

Photodimerization of cinnamic acids controlled by molecular assemblies of surfactant amine *N*-oxides

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UV irradiation of cinnamic acids **1** involving a complex with surfactant amine *N*-oxides (C_n DAO, $n = 12, 14$ and 16) as vesicles in water leads to the formation of cyclodimers (*i.e.* β -, δ -truxinic and/or α -truxillic acids[†]). Decreasing the molar ratios of **1** to C_n DAO causes the vesicles to transform into rod-like micelles and the yield of the cyclodimers decreases. The addition of HCl or NaOH to aqueous solutions of **1** and C_n DAO brings about sharp changes in the self-assembly structures from vesicles to micro emulsions or rod-like micelles, accompanied by a change in product distribution in the photolysis of the complex **1**. Upon addition of photoinactive carboxylic acids, phenylpropionic and palmitic acids to the **1** and C_{16} DAO system, the rod-like micelles change into vesicles by formation of a complex with C_{16} DAO leading to the observation of a dilution effect in the photodimerization upon addition of phenylpropionic acid. However, no dilution effect is observed for the palmitic acid. This is found to be attributable to the difference in degrees of mixing of **1** with the acids in the vesicles. These results show that photodimerization of **1** incorporated in C_n DAO is controlled by a variety of molecular assemblies, *i.e.* rod-like micelles and homogeneous or heterogeneous vesicles.

Introduction

Photocyclodimerizations of aromatic olefins have been reported to be significantly enhanced in micelles and related systems which act as the reaction environments.^{1–3} Furthermore, the stereochemistry of the resulting cyclodimers was found to change with a change in their aggregated structures. Cinnamic acids **1** have been revealed to be excellent probes for molecular orientations imposed by the organized reaction media.¹ Moreover, the stereochemistries of the cyclodimers from the photolysis of **1** can be compared with the mutual orientations of **1** in their variable crystal structures.⁴ Such a preorientation of the guest molecules has been confirmed to be effective in layered inorganic minerals⁵ as well as in normal or reversed micelles.¹

Alkyldimethylamine *N*-oxides, C_n DAO ($n =$ carbon number of alkylamines, *i.e.* 12, 14 and 16), are known to form various aggregates in water depending on the concentration, temperature and additive.^{6,7} Thus, it was noted that the aggregation behaviour of C_{16} DAO exhibited iridescent colours with surfactant concentration of 0.3–2 wt% in water at temperatures lower than 23 °C.^{6a,b} This iridescence was explained by the interference of light arising from Bragg reflection between the multi-lamellar layers. Such multilamellar aggregates provide an interesting reaction field for controlling the orientation of the guest molecules.

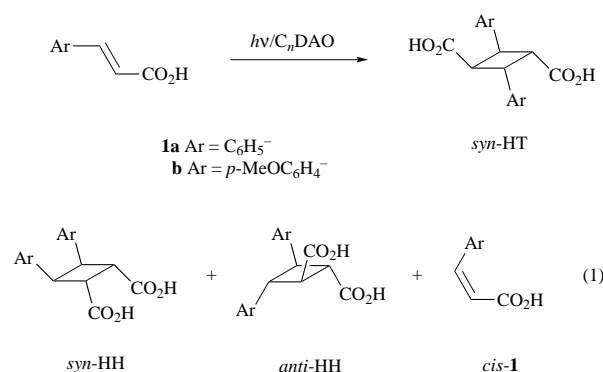
In the present paper, the authors report on the photocyclodimerization of **1** incorporated in the organized media of C_n DAO in water. The effect of the ratios of **1** and C_n DAO, the pH and the coadsorbates on aggregated structures and photoreactivities were investigated, and based on these results, the solubilization sites of **1** in the C_n DAO aggregates are presented.

[†] IUPAC names: truxinic acid = 3,4-diphenylcyclobutane-1,2-dicarboxylic acid, truxillic acid = 2,4-diphenylcyclobutane-1,3-dicarboxylic acid.

