Water-Participation in the Crystalline-State Photodimerization of Cinnamic Acid Derivatives. A New Type of Organic Photoreaction

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A new type of organic photoreaction, a water-participation reaction in the crystalline state, has been investigated. The photoirradiation of *p*-formylcinnamic acid (*p*-FCA) crystals in the presence of water leads to 4,4′-diformyl-β-truxinic acid (*p*-FCA dimer) which has one molecule of crystal water. A comparison of the photodimerization carried out in the presence/absence of water revealed the effects of the water molecule on the reaction. That is, the water molecule is incorporated into the *p*-FCA dimer during the photodimerization process. Furthermore, the water accelerates the reaction rate of photodimerization, leading to the formation of the crystalline dimer, whereas only the water-free amorphous dimer results in the absence of water. In addition, by heating at 100—110 °C, the *p*-FCA dimer with a water molecule is converted into a water-free crystalline dimer, which is not attainable from a water-free amorphous dimer. The photodimerization of several β-form crystals of cinnamic acid derivatives has been examined from the viewpoint of water-participation: *p*-nitro, *p*-chloro, and 3,4-dichlorocinnamic acid were found to photodimerize in the same manner as *p*-FCA.

Schmidt and his co-workers$^{1)}$ studied extensively the photodimerization of cinnamic acid in the crystalline state and established the field of a typical topochemical reaction in which the crystal structure of the compound plays a decisive role in the reactivity. In preparation for preparing the dimer of the *p*-phenylenediacrylic acid diethyl ester,$^{2)}$ we have attempted the photodimerization of *p*-formylcinnamic acid (*p*-FCA) in the crystalline state and found that it was converted into the dimer with one molecule of crystal water if it was irradiated in the presence of water.$^{3)}$

Although a few dimers from cinnamic acid derivatives, for example α-truxillic acid, and its dichloride have been reported$^{4)}$ to include a solvent molecule by the procedure of crystallization, the reaction is a new type of photoreaction in which water is incorporated into the dimer during the photodimerization process.

In this paper, further details of the reaction will be presented in order to reveal the overall view of characteristics of the crystalline-state water-participation reaction.

Experimental

Preparation of Cinnamic Acid Derivatives. *p*-FCA$^{5)}$ was prepared by the condensation of terephthalaldehyde and malonic acid in the presence of piperidine and was separated from its by-product, *p*-phenylenediacrylic acid, by the extraction of crude product with acetone.

Other cinnamic acid derivatives were prepared according to the Reference.$^{1)}$ All these compounds were recrystallized from the suitable solvents for preparing β-form crystals and were confirmed not to include any water in the original crystals.

Photodimerization. As a typical experiment, the photodimerization of *p*-FCA will be described.

Photodimerization in the Presence of Water. *p*-FCA crystals (0.3 g) were dispersed in water (100 ml) in a Pyrex flask. The flask was then irradiated with a 450-W high pressure mercury lamp at room temperature. Upon 60 minutes' irradiation the absorpotion maximum of *p*-FCA (295 nm) shifted to 254 nm and *p*-FCA was converted into the dimer quantitatively. NMR (DMSO-d_6) ppm: 3.8—4.5 (m 4, CH) 7.1—7.7 (m 8, C_6H_4) 9.8 (s 2, CHO). Found: C, 64.76; H, 4.76%. Calcd for $C_{20}H_{18}O_6+H_2O$: C, 64.86; H, 4.90%.

When the dimer was heated at 100—110 °C *in vacuo* for 10 h its elemental analysis changed as follows. Found: C, 68.48 H, 4.25%. Calcd for $C_{20}H_{18}O_6$: C, 68.18; H, 4.58%. The dimer can be recrystallized from ethanol–water.

Photodimerization in the Absence of Water. *Method 1*: *p*-FCA crystals were placed over phosphorus pentoxide in a petri dish with a glass cover. The dish was then irradiated with sun-light or a 450-W high-pressure mercury lamp until no further change was observed in the UV spectrum. Found: C, 67.71; H, 4.44%. Calcd for $C_{20}H_{18}O_6$: C, 68.18; H, 4.58%. *Method 2*: *p*-FCA crystals (0.3 g) were dispersed in thoroughly dried hexane (100 ml) and irradiated for 2 h in the way described above.

