Semiconductor Photocatalysis: Photodegradation and Trans-Cis Photoisomerization of Carotenoids

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In the presence of semiconductor CdS or ZnO particles, irradiation (>350 nm) of all-*trans-* β -carotene (**II**) in dichloromethane leads to rapid degradation of the carotenoid, which is relatively stable in the absence of the semiconductors. Canthaxanthin (**I**), however, undergoes significant photocatalyzed degradation only on ZnO, not on CdS. High-performance liquid chromatographic studies indicate that CdS catalyzes trans—cis photoisomerization of both **I** and **II**. As in the photoisomerization in the absence of semiconductor, the major cis isomers have the 9-cis and 13-cis configuration, but, under otherwise the same condition, the ratio of cis/trans isomers has doubled. In contrast to CdS, ZnO does not catalyze the photoisomerization of either **I** or **II**, although it enhances their rate of degradation. A photoisomerization mechanism involving carotenoid radicals formed by reaction with interstitial sulfur on the CdS surface is proposed.

Introduction

Carotenoids are widely distributed in green plants and animals; ~600 naturally occurring carotenoids having been isolated and identified.¹ They have the important biochemical and biological functions of light harvesting and photoprotection in green plants and have been found in all photosynthetic organisms that evolve O₂.^{2,3} Although carotenoids are generally present in their most stable form in which all double bonds in the backbone have the trans configuration, many mono- or dicis geometrical isomers, primarily at positions 7, 9, 13, 15, 13', and 9' (Scheme 1) are known. These cis isomers, together with trans isomers, are present in human as well as animal tissue and in pigment-protein complexes of photosynthesizing plants and bacteria, and are known to affect the biochemistry. For example, different configurations are found in spinach leaves, and $cis-\beta$ -carotene is bound to the reaction centers (RCs) of spinach Photosystem II and Photosystem I;^{4,5} cis isomers of spheroidene, neurosporene, and spirilloxanthin are bound to the RCs of the bacteria Rhodobacter sphaeroides 2.4.1, Rhb. sphaeroides GIC, and Rhodospirillum rubrum S1, respectively.6 Carotenoid cis isomers are also found in the thermophilic cyano bacterium Synechococcus valcunus copeland.^{7,8} The first cis carotenoids observed in animals were mono cis isomers of canthaxanthin localized in the ovaries, eggs, and hemolymph of the female brine shrimp Artemia. The presence of these cis isomers at specific sites of only reproductively active females implies that they are essential to reproduction and/or embryonic development.9

In vitro methods leading to formation of mixtures of cis and trans isomers include refluxing in organic solvents, melting of crystals, contact for prolonged periods with certain active surfaces, treatment with acids, and irradiation of solutions (often catalyzed by iodine).^{10,11} Recently it was found that electrochemical oxidation of all-*trans*-canthaxanthin and β -carotene, shown in Scheme 1, in dichloromethane also leads to significant trans-to-cis isomerization, with cis isomers accounting for ~40% of the carotenoid;¹² the proposed mechanism involves geometrical isomerization mediated by radical cations and/or dications. The same species are also generated by chemical

SCHEME 1: Structures of All-trans-Canthaxanthin (I) and Geometrical Isomers of β -Carotene (II) [(a) All-trans, (b) 7-cis, (c) 9-cis, (d) 13-cis, and (e) 15-cis]



oxidation; for example, treatment of all-trans carotenoids with $FeCl_{3}$, which results in the formation of cis isomers.¹³

During the past decade, the utilization of semiconductors as catalysts in photochemical transformations of organic and inorganic compounds has seen a tremendous growth.^{14–20} The participation of a semiconductor in a photocatalytic process can be either direct or indirect. Under band gap excitation, semiconductor particles act as short-circuit microelectrodes and directly oxidize or reduce the adsorbed substrates. Alternatively, they can promote a photocatalytic reaction by acting as mediators for the charge transfer between two adsorbed molecules (Scheme 2). This process is extensively employed in photoelectrochemistry and imaging science. In this case, the semiconductor accepts an electron from the excited state of an adsorbed dye and then transfers the charge to another substrate





 $(A \rightarrow A^{-})$. The energies of the conduction and valence bands of the semiconductor and the redox potential of the adsorbed molecule control the course of the photochemical reaction. Application of dye-sensitized semiconductor electrodes to a new type of photovoltaic cell, the dye-sensitized solar cell or Graetzel cell,²¹ has generated much current interest in the photochemistry community.²² Development of new semiconductor sensitizers that produce high conversion efficiency and low cost solar photovoltaic dye cells is a challenging task.

