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EFFECTS OF TEMPERATURE AND DISPERSANT ON PHOTOIRRADIATION OF p-FORMYLCINNAMIC ACID CRYSTAL

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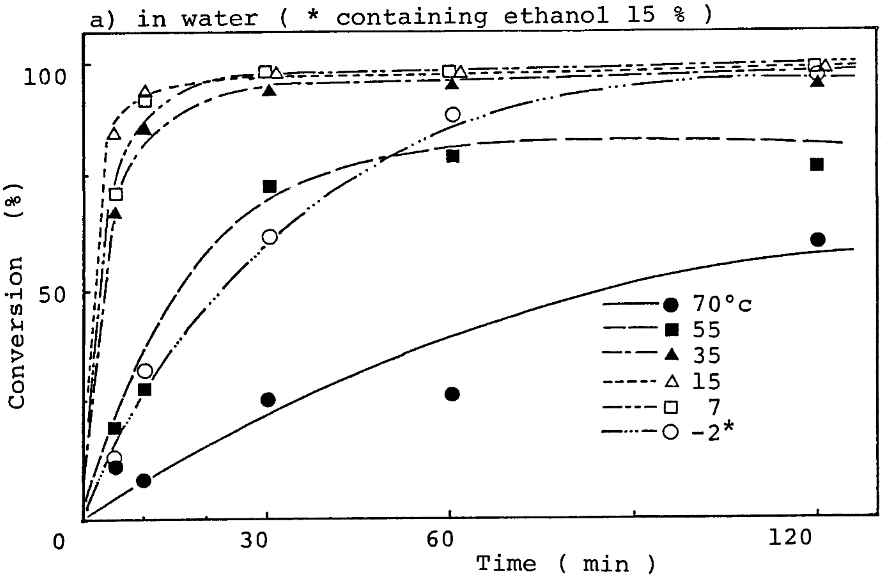
p-Formylcinnamic acid (p-FCA) crystal dimerizes quantitatively via the crystal lattice controlled photochemical process to form 4,4'-diformyl-β-truxinic acid (p-FCA dimer). The crystalline dimer was obtained quantitatively on photoirradiation of p-FCA crystal below 35°C in aqueous dispersant and included one mole of crystal water (p-FCA dimer·H_2O). In non-aqueous dispersant, the dimer was produced quantitatively below about 55°C; the amorphous dimer was produced in the range of about 55°C to 0°C, and the crystalline dimer below 0°C, the degree of crystallinity increasing with decreasing the reaction temperature. Maximal reaction rates were observed at 15°C in water and at 35°C in non-aqueous dispersants. Three kinds of dimers (crystalline p-FCA dimer·H_2O , and crystalline and amorphous p-FCA dimers) were interconvertible by appropriate treatments.

Several olefin crystals are photochemically converted into corresponding cyclobutane derivatives by cycloaddition reaction under a strict control of reacting crystal lattice (topochemical process).[1] Among those, of particular interest is the photodimerization of p-formylcinnamic acid (p-FCA) crystal in which the water molecule shows striking effect on the reaction behavior and, at the end of reaction, the molecule is taken into the p-FCA dimer (4,4'-diformyl-β-truxinic acid) crystal as a crystal water.[2],[3]

In order to elucidate the features of the reaction of p-FCA crystal to a further extent, the present study is focused on the effect of reaction temperature on kinetic behavior in the presence and in the absence of water, and on the morphology of final products. The crystals of β-form p-FCA (0.3 g) were dispersed in 100 ml of water or non-aqueous dispersants (silicone oil or n-hexane), then irradiated with a 120 W high pressure mercury lamp without a filter with constant stirring. Non-aqueous dispersants had to be thoroughly dehydrated, as trace amounts of water affected the crystallinity of the products.