Identification and Quantitative Analysis of Water in the Dimer. All the crude dimers, which has been prepared in the presence of water and has been confirmed to be free from monomers by a study of their UV spectra, were dried in a dessicator over phosphorus pentoxide for 2 days at room temperature *in vacuo*. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were carried out with a Rigaku Standard DSC-TGA instrument at the heating rate of 10 °C/min under nitrogen.

The amounts of water in the dimer were determined by titration with Karl Fischer reagent (Mitsubishi Kasei). An accurately weighed dimer was dissolved in a dehydrated solvent (Mitsubishi Kasei) and titrated with a Karl Fischer reagent. The amounts of water in the dimer were calculated by means of the following equation:

$$\text{Weight (\%) of water in the dimer} = \text{ml of Karl Fischer reagent consumed} \times \text{factor of Karl Fischer reagent/weight of the dimer}$$

Formation of Anhydride Dimer. The dimer (0.3 g) was refluxed in acetic anhydride for 5 h. After removal of acetic anhydride, the residue was washed with ethanol and dried. The obtained product showed the absorption peaks at 1880 and 1790 cm^{-1} on the IR spectrum.

Results and Discussion

Crystalline Modification of p-*FCA.* Two crystalline modifications were found in *p*-FCA crystals, depending on the crystallization procedure. From an ethanol solution, photo-active crystals (β-form) are obtained, while photostable crystals (γ-form) are obtained from an acetone solution. The two crystals give different intensities of absorption peaks (940, 990, and 1210—1230 cm^{-1}) in the IR spectra which are due to a carboxylic acid residue. The X-ray diffraction patterns are also different from each other (β-form, 17.2, 26.6°, γ-form, 16.9, 19.3, 23.6, 25.4, 26.8, 28.7°). However, both crystals show the same melting point (249 °C) and no phase-transition points have been observed by DSC analysis over the temperature range from room temperature to melting point.

Photodimerization of p-*FCA.* The product obtained by the irradiation of *p*-FCA crystals in the presence of water was identified as its dimer on the basis of the following data.

1. The IR spectrum of the product (Fig. 1) shows the disappearance of double bonds (1640 cm^{-1}, νC=C aliphatic).
2. In the NMR spectrum of the product, cyclobutane ring protons appear at 3.8—4.5 ppm.

However, the results of the elemental analysis of the product do not agree with the calculated value of the dimer and suggest the presence of one molecule of water in each dimer. The DSC diagram (Fig. 2-A) of the dimer shows three endothermic peaks at 105, 178, and 180 °C. The 105 °C peak which is broad and is accompanied by a weight loss, is considered to be the elimination of water from the dimer since the results of the elemental analysis of heat-treated dimer show that it has no water molecule and the DSC diagram shows two peaks at 178 and 180 °C, and no peak at 105 °C. The amounts of water in the dimer was determined to be 4.9% by means of the Karl Fischer reagent. This value indicates that each dimer has one molecule of water (Calcd 4.8%). Thus the presence of water in the *p*-FCA dimer was concluded. The peak at 178 °C was found to be due to the formation of cyclic anhydride from carboxylic acid residues; this was confirmed by the IR spectrum of the dimer heated up to 178 °C. The peak at 180 °C is its melting point. The IR spectrum of the water-free dimer is given in Fig. 1-B. The difference in the peaks at 3500, 1730, and 1350 cm^{-1} from those of the dimer with water (Fig. 1-A) is concluded to be due to the elimination of water. The X-ray diffraction patterns of the water-free dimer become different from those of the dimer with water.