Results and discussion

Photochemical cyclodimerization of **1** in aqueous C_n DAO solution

Irradiation of 5.0×10^{-3} mol dm⁻³ cinnamic acid **1a** in 5.0×10^{-3} mol dm⁻³ C_{16} DAO in water at $\lambda > 280$ nm for 19 h led to the formation of α -truxillic (*syn*-HT), β -truxinic (*syn*-HH), δ -truxinic acids (*anti*-HH) and the *cis*-isomer in yields of 6%, 17%, 31% and 46%, respectively [reaction (1)]. Similar



photochemical cyclodimerizations of **1** were observed in aqueous solutions of a series of C_n DAO with $n = 12, 14$ and 16 , and these are summarized in Table 1.

Cyclodimerization of **1a** gradually occurred after attaining a photostationary state (*trans*:*cis* ca. 2.2) after 30 min irradiation. A control experiment indicated that *cis*–*trans* isomerization was the only observable reaction in the photolysis of **1a** in methanol. It should be noted that the present C_n DAO surfactant systems improved the quantum efficiencies of the cyclodimers more than 10 times as much as that of the rod-like micelles of hexadecyltrimethylammonium cinnamate,^{1d} the cause of which is discussed below.

Table 3 Effect of pH on chemical yields for photocyclodimerization of **1a** in C₁₆DAO aggregates^a

pH ^b	Conversion (%)	Yields of products (%)			
		Dimers	(<i>syn</i> -HT : <i>syn</i> -HH : <i>anti</i> -HH) ^c	<i>cis</i>	<i>anti</i> -HH/ <i>syn</i> -HH
1.6	72	32	(4:46:50)	68	1.09
2.6	79	51	(—:42:58)	49	1.38
3.8	83	58	(8:24:58)	42	2.42
5.0	73	27	(—:29:71)	73	2.45
5.5	80	5	(—:—:—)	95	—

^a Irradiations were carried out with a Pyrex-filtered 300 W Hg lamp for 7 h for solutions of a concentration of 5.0×10^{-3} mol dm⁻³ **1a** and C₁₆DAO (1:1). ^b Control of the pH was performed by adding 5.0×10^{-3} mol dm⁻³ HCl or NaOH. ^c Figures in parentheses refer to the isomer distributions of the dimers.

Table 4 Aggregated structures of aqueous solutions of **1a** and C₁₆DAO in the absence or presence of coadsorbing carboxylic acids **2–4**^a

Coadsorbrates	[Coadsorbrates]:[1a] ^b		<i>M</i> ^c /g mol ⁻¹	<i>R</i> _G ^c /nm	<i>R</i> _H ^c /nm	Aggregated structures
	[C ₁₆ DAO]					
None	—:0.8 ^d		2.42×10^7	196	396	vesicles
	—:0.2		1.31×10^5	—	—	rod-like micelles
2	0.2:0.8		$>1.0 \times 10^7$	—	150	vesicles
	0.8:0.2		$>1.0 \times 10^7$	—	206	vesicles
3	0.2:0.8		$>1.0 \times 10^7$	—	160	vesicles
	0.8:0.2		$>1.0 \times 10^7$	—	158	vesicles
4	0.2:0.8		$>1.0 \times 10^7$	—	180	vesicles
	0.8:0.2		1.51×10^5	71.6	—	rod-like micelles

^a Light scattering measurements were carried out for solutions with a total concentration of 2×10^{-3} g cm⁻³ at 25 °C. The coadsorbates are phenylpropionic **2**, palmitic **3** and acetic acids **4**. ^b Concentrations of C₁₆DAO were equal to the sum of [**1a**] and [additive]; [**1a**] = 5.0×10^{-3} mol dm⁻³ (constant). ^c The molecular weight *M* and radius of gyration *R*_G were obtained from static light scattering measurements. The hydrodynamic radius *R*_G was obtained from dynamic light scattering measurements. ^d Cited from ref. 8d.

coincidence with the change in the aggregated structures from vesicles to micro emulsions, the major product from the vesicles being the *anti*-HH dimer.