Carotenoids absorb light in the range 380-520 nm, with molar extinction coefficients > 10⁵. The photodriven electron transport processes in synthetic triad and pentad molecules containing carotenoids^{23,24} and light-induced electron polarization and separation in carotenoid/solvent^{25,26} have been well studied. Carotenoid Langmuir-Blodgett (LB) films deposited on indinum tin oxide (ITO) have been shown to be photoactive electrodes.²⁷ These properties, together with their photoprotect characteristics, make certain carotenoids potential sensitizers in solar photovoltaic cells. Because carotenoids exhibit different stability in solution, it is essential to investigate the photochemical behavior as well as the stability of carotenoids in semiconductor/carotenoid/solvent systems.

In this study, we irradiated mixtures of carotenoids and semiconductor powders. It was found that in the presence of certain semiconductor powders, dichloromethane solutions of carotenoids show diverse photochemical behavior. Thus, with CdS particles, irradiation (> 350 nm) of all-*trans*-canthaxanthin (I) and β -carotene (II) in dichloromethane leads to significant enhancement of cis isomer formation. However, ZnO does not catalyze these photoreactions. Carotenoids I and II show different photostability with different semiconductors. In the presence of ZnO particles, rapid degradation of both I and II was observed under irradiation; with CdS, however, significant photodegradation of only II, not I, occurred.

Experimental Section

All-*trans*-canthaxanthin and β -carotene were purchased from Fluka. Anhydrous dichloromethane, HPLC grade acetonitrile, and cadmium sulfide and zinc oxide powder (<5 μ m) were obtained from Aldrich.

Optical absorption spectra in the range of 190 to 1100 nm were measured using a Shimadzu UV-1601 UV-vis spectrophotometer. A 250 W xenon lamp (ILC Technology) at a distance of 20 cm was used to irradiate the solutions. Deionized water contained in a cylindrical glass cell (path length, 10 cm) was used as an IR cutoff filter. An optical filter was used to cut off most of the UV light below 350 nm. The photoenergy at the external surface of the cuvette, measured with a Newport power meter (model 818-SL), was 0.4 W cm⁻². A closed continuous flow system (Figure 1), consisting of a 100-mL glass bottle with a flat glass window, a peristaltic pump (Rabbit, RAININ Instrument Company Inc.), and a flow cell (Shimadzu, 1-cm optical path length and 3-mm diameter), was used for irradiation of the solution and measurement of the spectra. A mixture of carotenoid and semiconductor powder in 50 mL of



Figure 1. Schematic of the flow system used for irradiation of carotenoid/semiconductor/ CH_2Cl_2 mixtures and optical spectra measurement.



Figure 2. Difference optical absorption spectra of $14 \,\mu$ M canthaxanthin in CH₂Cl₂ after irradiation for 2, 4, 6, 8, 10, 15, and 20 min with a xenon lamp (>350 nm) in the presence of (a) no semiconductor, (b) CdS powder (3 mg/mL), and (c) ZnO powder (3 mg/mL). The mixture was purged with N₂ to remove O₂ before irradiation. Arrows indicate increase of irradiation time.

dichloromethane was purged with nitrogen for 10 min prior to irradiation. During irradiation, the solution was stirred magnetically and continuously pumped through the flow cell connected by a 1-mm i.d. silicon rubber tube. A pump-inlet filter (stainless steel mobile phase filter for HPLC, 2 μ m) was used to prevent particles from entering the flow cell. The pump was stopped during the spectral measurements.