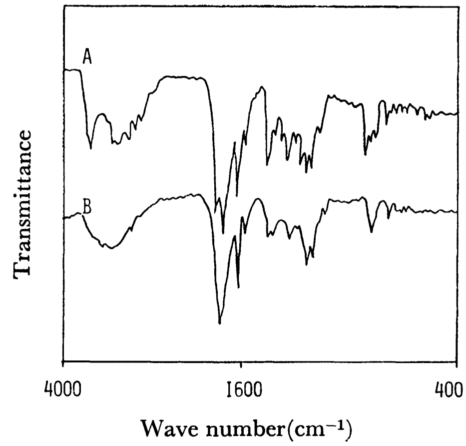


Fig. 1. IR spectra of *p*-FCA dimers.
A: The dimer obtained in the presence of water, B: the water-free dimer obtained by heating above dimer.

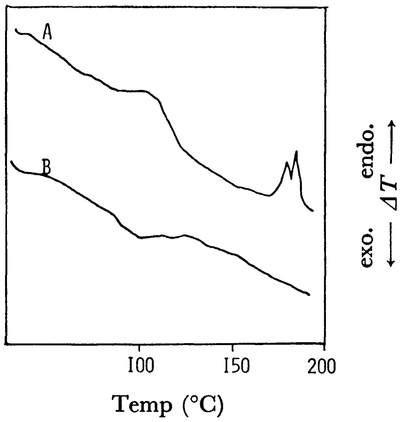
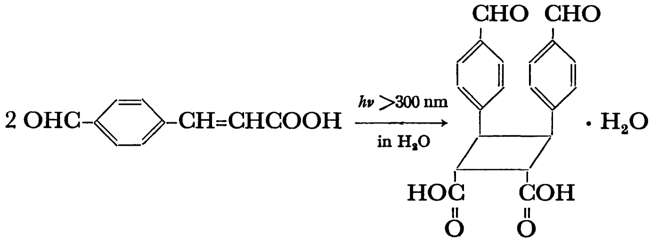


Fig. 2. DSC diagrams of *p*-FCA dimers.
A: The dimer obtained in the presence of water, B: the dimer obtained in the absence of water.

The structure of the dimer was dertermined by anhydride formation from carboxylic acid residues. The IR spectrum of anhydride dimer indicates the formation of five-membered-ring anhydride and the NMR spectrum of its cyclobutane-ring protons is symmetrical. These data indicate the formation of a β-truxinic acid type dimer (4,4′-diformyl-β-truxinic acid).



When the dimer in an ethanol or a dimethyl sulfoxide solution was irradiated with light (251 nm), it decomposed into *p*-FCA with cyclobutane-ring cleavage (Fig. 3).

The photodimerization of *p*-FCA crystals in the absence of water proceeds very differently in several points. The product obtained in the absence of water shows almost the same IR spectrum as that of the water-free dimer (Fig. 1-B) and the same NMR spectrum as that obtained in the presence of water.

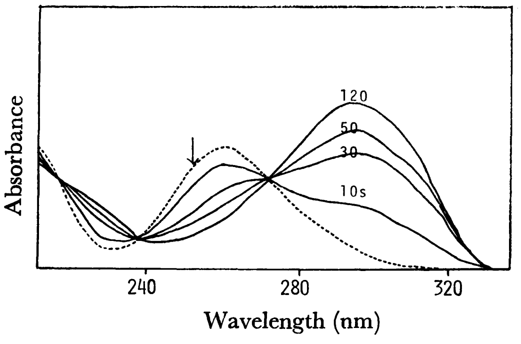


Fig. 3. Change in UV spectrum on irradiation of *p*-FCA dimer in ethanol solution.
------: Before irradiation, ——: after irradiation.

In the DSC diagram (Fig. 2-B) only the exothermic peak (100—110 °C) was observed, and there was no weight loss. The elemental analysis of the product agreed with the calculated value of the dimer without water molecule. From these data it may be concluded that the product obtained in the absence of water is the same β-truxinic acid-type dimer, but without water.

Remarkable differences connected with both dimers were found in the rates of photodimerization and crystallinity. It is interesting to note that photodimerization proceeds very rapidly, forcibly taking up the surrounding water. For example, *p*-FCA crystals embedded in the KBr pellet photodimerize in about 10 min, with the incorporation of the water which is absorbed in KBr.

