Photoisomerization of 7-*cis*-Retinal. The Concentration Effect

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A triplet quantum chain process is believed to be responsible for the concentration dependent quantum yield of isomerization of 7-*cis*-retinal.

Photoisomerization of retinal has been studied extensively either as a model system for the visual chromophore[1,2] or as a representative polyene in studies of factors controlling regioselectivity of the isomerization process.[3] Past studies have been limited to the all-*trans* and the more readily available 13-*cis*, 11-*cis*, and 9-*cis* isomers.[1—6] We have now conducted a study with the sterically crowded 7-*cis* isomer.[7] In the process we detected an unexpectedly large quantum yield of isomerization and its dependence on concentration of the polyene. The effect may be of general importance and is described below.

Direct irradiation (365 nm) of a hexane solution of

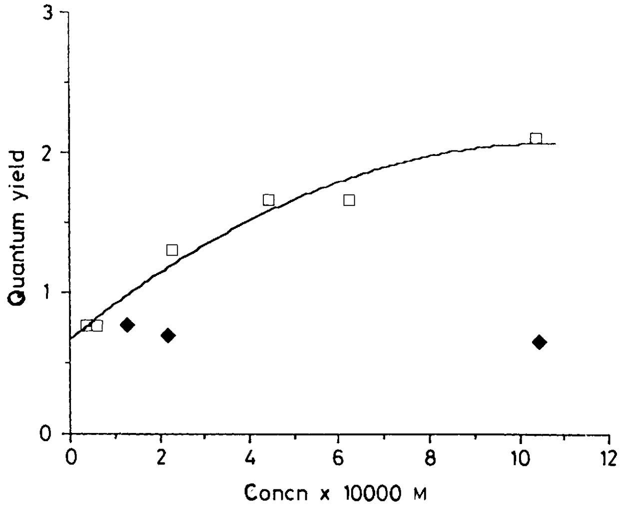

Figure 1. Quantum yield of isomerization (0.7—2.1) of 7-*cis*-retinal in hexane as a function of retinal concentration (4.4×10^{-5}—1.04×10^{-3} M) with 365 nm light. (□, Degassed samples after five cycles of freeze–pump–thaw; ◆, aerated samples.) Data are the averages of three samples for each concentration, the average error limit is ±18%. HPLC analyses carried out on a 5 μ Dynamax Microsorb Si-80 column (1.2% methyl t-butyl ether in Freon 113).[7] Areas corrected for different molar absorptivities (at 360 nm) of isomers.[3]

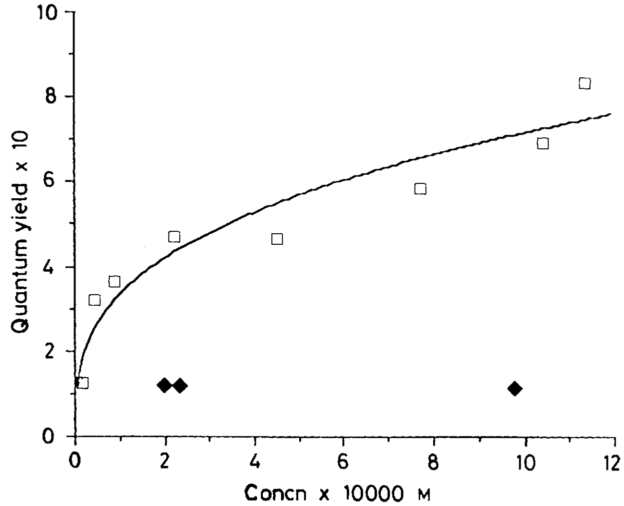

Figure 2. Quantum yield of isomerization (0.13—0.84) of all-*trans*-retinal in hexane as a function of retinal concentration (1×101^{-5}—1.14×10^{-3} M) with 360 nm light. (□, Degassed samples; ◆, aerated samples.) Averaged error limit is ±10%.

7-*cis*-retinal (purified by preparative HPLC before use) was found to give primarily the all-*trans* isomer accompanied by minor amounts of the 13-*cis*, 7,13-di-*cis*, and 9-*cis* isomers (analysed by HPLC).[3,8] Hence one-bond isomerized products appear to dominate but two-bond isomerized products are also present. Quantum yields of isomerization of 7-*cis*-retinal [iron(III) oxalate as an actinometer system],[9] conducted with degassed hexane solutions of different concentrations of 7-*cis*-retinal, have been determined (Figure 1). The data clearly show an increase of efficiency of isomerization at higher concentrations of the polyene. In fact in most cases the quantum yield was found to be greater than one! Lower values, independent of retinal concentration, were found for the aerated samples.

These observations were unexpected because in no instances were we aware of reports on dependence of quantum yield of isomerization of any of the retinal isomers on its concentration or dissolved oxygen. In fact, it has generally been assumed that aeration has little effect on the isomerization process.[5,10] To test whether the observed effect is limited to the hindered 7-*cis* isomer, we conducted a similar study with all-*trans*-retinal. The results shown in Figure 2 reveal a similar, though somewhat less dramatic trend, *i.e.*, quantum yield of isomerization increases at higher retinal concentrations, and decreases when aerated.

The large quantum yield value and the oxygen effect led us to suspect that the increased quantum efficiency is a consequence of a triplet quantum chain process,[11] knowing that in a non-polar solvent the triplet yields of all-*trans*-retinal (0.43 ± 0.08) and the three common mono-*cis* isomers are high (0.39—0.61).[12] We have therefore carried out a product study of triplet sensitized (532 nm light with zinc octaethylporphyrin as photosensitizer $E_T = 40.4$ kcal mol^{-1})[6] irradiation of 7-*cis*-retinal for comparison with that from direct irradiation. Results of the distribution of initial products (1—10% conversion) show the following notable trends. The hindered 7,13-di-*cis* isomer, a one-bond isomerized product, was formed only under direct irradiation, a likely singlet state product. The ratio between the two two-bond isomerized products remained the same (13-*cis*:9-*cis* = 1.6) under the two different conditions of irradiation. This is only consistent with the involvement of the triplet state for these products. A likely mechanistic pathway for their formation is the conversion of the 7-*cis* triplet (formed by intersystem crossing upon direct excitation of 7-*cis*-retinal or sensitization) to the all-*trans* triplet which undergoes isomerization to the 9-*cis* or 13-*cis* isomer. A quantum chain process then involves secondary energy transfer from the all-*trans* triplet to a second 7-*cis*-retinal molecule.

The effect reported here does not necessarily contradict earlier reports of lack of a variation of quantum yield of isomerization in the presence or absence of dissolved oxygen because they were conducted at lower concentrations of retinal.[5,10] The effect is smaller for the unhindered isomers. Nevertheless the present study suggests a need to re-examine other retinal isomers (in particular the hindered 11-*cis* isomer). It should also be noted that a similar concentration dependent triplet quantum chain process has been observed in other simpler dienes and trienes.[13]

The work was supported by a grant from the Nationa Science Foundation (CHE-16500).

Received, 5th September 1989; Com. 9/03783G

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Typeset and printed by Black Bear Press Limited, Cambridge, England