Effects of the coadsorption of photoinactive carboxylates on the photocyclodimerization

Olefins **1** incorporated in the surfactant aggregates are subject to the above-mentioned [2 + 2] photocyclodimerization with high efficiencies and high regioselectivities (*i.e.* the formation of HH dimers). These results imply that the olefin molecules are aligned in a parallel orientation in the aggregate interior. In order to elucidate the molecular packing of the interior in more detail, the effect of the addition of photoinactive carboxylates was studied. Table 4 indicates that the aggregated structures are all vesicles when the remaining vacant sites of C₁₆DAO are involved in a complex with phenylpropionic **2** or palmitic acid **3**. On the other hand, acetic acid **4** had no effect on the aggregated structures of **1a** and C₁₆DAO. Water soluble **4** was definitely seen to be dissolved in the aqueous bulk solution and seems not to form any ion-pairs with C₁₆DAO. Therefore, the mixture of **1a**, C₁₆DAO and **4** experiences circumstances similar to the case without the additive, resulting in no noticeable influence on the aggregated structures. In contrast, the addition of higher carboxylic acid, **2** or **3**, changed the rod-like micelles to vesicles. This fact reflects the adequate hydrophobicity of the acid to form vesicles of 1:1 ion-pairs with C₁₆DAO.

In order to investigate the effect of vesicle formation on the photodimerization, UV irradiations were carried out for the systems with additives **2** and **3**. Fig. 1 shows the interesting effect of added carboxylates, **2** and **3**, on the yields and isomer selectivities of the cyclodimers. In the absence of additives, the yield of the photocyclodimers dropped sharply at a 0.2:1 ratio of **1a** and C₁₆DAO due to the change in the aggregates from vesicles to rod-like micelles. It is interesting to note that the addition of photoinactive carboxylates resulted in a remarkable effect on the photodimerization, *i.e.* a significant increase in cyclodimer yields and selectivity of *syn*-HH.

A clear contrast in behaviour between additives **2** and **3** can, however, be observed for the photochemical dimerization of **1a**.

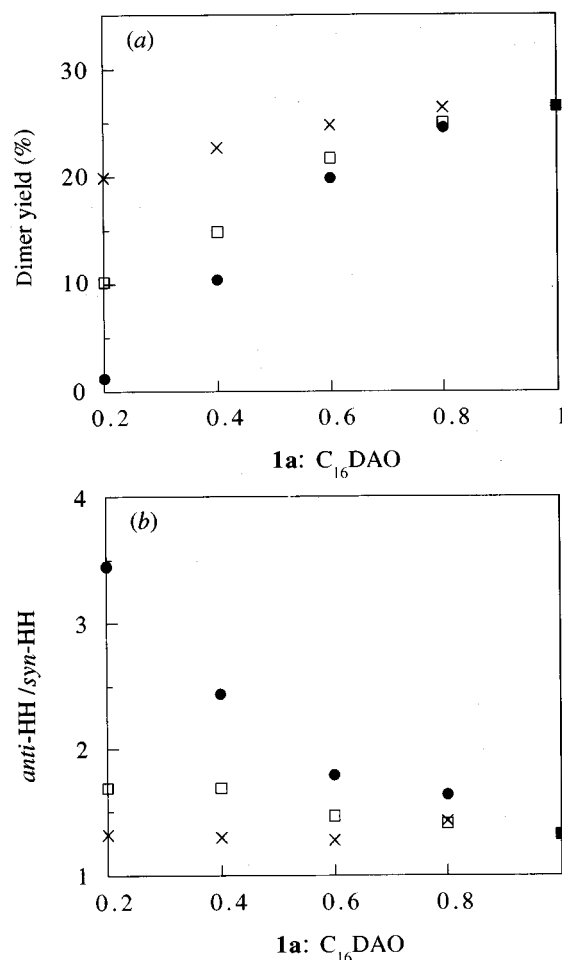


Fig. 1 The effect of additives **2** (□) and **3** (×), (●, no additive), on the photocyclodimerization for aggregates of **1a** and C₁₆DAO upon irradiation for 10 h; (a) yields and (b) selectivities. Concentrations of C₁₆DAO were equal to the sum of [**1a**] and [additives]; [**1a**] = 5.0×10^{-3} mol dm⁻³ (constant).

