The Metastable State of β-Carotene Excited by Pulse Radiolysis

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Summary Using pulse radiolysis the life-time and extinction coefficient of the β-carotene triplet absorption at 515 nm, have been estimated to be 9 μsec. and *ca.* 2×10^5 $M^{-1}cm^{-1}$.

AN excited state of all-trans-β-carotene can be produced by photosensitization;[1] this excited state is assumed to be the lowest triplet and absorbs with λ_{max} 515 nm and unknown extinction coefficient. Pulse radiolysis of β-carotene in hexane has allowed us to observe the same absorption without the use of a sensitizer. The first-order decay constant for the carotene triplet has been found to be $1{\cdot}1 \pm 0{\cdot}1 \times 10^5$ $sec.^{-1}$. This is similar to the first-order rate of decay of retinene and retinol triplet,[2-4] and would not be too fast to be observed in previous flash spectroscopic studies.[5-7] It has been suggested[1] that the previous failure to observe a β-carotene triplet absorption when carotene is flashed alone is due to the triplet state decaying to the ground state in less than about 1 μsec. The value we have now obtained discounts this idea, and a more likely explanation is that the S → T crossover efficiency of this molecule is very low. High-energy excitation in aliphatic hydrocarbons yields some solute triplets formed independently of the singlet state.[8]

We have also observed a depopulation of the singlet state of β-carotene between 380 and 500 nm in experiments both with and without sensitizers. This has allowed us to estimate a value of the extinction coefficient of the β-carotene triplet at 515 nm of about $2{\cdot}3 \times 10^5$ M^{-1} cm^{-1}. This value is a maximum value and would be lower if there is any triplet absorption in the 380—500 nm region. We have also estimated a value of the extinction coefficient of β-carotene in the presence of naphthalene using the technique described by Land.[9] This leads to a value of about $1{\cdot}7 \pm 0{\cdot}4 \times 10^5$ M^{-1} cm^{-1}. Mathis[6] observed a depopulation of lutein, a molecule similar to β-carotene, using laser-flash spectroscopy. From this an extinction coefficient at 518 nm of 4×10^5 M^{-1} cm^{-1} was estimated.

There is considerable interest in the energy level of the lowest triplet state of β-carotene. Energy-transfer studies using flash spectroscopy have shown that the level is below that of naphthacene (E_T = 29 kcal. $mole^{-1}$).[1] We have observed that oxygen quenches the carotene triplet at a rate comparable with the oxygen quenching of naphthalene triplet. If this reaction leads to the formation of singlet oxygen ($^1\Delta_g$), the energy level of the carotene triplet would be located at $25{\cdot}5 \pm 3$ kcal. $mole^{-1}$. Since we have also shown that carotene quenches the triplet state of pentacene[10] at rates approaching the diffusion limit the carotene triplet energy level would be at the lower end of the above range. These observations are difficult to correlate with the quenching by β-carotene of the reaction of singlet oxygen ($^1\Delta_g$) reported by Foote and Denny.[11]

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