A Metastable State of Retinol (Vitamin A)

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Summary A strong triplet–triplet absorption spectrum of retinol is observed between 370 and 430 nm.; the absorption only occurs if a triplet sensitizer is present.

POLYENES with five conjugated double bonds such as retinal (retinene) and retinol (vitamin A) are of importance in the visual cycle.[1] Several workers[2-4] have studied the *in vitro* photochemistry of these compounds by flash photolysis and other techniques. A strong, short-lived transient, presumably triplet absorption of retinal has been reported, but these workers report no similar absorption from retinol or Schiff base complexes of retinal.

We now report a transient absorption from retinol, observed in the presence of a hydrocarbon, presumably after an energy transfer reaction from the hydrocarbon triplet state.

All-*trans*-retinol (Sigma, synthetic crystalline) and all-*trans*-retinal were used without further purification. A photoelectric flash apparatus with flash energies of about 25 J and flash durations of 2—3 × 10^{-6} sec. was used. Solutions, in redistilled dried hexane, were outgassed to a pressure of 10^{-6} mm. Hg. Concentrations of retinol used varied from 2 × 10^{-6} to 25 × 10^{-6}M and of hydrocarbons from 50 × 10^{-6} to 100 × 10^{-6}M.

Kinetic measurements of the triplet decay of 1,2-benzanthracene (E_T = 49 kcal.mole^{-1}) both in the presence and absence of retinol show that retinol quenches the hydrocarbon triplet at a rate ($k_2 = 0{\cdot}5 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$) close to the diffusion limit.

The overall reaction scheme can be illustrated qualitatively by the following mechanism.

$$\begin{array}{ll} D^T \rightarrow D^S & k_1\,(D^T) \\ D^T + A^S \rightarrow A^T + D^S & k_2\,(A^S)(D^T) \\ A^T \rightarrow A^S & k_3\,(A^T) \end{array}$$

where D^T and D^S represent the hydrocarbon donor in its triplet and singlet states and A^T and A^S represent the acceptor, retinol, in its triplet and singlet state. The quenching rate constant (k_2), being close to the diffusion limit, indicates that the lowest triplet state of retinol is below 46 kcal.mole^{-1}.

Flash experiments on retinol alone produced no transient absorption in the region 350—900 nm. However, in the presence of 1,2-benzanthracene a strong transient absorption between 370 and 430 nm. was observed with maxima at 402 and 382 nm. The hydrocarbon itself has little or no triplet absorption in the 370—430 nm. region. The Figure shows the triplet absorption spectrum of 1,2-benzanthracene together with the transient absorption obtained in the presence of retinol.

Results on other hydrocarbon–retinol systems are more difficult to interpret because the hydrocarbon triplets themselves absorb in the region 370—430 nm. Usually, in the presence of a high concentration of an efficient quencher there is a large reduction in the observable triplet absorption of the hydrocarbon, due to considerable quenching during the flash lifetime. However, for the naphthalene (E_T = 60 kcal. mole^{-1})–retinol system, little or no reduction was detected and a strong transient absorption is observed between 370 and 430 nm. even at large retinol concentrations. In fact, for some retinol–naphthalene concentration ratios the transient absorption, monitored at 412 nm. at times *ca.* 20 × 10^{-6} sec. after the flash, was more intense than with naphthalene alone. The quenching constants obtained for the naphthalene–retinol system are somewhat ambiguous since, after adding retinol, the transient absorption observed at 412 nm. is due to both naphthalene and retinol triplets. Certainly at low retinol concentrations the transient decay at 412 nm. yields a value of the quenching constant ($k_2 = 1 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$) close to the diffusion limit.

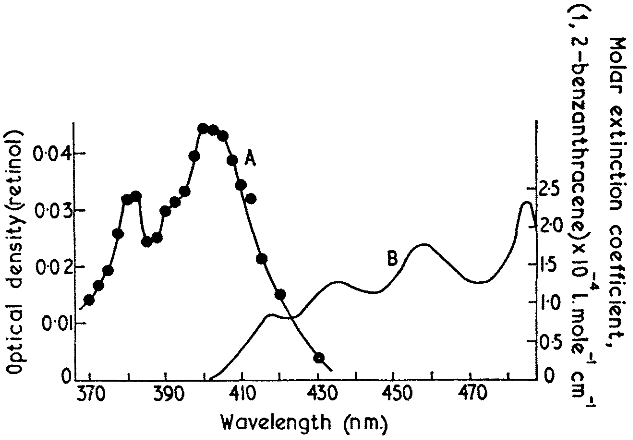

FIGURE. *Triplet–triplet absorption spectra in hexane at 25°: A, all-*trans*-Retinol, recorded* 50 × 10^{-6} sec. *after the flash; B, 1,2-benzanthracene (after Porter and Windsor*[6]*).*

The fact that no transient absorption is observed when retinol alone is flashed means that either the triplet state is not populated or that its mean lifetime is less than 5 × 10^{-6} sec. Abrahamson and co-workers prefer the first explanation and suggest that the inefficiency of triplet formation is due to the lack of a suitably placed n–π^* state. However Livingston and co-workers[4,5] have pointed out that this interpretation leaves unexplained how the molecule loses its energy of excitation. The alternative explanation, that the mean lifetime of the triplet state is less than 5 × 10^{-6} sec., appears to require fewer *ad hoc* postulates.

The present work has allowed us to estimate the lifetime of the retinol triplet by choosing concentrations in the benzanthracene–retinol system such that there is no benzanthracene triplet after 10—20 × 10^{-6} sec. With these conditions, the transient monitored at 402 nm. could still be detected after 100 × 10^{-6} sec. The rate of decay of this transient after 20 × 10^{-6} sec. should be that of the retinol triplet alone. The corresponding first-order rate constant we have obtained is approximately 6 × 10^4 sec.$^{-1}$; no second-order component was detectable. This value is comparable with the rate constant for the decay of the retinal triplet which Livingston and co-workers[4] found to be $9{\cdot}6 \times 10^4$ sec.$^{-1}$ in hexane at 25°. We have repeated their work on retinal in hexane and obtained a very similar value ($9{\cdot}2 \times 10^4$ sec.$^{-1}$). The rate constant we now report for the decay of the retinol triplet does not preclude direct observation of this triplet.

Our results still leave unexplained the failure of retinol to exhibit a triplet–triplet absorption spectrum when flashed alone, since it is not apparent why the first excited singlet state of retinol should undergo a much faster non-radiative transition to the ground state than to the lowest triplet state. However, both the kinetics of the retinol triplet decay and the overall mechanism may not be as simple as suggested above.

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