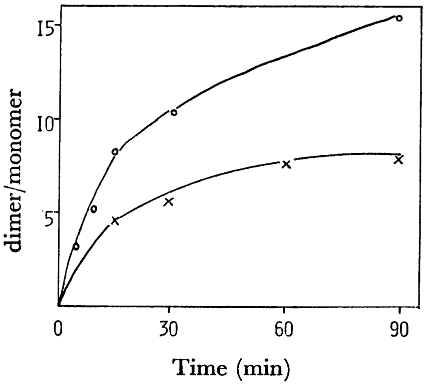


Fig. 4. Plot of dimer/monomer *vs.* time.
—○—: In water, —×—: in hexane.

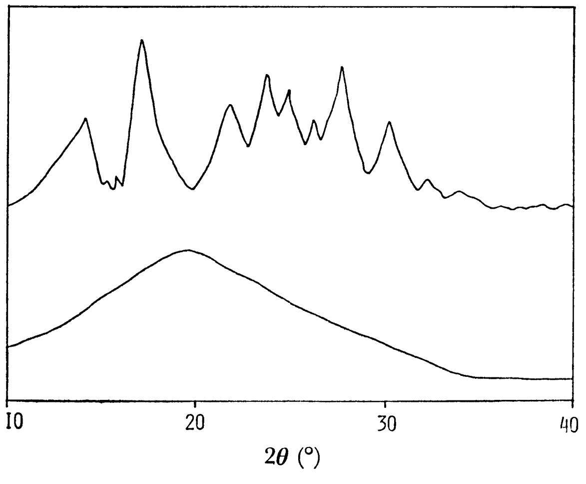


Fig. 5. X-Ray diffraction patterns of *p*-FCA dimers.
A: The dimer obtained in the presence of water,
B: the dimer obtained in the absence of water.

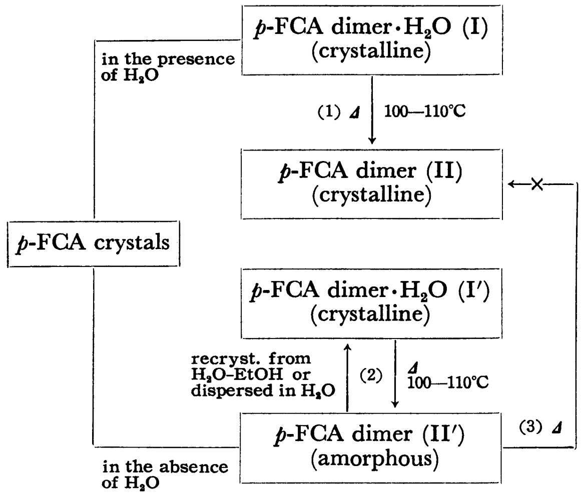
The plot of the dimer/monomer rate *vs.* the reaction time in water and hexane is shown in Fig. 4. The presence of water apparently accelerates the reaction. With respect to the crystallinity there is a prominent difference between two dimers (Fig. 5). The crystalline dimer was obtained in the presence of water, while amorphous one was obtained in the absence of water. It seems that the water molecule assists to crystallize the dimer, as is often observed in protein molecules.

The relationship of these two kinds of dimers is shown in Scheme 1.

(1) The dimer with one molecule of water (I) can be converted into the water-free crystalline dimer (II) by heating 100—110 °C *in vacuo*.

(2) The water-free amorphous dimer (II′) becomes the crystalline dimer with water (I′) by dispersing it in water as long as the irradiation time or by recrystallization from a water–ethanol solution. This process is not affected by light. The IR spectrum and X-ray diffraction patterns of the dimer (I) and the dimer (I′) are nearly identical; however, their thermal behavior is peculiarly different. The DSC diagram of the dimer (I′) shows only an endothermic peak at 100—110 °C, and it is dehydrated at that temperature not into the dimer (II) but into the water-free amorphous dimer (II′). In this point, the dimer (I′) is different from the dimer (I).

(3) The DSC diagram (Fig. 2-B) of the water-free amorphous dimer (II′) shows only an exothermic peak at 100—110 °C, which may be due to crystallization. However, it could not be converted into the water-free crystalline dimer (II) by heating at that temperature.