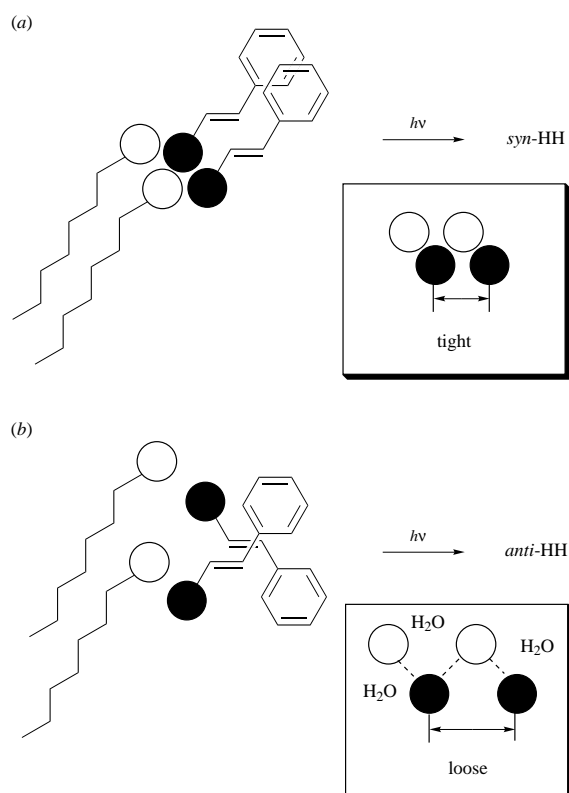


Fig. 2 Packing models for the formation of (a) *syn*-HH and (b) *anti*-HH dimers

Thus, the dilution effect of **1a** with carboxylic acids on the yields of the cyclodimers was significant for the case of **2** while only a slight effect could be observed for **3**. The former case is understandable since the molecular structure of **2** is similar to that of **1a** and they may be mixed homogeneously with each other in vesicles. The case of **3** is different in that the flexible structure of aliphatic acid **3** is different from that of cinnamic acid **1a**. Moreover, it is important to note that **3** is a surfactant in itself and ion-pairs of C_{16} DAO and **3** should act as double-chain surfactants to form stable vesicles.¹¹ Hence, it is probable that the almost total lack of any dilution effect in the case of **3** is due to the formation of nonhomogeneous molecular aggregates of **1a** and **3**. In other words, molecules **1a** and **3** are located at different sites within the vesicles, leading to a slight dilution effect of **3** on the photodimerization.

The selectivities of *syn*-HH are larger in the vesicle system reflecting its more rigid aggregated structure than that in the rod-like micelles. McNeil and Thomas¹² have reported that the head groups of didodecyldimethylammonium bromide vesicles are in closer proximity than those of hexadecylammonium bromide micelles, leading to the exclusion of water from the head group region. Likewise, molecules **1a** in the vesicles are more tightly aligned than those in the rod-like micelles. The formation of the *syn*-HH dimer requires closer packing of the **1a** molecules, as pictured in Fig. 2. We have previously reported that reversed micelles formed from **1a** and laurylamine in carbon tetrachloride gave a *syn*-HH dimer upon UV irradiation, but the addition of small amounts of methyl alcohol caused the major product to change dramatically to *anti*-HH, reflecting the looseness of the ion-pairs between **1a** and laurylamine.^{1d} The same picture is applicable to the present case of product change which depends on the aggregate forms from vesicles to rod-like micelles.

