The Triplet State of Lycopene

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Summary The triplet–triplet absorption spectrum of lycopene is observed between 505 and 550 nm., the shape of the spectrum varies with the degree of *cis-trans*-isomerization.

CONJUGATED polyenes, including lycopene, are of importance in biological systems, but little is known of their *in vitro* photochemistry. Lewis and Kasha[1] reported a phosphorescence emission from lycopene, but this was only observed after lycopene had been heated with iodine, and they assumed it was due to the presence of a *cis–trans*-isomeric mixture. Pariser[2] has suggested that the isomerization of lycopene has greatly increased the excited singlet-to-lowest-triplet transition rate. However, Evans[3] has suggested that this emission is due to an impurity and not to emission from the lycopene triplet state, and that an emission of the latter type should occur in the i.r. region. Claes[4] has found that several conjugated polyenes, including lycopene, protect chlorophyll-a from photo-oxidation. This suggests that the lowest triplet state of lycopene is below about 30 kcal. mole^{-1}. However, some of the results obtained by Claes are not fully compatible with a diffusion energy-transfer mechanism.

We have studied lycopene (Hoffmann–La Roche) using a flash-spectroscopic technique. Flash energies of about 25 J with a half-duration of 2—3 × 10^{-6} sec. were used. The scanning beam, after passing through a vertical sample cell of the type described by McClure,[5] was rendered monochromatic with a Hilger and Watts D292 monochromator and focussed on to a Hama Matzu R213 photomultiplier. Transient absorptions were displayed on a Cossor CDU110 oscilloscope and recorded photographically. Solutions (in redistilled, dried n-hexane) were outgassed to a pressure of 10^{-6} mm. Hg.

Flash spectroscopic experiments on *all-trans-* or a *cis–trans-* mixture of lycopene alone showed no transient absorption in the region 300—900 nm. However in the presence of the aromatic hydrocarbons naphthalene (E_T 60 kcal. mole^{-1}), anthracene (E_T 42·5 kcal. mole^{-1}), and naphthacene (E_T 29·5 kcal. mole^{-1}) a strong transient absorption in the region 505—540 nm. was produced. The hydrocarbons alone showed no transient absorption in this region.

Kinetic measurements of the triplet decay of the hydrocarbon both in the presence and in the absence of lycopene show that lycopene quenches the triplets of the hydrocarbons at rates approaching the diffusion limit, which is about 2 × 10^{10} l.mole^{-1} sec.$^{-1}$ for hexane at 25°. The rate constants obtained are given in the Table, where k_1^D is the first-order rate constant for the decay of the hydrocarbon triplet in the absence of lycopene, k_1^L is the first-order decay constant of the sensitized lycopene triplet, and K_q is the second-order quenching constant.

These results indicate that the transient absorption at 505—540 nm. is due to absorption by lycopene triplet which has been produced by a simple diffusion-controlled energy-transfer process from various donors.

Triplet decay and quenching rate constants (25°)

Donor	Donor M(× 10^5)	Lycopene M(× 10^6)	$k_1^D \times 10^{-3}$ sec.$^{-1}$	$k_1^L \times 10^{-4}$ sec.$^{-1}$	$k_q \times 10^{-10}$ l.mole^{-1} sec.$^{-1}$
Naphthalene	8·5	0·75	2·4	2·6	1·5
Anthracene	7·1	1·2	1·0	2·3	1·7
Naphthacene	2·5	0·75	2·0	1·2	1·1

The Figure shows two triplet–triplet absorption spectra of lycopene with anthracene as the donor. Spectrum (a) was obtained by use of fresh *all-trans*-lycopene and was recorded after a minimum exposure to light and heat. Spectrum (b) was obtained after many flashes; it could also be obtained by use of lycopene which had been stored at 0° in hexane for several weeks. Heating solutions of *all-trans*-lycopene produces a *cis–trans*-isomeric mixture, which gives a triplet spectrum identical to (b). It thus appears that the triplet–triplet absorption peak at 527 nm. is a characteristic of the *trans*-isomer. Spectra obtained with other donors were generally similar to (b). However, a shoulder was observed at 527 nm. which disappeared after several flashes.

A few measurements were made at −20° and −60° with anthracene as a donor. The spectra were similar to (b), except that the peak was shifted to the red, being about 525 nm. at −20° and 530 nm. at −60°. The relative absorptions, and values of k_1^L are decreased with decreasing temperature as would be expected for a diffusion-controlled reaction.

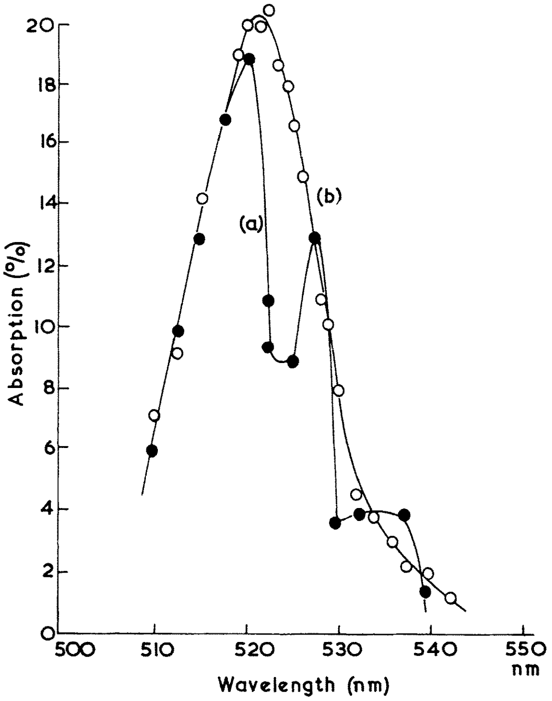

FIGURE. *Triplet–triplet absorption spectra* (25°): (a) *all-*trans*-lycopene*; (b) cis–trans-*lycopene.*

The phosphorescence observed by Lewis and Kasha from a *cis–trans*-mixture of lycopene corresponds to a triplet energy level of 52 kcal. mole^{-1} for lycopene. However, since we have direct evidence of energy transfer from naphthacene triplet to lycopene, the energy of the lowest triplet of lycopene is not greater than 29·5 kcal. mole^{-1}. Thus the emission observed by Lewis and Kasha is not from the lowest triplet state of lycopene and may well be due to some impurity.

Chessin, Livingston, and Truscott[6] have observed a sensitized transient absorption for β-carotene, a molecule similar to lycopene. Their work indicates the lowest triplet of β-carotene also lies below 29·5 kcal. mole^{-1}. However, Cherry, Chapman, and Langelaar[7] have studied β-carotene by use of delayed fluorescence techniques, and their results indicate a triplet energy level of 48·7 kcal. mole^{-1}. If this corresponds to the lowest triplet state of β-carotene, as it presumably does, the two sets of results are difficult to correlate. The present results on lycopene indicate a diffusion-controlled energy-transfer mechanism and are not likely to be due to some lycopene–hydrocarbon complex.

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