A Vydac 201TP54 polymeric C_{18} column (250 × 4.6 mm i.d.) packed with 5- μ m particles (Hesperia, CA) and a Shimadzu LC-600 pump with a SPD-6AV UV-vis detector were used for the HPLC separation and detection. Acetonitrile was used as the mobile phase. The detector was set at 465 and 450 nm for canthaxanthin and β -carotene, respectively, near the maximum absorbance of the neutral cis carotenoids.

Results and Discussion

Photodegradation Catalyzed by Semiconductor Powders. Figure 2 shows the difference optical absorption spectra $(A_t - A_0)$ of 14 μ M canthaxanthin (I) in CH₂Cl₂ after irradiation with a xenon lamp (>350 nm) for increasing periods of time. In the absence of semiconductor powders, irradiation of the solution leads to the gradual disappearance of I (Figure 2a). The rate of decrease in the concentration of I increases somewhat in the presence of CdS powder (Figure 2b), and much more so in the presence of ZnO powder (Figure 2c). The decrease in concentration of neutral canthaxanthin shows a linear dependence on irradiation time (Figure 3a, curves 1–3) during the early stages ($\leq t_{1/2}$); that is, the photodegradation reaction appears to be zero-



Figure 3. Photodegradation of (a) 14 μ M canthaxanthin and (b) 14 μ M β -carotene by irradiation for increasing periods of time, in the presence of (1) no semiconductor, (2) CdS powder, and (3) ZnO powder. Data from Figures 2 and 4, respectively.



Figure 4. Difference optical absorption spectra of $14 \,\mu M \,\beta$ -carotene in CH₂Cl₂ after irradiation for 2, 4, 6, 8, 10, 15, 20 min with xenon lamp (>350 nm), in the presence of (a) no semiconductor, (b) CdS powder (3 mg/mL), and (c) ZnO powder (3 mg/mL). The mixture was purged with N₂ to remove O₂ before irradiation. Arrows indicate increase of irradiation time.

order in carotenoid. The apparent rate constants, k_{obs} , are 0.05, 0.08, and 0.23 μ M min⁻¹ in the presence of no powder, CdS powder, and ZnO powder, respectively. It may be noted that changes in absorption due to concurrent formation of cis isomers were ignored because both λ_{max} and extinction coefficients of cis and trans isomers are similar ($\Delta\lambda_{max} = 5-7$ nm). The difference spectrum after irradiation for 20 min approaches that of pure *trans*-canthaxanthin, which shows no fine structure at its maximum near 475 nm in CH₂Cl₂. The spectral results of similar experiments with β -carotene (**II**) are shown in Figure 4. The difference spectrum after irradiation for 20 min shows the fine structure characteristic of **II** in CH₂Cl₂. Comparison of Figures 2 and 4 leads to the conclusion that both CdS and ZnO exert a greater catalytic effect on the photodegradation of



Figure 5. (a) High-performance liquid chromatograms of 0.3 mM alltrans-canthaxanthin in CH_2Cl_2 after irradiation for 15 min. The solution contained (···) no powder, and (–) CdS powder when irradiated. Solution was filtered before injection (mobile phase, CH₃CN; injection volume, 5 μ L; flow rate, 1 mL/min; temperature, 22 °C). (b) Same as a, except with ZnO powder.

 TABLE 1: Approximate cis-trans Ratios of Carotenoids

 Formed by Photoisomerization from All-trans Carotenoids

 in the Presence of Semiconductors

		cis/trans ratio (± 0.01)		
carotenoid isomer		without semiconductor	ZnO	CdS
\mathbf{I}^{a} \mathbf{II}^{b}	9-cis 13-cis 9-cis 13-cis 15-cis	0.07 0.03 0.05 0.04 0.03	0.07 0.03 0.05 0.04 0.03	0.15 0.12 0.12 0.09 0.06

^a Irradiation for 15 min. ^b Irradiation for 10 min.