Fig. 1, (a) and (b), shows the plots of time versus conversion in water and in the silicone oil (Shinetsu Chem. KF-96L) at various temperatures. The conversion was determined by UV spectroscopy. The dimerization proceeded quantitatively below about 55°C in the silicone oil. With increasing the temperature the dimer yield gradually decreased. As far as the dimer yield is concerned, the temperature dependence of the time versus conversion curve seems to be explained in terms of topochemi-

a) in water (* containing ethanol 15 %)



b) in the silicone oil

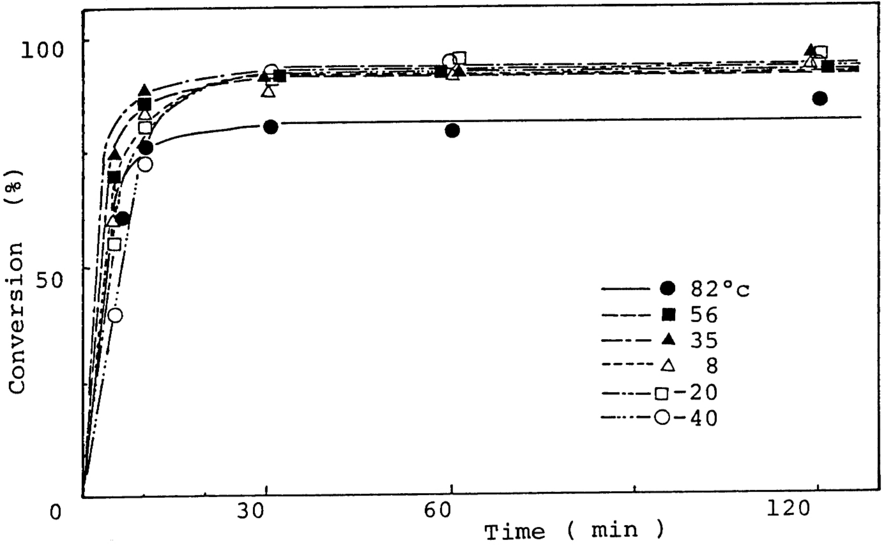


Fig. 1. Temperature effect on conversion of p-FCA crystal photoirradiated in respective dispersant.

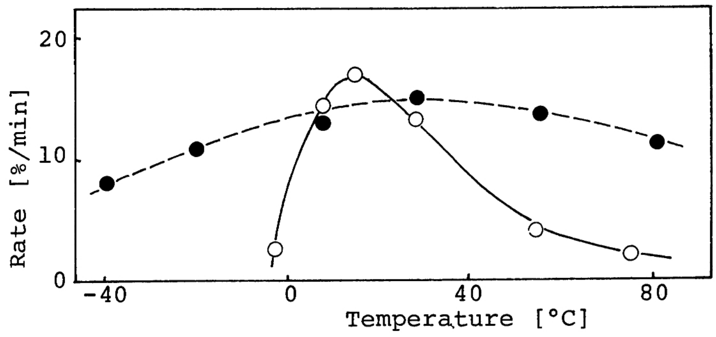


Fig. 2. The initial reaction rates of dimer formation. (○: dispersed in H_2O, ●: in the silicone oil)

cal process which requires the rigid crystal lattice of reactant.[4)]

However, p-FCA showed unique behaviors in water. The p-FCA dimer formed in water was highly crystalline irrespective of reaction temperature, in spite of the fact that the p-FCA crystal fairly soluble in water (solubility; 0.17 g p-FCA/ 100 ml water, 55°C), and that the stoichiometric amount of water was not included in the resulted dimer (0.3 H_2O at 55°C). The reaction rates were estimated from the conversion at 5 minutes' photoirradiation (Fig. 2). In water the maximal rate (16.9 % / min) is seen at about 15°C which is a little lower than the temperature where the final dimer yield begins to decrease. The observed optimal temperature for the maximal reaction rate suggests that a certain degree of thermal vibration of the molecules in the crystal is necessary for the most effective lattice controlled photodimerization.

