Mechanism for the Two-bond Isomerization in the Photoirradiation of 7,9-Di-*cis*-retinal

Robert S. H. Liu* and Yun Zhu

Department of Chemistry, 2545 The Mall, University of Hawaii, Honolulu, HI 96822, USA

The two-bond isomerization process of 7,9-di-*cis*-retinal to all-*trans*-retinal has been shown to proceed by way of an adiabatic, stepwise process.

Recently, in a study of primary photoproduct distribution for all sixteen isomers of retinal,[1] two- (and multiple-) bond isomerized products were shown to accompany one-bond isomerized products. In cases by poly-*cis* hindered isomers, such products constituted the major products. Possible mechanisms for their formation are a concerted two-bond twist (*e.g.*, the 'bicycle pedal' mechanism)[2] or a stepwise process, either in the form of an excited adiabatic process or a non-adiabatic process of two-photon excitation:

Concerted: *cis,cis* to *cis,cis** to *trans,trans*
Adiabatic stepwise: *cis,cis* to *cis,cis** to *cis,trans** to *trans,-trans*
Non-adiabatic (two-photon) stepwise: *cis,cis* to *cis,cis** to *cis,trans* to *cis,trans* to *trans,trans*

We have now measured changes of product distribution during irradiation of 7,9-di-*cis*-retinal in hexane between 298 and 193 K, and determined quantum yields of isomerization at these temperatures. We believe that the results clarify the specific mechanism involved in formation of the two-bond isomerized product.

The product distributions for the hindered 7,9-di-*cis* at the two extreme reaction temperatures (298 and 193 K) for this study are shown in Figs 1 and 2. All-*trans*, a two-bond isomerized product, was the major product in both cases, especially at room temperature. The three-bond isomerized 13-*cis* isomer was detectable only at the higher temperature. Quantum yields of isomerization as a function of reaction temperature have been reported for the all-*trans* isomers.[3] The values for the hindered 7,9-di-*cis*-retinal have now been determined (Table 1) showing in most cases the usual trend of decreasing quantum yields of product formation at lower temperatures. The only exception is the 9-*cis*, its quantum yield increasing by three-fold upon lowering of reaction temperature.

These combined results are consistent with the above adiabatic stepwise process. First, the simultaneous appearance of one-, two- and three bond isomerized products clearly cannot be accounted for solely by the concerted two-bond mechanism. Of the two stepwise processes, the two photon process is inconsistent with the pattern of product distribution during the irradiation period. Both Figs 1 and 2 show no signs of accumulation of the 9-*cis*-isomer at the early stages of irradiation, as expected for a two-photon process. Instead, all products remained in same proportions throughout (up to 10% conversion). Also, it was shown earlier that the amount of the two-bonds isomerized product was not enhanced by higher light intensity.[1] Most revealing are the unusual 9-*cis* quantum yield data. The increased quantum yield at lower

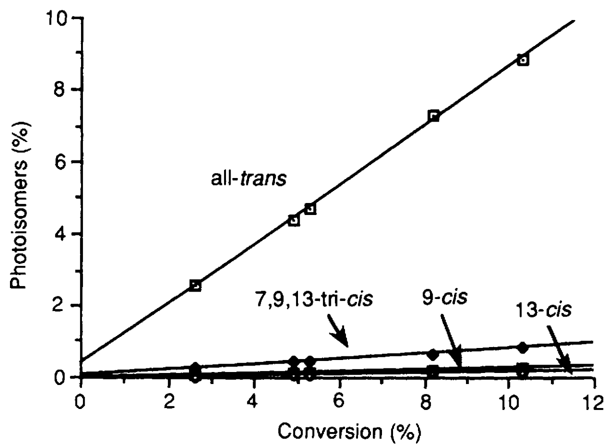

Fig. 1 Progress of product formation during direct irradiation (366 nm, Applied Photophysics 'Merry-go-round' apparatus) of 7,9-di-*cis*-retinal in hexane at 298K. The product mixtures were determined by HPLC analyses. HPLC conditions and correction factors for different absorbance of retinal isomers at 360 nm are those from ref. 9.