The ratios of *anti*- and *syn*-HH were different between additives **2** and **3**, although both of them formed vesicles. The lower ratios for additive **3** seems to indicate that the $3-C_{16}$ DAO complex forms a tighter aggregate than that of $2-C_{16}$ DAO. This is because the ion-pairs of **3** and C_{16} DAO behave as double-

chained surfactants to form stable vesicles, as mentioned above. On the other hand, the slightly higher ratio of *anti*- and *syn*-HH dimers indicates that the aggregates of $1a-2-C_{16}$ DAO are less tightly bound to each other. It can thus be seen that **1a** molecules in $1a-3-C_{16}$ DAO vesicles are more tightly bound to a neighbouring **1** favourably to form the *syn*-HH dimer. In conclusion, the present results show that photodimerizations of olefin molecules are controlled not only by their aggregated structures, micelles and vesicles, but also by the relative miscibility properties of the various components.

Experimental

General

Irradiations were carried out by means of a Eikosha PIH-300 medium mercury arc lamp (300 W) through a Pyrex vessel. HPLC was recorded on a Shimadzu LC-6A chromatograph with a CAPCELL PAK C18 UG120 S-3 μ m, Shiseido Co., Ltd. IR spectra were recorded on a Jasco FT/IR-300E. Static and dynamic light scatterings were recorded on a Otsuka Electronics DLS-700 dynamic light scattering spectrophotometer.

Materials

Unsubstituted and *p*-methoxycinnamic acids **1a** and **1b** were purchased from Tokyo Kasei Co., Ltd. and were recrystallized twice from benzene. C_{12} DAO was purchased from Fluka Chemie AG and was used without further purification. C_{14} DAO and C_{16} DAO were synthesized in accordance with the literature.¹³ Acids **2-4** were purchased from Nacalai Tesque, Inc. and were used without further purification. The photodimers of **1**, *syn*-HH, *anti*-HH and *syn*-HT were synthesized in accordance with the literature.^{4b,14}

Photoirradiation of **1** in aqueous C_n DAO solution

10 cm³ aqueous solutions of **1** and C_n DAO were prepared by sonication at 50–60 °C in an ultrasonic bath (BRANSON 5210) for several hours. The concentration of **1** was held constant at 5.0×10^{-3} mol dm⁻³ and the ratios of **1** to C_n DAO were varied from 0.2 to 1. For the study on the pH effect, adjustments of the pH of the solutions were performed by adding 5.0×10^{-3} mol dm⁻³ HCl or NaOH. The effect of coadsorbed carboxylates were investigated by adding photoinactive carboxylic acids to form ion complexes with the remaining C_{16} DAO; e.g., when the ratio of **1a** to C_{16} DAO was 0.2, the ratio of coadsorbed carboxylates to C_{16} DAO was 0.8. The solutions obtained were placed in Pyrex tubes and purged by argon gas for 15 min and were then irradiated with a 300 W medium-pressure Hg lamp at ambient temperature. The irradiated solutions were analysed by HPLC and detected at λ 225 nm using an eluent with the following ratio: a phosphoric acid solution (3.0×10^{-2} mol dm⁻³):methyl alcohol = 55:50 (pH = 3.5) at a flow rate of 0.5 cm³ min⁻¹; retention times (min), **1a**, 15; *cis*-isomer of **1a**, 10; *syn*-HH, 45; *anti*-HH, 65; *syn*-HT, 16.5.

Light scattering measurements and VEM observations

The aggregated structures of **1** and C_n DAO in aqueous solution were analysed by static and dynamic light scatterings reading at a total concentration of 2×10^{-3} g cm⁻³. A light of 488 nm wavelength from an argon ion laser was used, and the scattering angles were changed from 30° to 150°. The cell housing was filled with di-*n*-butyl phthalate and kept at 25 °C. Solvent and solutions were filtered through a membrane filter (Advantec; pore size, 0.45 μ m). Measurement of specific refractive index increment was carried out at 25 °C on an Otsuka Densi Differential Refractometer RM-102 with an iodine lamp at 488 nm using a Brice-type cell. The apparatus was calibrated by aqueous solutions of sucrose. VEM observations were carried out on a Nikon NTF-2 transmission differential interference contrast optical microscope attached to a video camera and cabled to a real-time digital image processing system. Details of the

measurements and analyses have been described previously in the literature.^{6b,8a,d}

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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Paper 7/02413D

Received 8th April 1997

Accepted 3rd September 1997