X} + \text{Q} \xrightarrow{k_q} \alpha tt + (1-\alpha)tc + \text{Q}$$

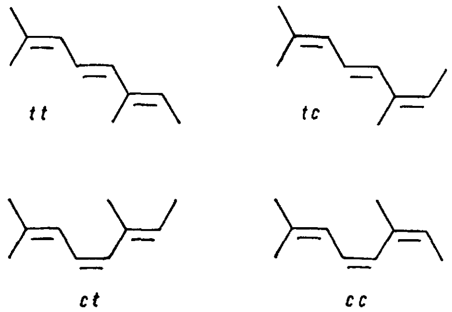
$$\text{X} + (\text{I}) \xrightarrow{k_9} \beta tt + (1-\beta)tc + (\text{I})$$

where X is the common triplet intermediate.[5]

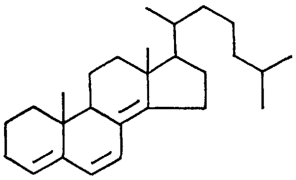
Assuming that k_{1-4} and k_q are diffusion controlled ($6{\cdot}2 \times 10^9\ \text{M}^{-1}\,\text{s}^{-1}$)[6] as is commonly accepted in exothermic energy transfer processes, we calculated the decay constants. The average lifetime (at 28°), τ is thus found to be $2{\cdot}9 \times 10^{-7}$ s. Clearly, the triplets are too short lived for direct detection by conventional flash-photolysis set-ups at room temperature, but sufficiently long lived to encourage studies under conditions where natural decay processes are inhibited.

Flash-photolysis measurements[7] of triplet lifetimes of (I) and (II) were attempted both at liquid nitrogen temperature in glass-forming solvents (6:1 isopentane/3-methylpentane; $\eta = 6{\cdot}9 \times 10^6$ P at 77 K[8]) and at room temperature in benzene solution. In the rigid glasses at 77 K, flash excitation of (I) and (II) with no triplet sensitizer present generated transient species believed to be the respective triplet states of these two compounds with respective average lifetime 2·0 and $3{\cdot}0 \times 10^{-3}$ s. At 23° in benzene, the cholestatriene triplet was detected, but only in the presence of a triplet sensitizer (10,10-dimethylanthrone). The allo-ocimene triplet, in agreement with the photochemical results, was not detected even in the presence of a sensitizer. In all cases the transient absorption maxima occurred near 365 nm. In contrast to earlier reports[9] that polyene triplets can only be generated by pulse excitation in the presence of a triplet sensitizer, the triplets of allo-ocimene and cholestatriene were generated directly without the intermediacy of a sensitizer, but apparently only at liquid nitrogen temperature.

Under identical conditions, the triene triplet lifetimes are greater in the rigid model compound, cholestatriene, than in allo-ocimene indicating that flexibility or twisting in the triene triplet states provides an important pathway for their radiationless deactivation. Also, we found an increase in lifetime of allo-ocimene triplets with solvent viscosity ($2{\cdot}4 \times 10^{-3}$ s in 2:3 isopentane/3-methylpentane, $\eta = 5{\cdot}1 \times 10^9$ at 77 K[10]) thus providing evidence that, as with stilbene,[1] solvent viscosity is also important in limiting the triplet deactivation process.



(I)



(II)

In cholestatriene, the rate of transient depopulation is independent of wavelength, whereas with allo-ocimene, the transient lifetime increases substantially at wavelengths longer than 400 nm. This difference between the two trienes is most likely due to the presence in allo-ocimene of more than one geometric isomer[4,5] with different triplet absorption spectra and lifetimes, but this point must be verified experimentally. Since the allo-ocimene triplet has its absorption maximum at nearly the same wavelength as the cholestatriene triplet and since, at this wavelength, there is no detectable contribution from longer-lived

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† Part of this work was presented in a plenary lecture at the 23rd IUPAC Congress, Boston, U.S.A., July 1971.

transients, we believe that the measured allo-ocimene triplet lifetimes correspond to the *ct* and/or *cc* allo-ocimene isomer(s) where the triene geometry is similar to that in cholestatriene.

The work done at UH was partially supported by a grant from the National Science Foundation.

(*Received*, 13*th August* 1973; *Com.* 1163.)

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