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# WATER PARTICIPATION IN THE CRYSTALLINE STATE PHOTOREACTION PHOTODIMERIZATION OF p-FORMYLCINNAMIC ACID

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p-Formylcinnamic acid ( p-FCA ) crystal photodimerizes with incorporation of water to give rise to the monohydrated dimer crystal. When p-FCA crystal is photoirradiated in the absence of water, water-free amorphous dimer is obtained. p-Nitro- and p-chlorocinnamic acids were found to dimerize in the same manner as p-FCA.

p-Formylcinnamic acid$^{1)}$ was found to dimerize in the crystalline state. The reaction is quite novel in the view of crystalline organic reaction influenced by the water in the atomosphere. That is, water molecule is participated in the photodimerization of p-FCA crystal resulting the dimer crystal which includes one molecule of water per dimer molecule.

Two crystal modifications were found in p-FCA depending on crystallization procedure as is the case of cinnamic acid.$^{2)}$ From ethanol solution photo-active crystal is obtained while photo-stable crystal from acetone solution. It was confirmed by elemental analysis that these crystals do not have water of crystallization. Both crystals give the different x-ray diffraction patterns and show the different intensity of absorption in IR spectrum due to carboxylic acid ( 940, 990 and 1210-1230 cm$^{-1}$ ). However both crystals show the same melting points ( 249°C ) and any phase transition point has not been observed by differential scanning calorimetry ( DSC ) over a temperature range from room temperature to melting point.

In a typical experiment, crystal of p-FCA ( 0.3 gr ) was dispersed in water ( 100 ml ) using pyrex flask and irradiated with 500 W high pressure mercury lamp at room temperature. p-FCA has its absorption maximum at 295 nm in ethanol

( $\epsilon$ 31,000 ). The photodimerization proceeds very rapidly and is completed after 30 minutes in quantitative yield. On irradiation absorption maximum at 295 nm shifted to 254 nm in ethanol ( $\epsilon$ 26,000 ) as shown in Fig. 1.

The product is crystalline white with the melting point of 180°C. Its nmr spectrum shows aldehyde proton ( 9.8 ppm, 2H ), benzene protons ( 7.1-7.7 ppm, 8H ) and cyclobutane protons ( 3.8-4.5 ppm, 4H ). IR spectrum ( Fig. 2-A ) indicates disappearance of -C=C- bonds ( 1640 cm$^{-1}$ ). From these data it is reasonable to conclude that the product is the dimer of p-FCA formed by cycloaddition of two double bonds. However, the result of elemental analysis of the product does not agree with the calculated value of the dimer and suggests the presence of additional one molecule of $H_2O$ in each dimer unit. ( Calcd. for $C_{20}H_{18}O_6$ ( % ), C;68.18 H;4.58, Calcd. for $C_{20}H_{18}O_6 + H_2O$ ( % ), C;64.86 H;4.90, Found ( % ), C;64.74 H;4.76 ).

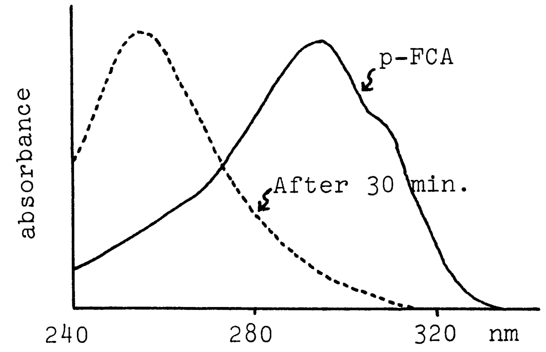


Fig. 1 The change of UV spectrum on irradiation.