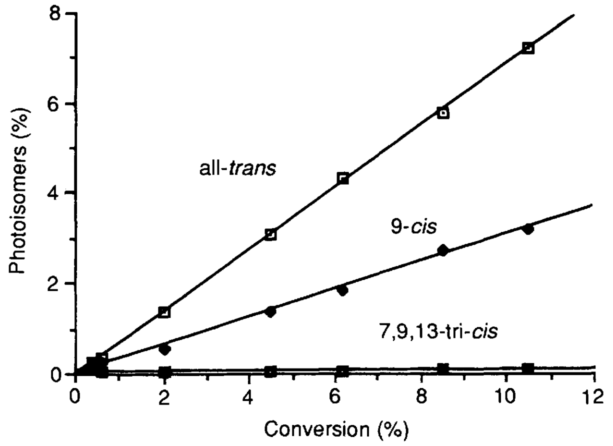

Fig. 2 As Fig. 1 except that the irradiation was carried out at 193K

Table 1 Quantum yields[a] of photoisomerization of 7,9-di-*cis*-retinal (1×10^{-3} mol dm^{-3} in hexane) at 298 and 193 K

	Φ (from 7,9-di-*cis*[b])			
T/K	7,9,13-tri-*cis*	9-*cis*	*trans*	total
298	0.04	0.02	0.51	0.57
193	0.01	0.06	0.13	0.20

[a] Error estimate, ± 10% relative to those of all-*trans*-retinal.[3,8] [b] The reported values for all-*trans*-retinal are: $\Phi_{13\text{-}cis}$ & $\Phi_{9\text{-}cis}$ = 0.10, 0.015 (298 K) respectively and 0.018, 0.0014 (193 K).[3]

temperature is consistent only with the above adiabatic process. Torsional relaxation of the 7-*cis* bond of the excited 7,9-di-*cis*-retinal should be rapid, assisted by relief of severe steric crowding at this centre[4] (supported by the fact that 9-*cis* was the only mono-*cis* product in the irradiation mixture), giving first the excited 9-*cis*. Subsequent conversion from 9-*cis* into all-*trans* should be more volume-demanding and more activated[5] (see sketch in Fig. 3). Hence, at the lower temperature, the latter conversion becomes competitively less favoured than vertical decay to the ground state 9-*cis*-retinal. This would lead to the seemingly surprising result of the increased quantum yield at a lower temperature.

The current photochemical data do not specify the excited state responsible for the two-bond isomerization process. However, based on known spectroscopic properties of retinal, we suspect that the triplet state was involved. Thus, intersystem crossing efficiency of retinal in a non-polar solvent is high (close to 0.5),[6] and time-resolved UV–VIS absorption studies[7] show that the triplets of hindered isomers of retinal are short lived (~psec) converting rapidly into the more stable and longer lived (μsec) triplets of unhindered isomers. Consequently, the three-bond isomerized 13-*cis* isomer should be formed by two consecutive activated rotational processes in the excited state potential surface. Its complete disappearance at the lower temperature is, therefore, not surprising.

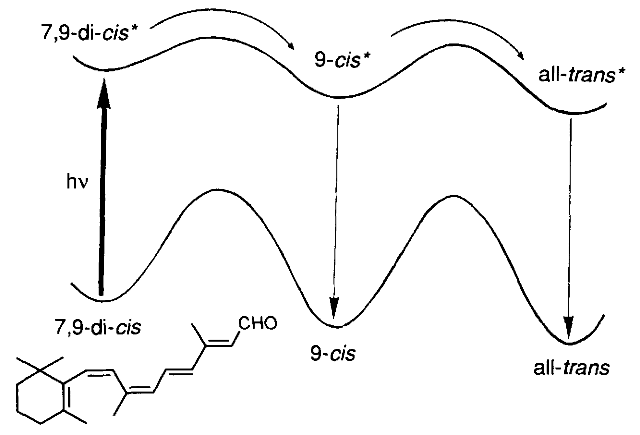

Fig. 3 Sketch of a possible torsional potential curve and pathway for conversion of 7,9-di-*cis*-retinal into all-*trans*-retinal

Whether the adiabatic mechanism is also applicable to reactions of protein-bound polyene chromophores remains to be seen.

The work was patially supported by grants from the U.S. Public Health Services (DK-17806) and HFSPO.

Received, 3rd August 1993; Com. 3/04631A

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