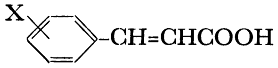
Scheme 1.

The observation (2) and the fact that a water solution saturated with *p*-FCA does not yield the dimer on irradiation imply that water molecule is incorporated into the dimer not after the formation of the dimer but during the photodimerization process.

Though the details of the reaction mechanism are not established yet, it is probably similar to that proposed for the solid-gas reaction of carboxylic acid and ammonia.[6] That is, if *p*-FCA crystals are exposed to light in an atmosphere of water, a dimer would be formed with the incorporation of the water molecule; at the same time, the disorientation of the crystal layer occurs sufficiently to permit the water molecule to diffuse into the next layer of *p*-FCA crystals, where the process is repeated.

Survey of Water Participation Crystalline Photodimerization of Other Cinnamic Acid Derivatives. In order to extend this new type of photodimerization of *p*-FCA to other compounds, the photodimerization of several other cinnamic acid derivatives was reinvestigated from the

Table 1. Photodimerization of cinnamic acid derivatives

	Elemental analysis (%)	Endo peaks on DSC diagrams (°C)	Amounts of water (%)
Photodimerization with water participation			
p-CHO-	C, 64.86, H, 4.90[a]	100—120,[e] 178,[f] 180[g]	4.9 (4.8)[a]
	C, 64.74, H, 4.76[b]		
p-NO_2-	C, 53.47, H, 3.99, N, 6.93[a]	100—120,[e] 216,[f] 226[g]	5.4 (4.5)[a]
	C, 53.52, H, 3.95, N, 6.71[b]		
p-Cl-	C, 58.03, H, 4.00[c]	85—100,[e] 200[h]	3.0 (4.7)[a]
	C, 57.60, H, 4.42[b]		
3,4-diCl-	C, 48.79, H, 2.69[c]	90—100,[e] 149[h]	2.5 (4.0)[a]
	C, 48.86, H, 2.82[b]		
Photodimerization without water participation			
p-H	—	212—213[h]	
p-Br	C, 47.60, H, 3.11[d]	212—214,[f] 224[g]	
	C, 47.36, H, 3.36[b]		
m-NO_2-	C, 55.96, H, 3.65, N, 7.25[d]	206[h]	
	C, 54.12, H, 3.66, N, 6.89[b]		
o-Cl-	C, 59.08, H, 3.73[d]	215—216[h]	
	C, 59.20, H, 3.87[b]		
2,4-diCl-	C, 49.80, H, 2.80[d]	240[h]	
	C, 50.39, H, 2.65[b]		
2,6-diCl-	C, 49.80, H, 2.80[d]	224[h]	
	C, 49.22, H, 2.45[b]		

a) Calcd as including one molecule of H_2O. b) Found. c) Calcd as including 1/2 molecule of H_2O. d) Calcd for dimer. e) Peak due to dehydration. f) Peak due to formation of anhydride. g) Melting point of anhydride. h) Melting point of dimers

viewpoint of water participation. Since the 1,2-*cis* conformation of carboxylic acid residues on a cyclobutane ring seems to be important factor in the incorporation of water, the photodimerization of several β-form crystals of cinnamic acid derivatives has been attempted in a water dispersant. The water participation was checked by the method described before. The results are given in Table 1. *p*-Nitro, *p*-chloro, and 3,4-dichlorocinnamic acid were found photodimerize in essensially the same way as *p*-FCA. The dimers from these monomers have more or less the same properties as those described in Scheme 1. However, the amounts of water incorporated into the dimer are different depending on the dimer. The dimers from β-form crystals of cinnamic acid, *o*-chloro, *m*-nitro, *p*-bromo, 2,4-, and 2,6-dichlorocinnamic acid did not incorporated any water during the photodimerization process.

Summarizing the results of the survey on the compounds which photodimerize with water participation, it can reasonablly be suggested that there is a possibility that the β-form crystals of *para*-substituted cinnamic acids photodimerize in this manner.

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