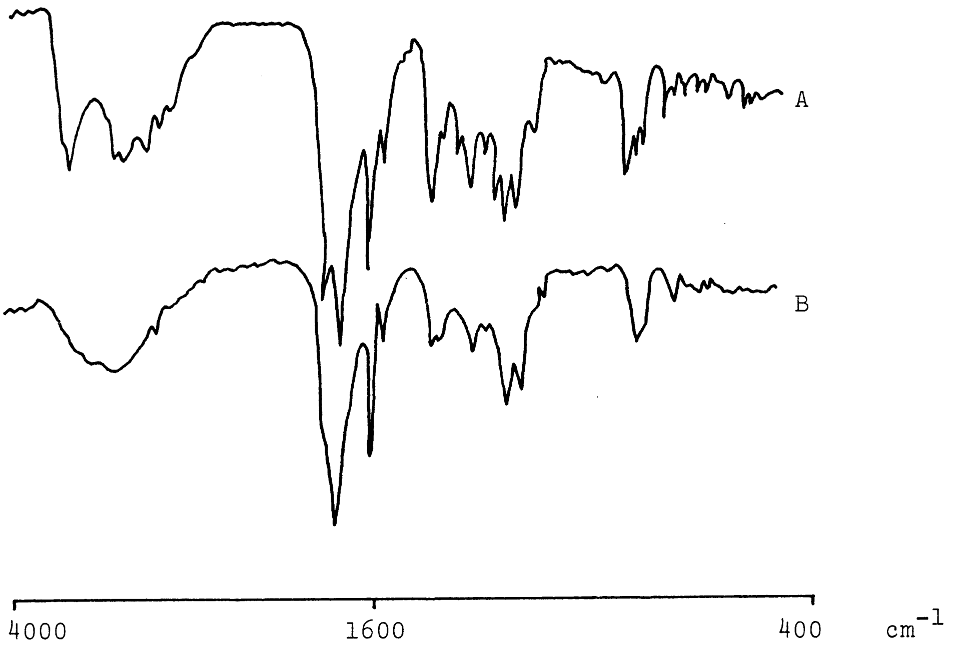


Fig. 2 IR spectra of p-FCA dimer with crystal water-A and water-free dimer-B

DSC analysis of the dimer shows three endothermic peaks at 105°C, 178°C and 180°C. The peak ( 105°C ) which is broad and accompanies with the weight loss, could be due to the elimination of water from dimer crystal.
In order to confirm this assignment of the peak at 105°C, the dimer was heated at 100-110°C in vacuo for 10 hours. DSC analysis of the dimer thus treated shows two peaks at 178°C and 180°C and no peak at 105°C, and thus, supports the assignment to the DSC curve of the dimer with crystal water. Its elemental analysis also shows water-free dimer was obtained by this treatment. ( Calcd. for $C_{20}H_{18}O_6$ ( % ), C;68.18 H;4.58, Found ( % ) C;68.46 H;4.25 ).
The peak at 178°C was found to be due to the formation of cyclic anhydride from carboxylic acid residues which was confirmed by IR spectrum of the dimer heated up to 178°C. The peak at 180°C is its melting point.
IR spectrum of water-free dimer is given in Fig. 2-B. The difference in peaks at 3500, 1730 and 1350 $cm^{-1}$ from those of the dimer with crystal water is considered to be due to the elimination of water. The x-ray diffraction patterns of water-free dimer became different from that of monohydrated dimer.

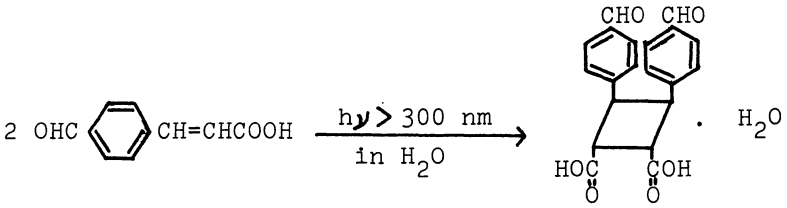
From these data it is concluded that the photodimerization of p-FCA crystal proceeds with incorporation of one molecule of water in each dimer.

When the crystal of p-FCA is photoirradiated in the absence of water, dimerization proceeds very differently. For example, p-FCA crystal dispersed in thoroughly dried n-hexane photodimerizes more slowly in 85 % yield.
The dimer thus obtained was found to be water-free dimer ( Fig. 2-B ) by IR spectrum and has the same steric configuration of cyclobutane as that of the dimer obtained in the water dispersant.
However, obvious difference between two dimers is that the dimer obtained in the absence of water is completely amorphous by x-ray diffraction analysis.
Furthermore, recrystallization from the solvent containing water converted the water-free dimer into the dimer with one molecule of water in the crystal.

From these observation it is evident that the water molecule plays important role to accelerate this type of photodimerization and/or to crystallize the dimer.

The structure of the dimer was determined by anhydride formation from carboxylic acid residues. The anhydride derived by heating the dimer in acetic anhydride indicates the exsistance of five membered ring anhydride on IR spectrum ( 1880 and 1790 $cm^{-1}$ ). Nmr spectrum of cyclobutane protons of thus obtained anhydride dimer is symmetrical.

These facts suggest the structure of the dimer is trans, head to head type like β-truxinic acid.



This is the first example of water participation in crystalline state organic reaction that is of particular interest in the view of crystal deterioration by the action of sunlight in the ordinary atomosphere.

Furthermore, the crystalline state photodimerization which yields derivative of β-truxinic acid1), 3) was re-examined from the view point of water participation. As the result, p-nitro- and p-chlorocinnamic acids dispersed in water were found to dimerize in the same manner as p-FCA.

( Elemental analysis; p-nitrocinnamic acid dimer Calcd. for $C_{18}H_{14}O_8N_2$ + $H_2O$ ( % ), C;53.47 H;3.99 N;6.93, Found ( % ) C;53.52 H;3.95 N;6.71

p-chlorocinnamic acid dimer Calcd. for $C_{18}H_{14}O_4Cl_2$ + $H_2O$ ( % ), C;56.41 H;4.20, Found ( % ) C;57.60 H;4.42 )

Further detail of this type of photodimerization will be described later.

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