II than I. In the absence or presence of CdS powder, the decrease in concentration of II also shows a linear dependence on the irradiation time in the early stages (Figure 3b, curves 1 and 2), and the apparent zero-order rate constants k_{obs} are 0.07 and 0.25 μ M min⁻¹, respectively. With ZnO powder, however, the decrease of β -carotene concentration shows a logarithmic dependence on the irradiation time, indicating that it is a first-order reaction ($k_1 = 0.05 \text{ min}^{-1}$). These results show that canthaxanthin is photochemically more stable than β -carotene in the presence of semiconductors.

Trans-Cis Photoisomerization by Semiconductor Powders. Figure 5a shows the HPLC results after irradiating a 0.3 mM solution of I for 15 min, in the absence (dotted line) and the presence (solid line) of CdS powder in the solution. The two new major components were identified to be the 9-cis and 13cis isomers by comparison with previous results.^{28,29} Although in both cases cis isomers were formed during irradiation of trans-canthaxanthin, the ratio of cis/trans products formed in the presence of CdS powder is several times larger than that obtained in its absence during the same time of irradiation. The 9-cis/all-trans ratio increased from 0.07 to 0.15, and the 13cis/all-trans ratio increased from 0.03 to 0.12 (Table 1). For β -carotene, similar results were obtained. After irradiation three new components were identified to be the 9-cis, 13-cis, and 15-cis isomers. The ratio of cis/trans products formed in the presence of CdS powder increased from 0.05 to 0.12 (9-cis),

SCHEME 3: Energy Levels of the Conduction and Valence Bands of CdS and ZnO, and Oxidation and Excited States of Canthaxanthin (I) and β -Carotene (II)



0.04 to 0.09 (13-cis), and 0.03 to 0.06 (15-cis; Table 1). These results indicate that the extent of carotenoid geometrical photoisomerization is enhanced significantly in the presence of CdS powder. In our experiments, in the absence of CdS powder, the cis/trans ratio of products of photoisomerization of carotenoids is relatively low; such isomerization is believed to follow a triplet mechanism.³⁰

On the other hand, the HPLC result after irradiating a 0.3 mM solution of I for 15 min in the presence of ZnO powder (Figure 5b, solid line) showed no observable difference in the cis/trans ratio of isomers compared with that obtained in the absence of ZnO powder (Figure 5b, dotted line; Table 1). However, two as yet unidentified components with much shorter retention times (between 5 and 8 min) were generated upon irradiation in the presence of ZnO (Figure 5b, solid line). Similar results were obtained for β -carotene isomerization (Table 1). These observations lead to the conclusion that ZnO exerts little, or no, catalysis on the photoisomerization of carotenoids, although it obviously catalyzes other reactions (e.g., photodegradation). The possibility that the two new components are carotenoid geometrical isomers is unlikely because of their very short retention times. Further investigations need to be carried out to identify these new products.

Semiconductor-Catalyzed Photodegradation and Photoisomerization Mechanism. It has been demonstrated previously that the degradation of carotenoids oxidized by FeCl₃ occurs by formation of carotenoid radical cations and that the decay rate of these radical cations is greatly enhanced by irradiation.²⁸ It is also known that large-band gap semiconductors such as ZnO can be sensitized with various dye molecules that became oxidized in the process.^{31,32} The semiconductorcatalyzed photodegradation mechanism could involve photochemical formation of carotenoid radical cations by a sensitization process. In such a process, an electron from the excited carotenoid molecule is injected into the conduction band of the semiconductor to form a carotenoid radical cation that, upon further irradiation, undergoes rapid degradation. Such an electron transfer to the semiconductor process is feasible according to the relative energies of the semiconductor band edges and the carotenoid excited states. Scheme 3 shows the energy levels of the conduction and valence bands of CdS and $ZnO^{33,34}$ and the excited states of carotenoids I and II, as well as the oxidation potentials of I and II which were determined by cyclic voltammetry using SCE as the reference electrode.³⁵ In the excited states, these oxidation potentials correspond to -1.98 and -2.21 V for I and II, respectively. Thus, the energy gained from the light excitation provides sufficient driving force $(\Delta E,$ the potential difference between carotenoid excited states and semiconductor conduction bands) to inject electrons from Car* into the conduction band of the semiconductor particles. The degradation rate of the carotenoids will be determined by the formation rate of their radical cations, which is related to SCHEME 4: CdS-Catalyzed cis-trans Photoisomerization of Carotenoids



the driving force (ΔE) of a particular semiconductor/carotenoid pair. Thus, it is expected that under the same irradiation conditions, **II**/ZnO would give the fastest rate of the photochemical reactions, and **I**/CdS would give the slowest. The experimental results bear out this expectation and lend support to the proposed mechanism.

Depending on the method used to effect cis-trans isomerization of carotenoids, several mechanisms have been proposed; for examples, triplet energy transfer³⁰ and formation of singlet biradicals³⁹ and radical cations.^{12,13} The proposed radical cation mechanism is based in part on AM1 calculations that show that the barrier to rotation about certain bonds in the carotenoid radical cations, compared to the neutral species, is greatly reduced. The isomerized radical cations are then transformed to neutral cis-carotenoids by exchanging one electron with neutral carotenoids (which are converted to radical cations). Such reactions could also be involved in the photoisomerization because, as already discussed, carotenoid radical cations can be photoproduced by CdS and ZnO semiconductor particles. However, if this were the only mechanism, both CdS and ZnO should catalyze trans-cis photoisomerization of carotenoids, but only CdS, not ZnO, particles enhance the photoisomerization. An additional mechanism must occur, presumably at the surface of CdS.

It has been shown that CdS powder can induce efficient cistrans photoisomerization of alkenes.^{31,33,36–38} Two mechanisms have been invoked previously. For the photoisomerization of styrene derivatives in the presence of CdS, the intermediacy of styrene radical cations, formed by electron transfer from styrene to valence band holes in the irradiated CdS, was proposed.³⁷ In a later investigation of the photoisomerization of nonaromatic monoalkenes catalyzed by CdS, it was proposed that the active sites for the cis-trans photoisomerization are photoproduced radicals from surface states, and that surface defects such as interstitial sulfur (I_s) play important roles in their formation.³³ A trapped hole would be produced if I_s donates an electron to the photoformed hole in the valence band before the recombination. The trapped holes arising from I_s can be regarded as sulfur radical cations (I_{s}^{+}) . Addition (and subsequent elimination) reactions of alkenes should occur to sulfur radicals on the surface of catalysts, leading to the catalytic cis-trans isomerization. A similar mechanism fits the CdS-catalyzed photoisomerization of carotenoids. As shown in Scheme 4, upon irradiation of CdS particles, surface defects such as interstitial sulfur (I_s) form sulfur radical cations (I_{s}^{+}) by donating electrons to the photoformed holes in the valence band.³³ An electron from a double bond in the carotenoid backbone could combine with I_{s} .⁺ to form a S⁺-C bond and carotenoid radicals that can easily undergo geometrical isomerization to form various cis configurations. According to AM1 molecular orbital calculations, the energy barriers of configurational transformation in the gas phase from trans to cis are much lower in the radicals than in the neutral molecule.12

As discussed above, in the CdS/carotenoid case, there exist two competing reactions; that is, photoisomerization via formation of attached carotenoid radicals on CdS surface-active sites, and photodegradation via formation of carotenoid radical cations by the sensitization process. For the ZnO/carotenoid system, however, either the photodegradation process is much faster than the photoisomerization, or the latter does not occur.

Conclusions

It has been shown that canthaxanthin and β -carotene can undergo charge transfers on ZnO and CdS particle surfaces, leading to significant photodegradation of β -carotene on both ZnO and CdS, and for canthaxanthin only on ZnO. The photodegradation rate is related to the energy difference between the semiconductor conduction bands and the excited states of carotenoids. CdS also catalyzes geometrical photoisomerization of all-*trans*-canthaxanthin and β -carotene, to form mainly 9-cis and 13-cis isomers. Active sites, such as interstitial sulfur (I_s), of the CdS particles have been proposed to play an essential role in the isomerization.

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