Although it was reported in the previous paper[3)] that water accelerated the photodimerization rate of p-FCA crystal, such an accele-

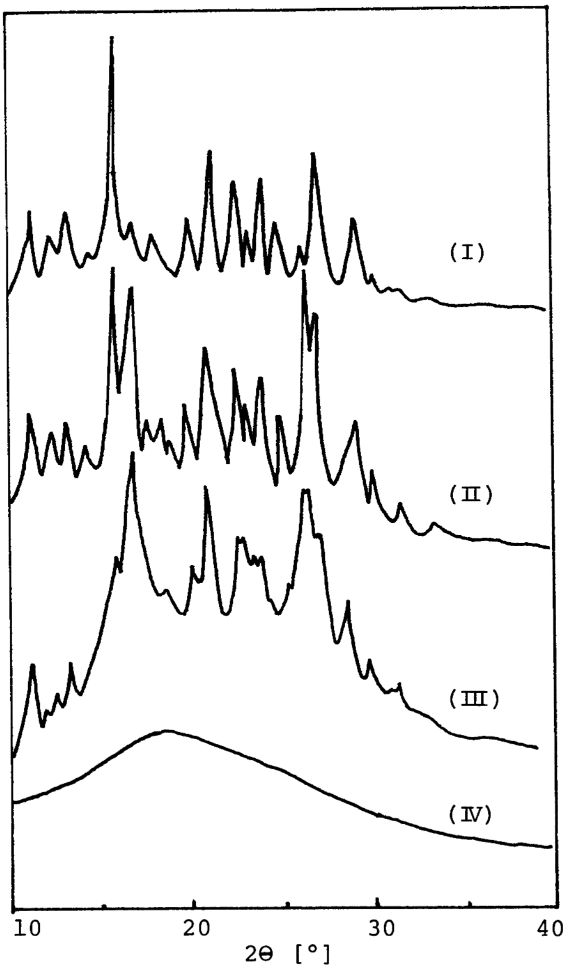


Fig. 3. X-ray diffraction patterns of p-FCA dimers. (I) Dimer•H_2O prepared by photoirradiation at 15°C in water. (II) Water-free dimer obtained by heating the dimer (I) at 100°C for about 1 hour. (III) Water-free dimer prepared by photoirradiation at -45°C in the silicone oil. (IV) Water-free dimer prepared by photoirradiation at 35°C in the silicone oil.

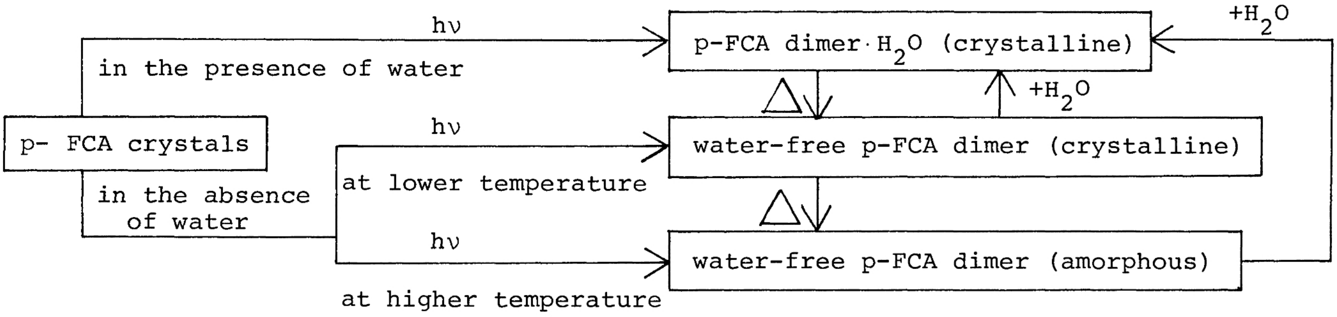
rating effect is not generally observed over a wide range of temperature as seen in Fig. 2. The temperature for the maximal rate in the silicone oil (15 % / min) is about 35°C. The temperature is also about 35°C when n-hexane was used in place of silicone oil.

X-ray diffraction patterns of four kinds of p-FCA dimers are shown in Fig. 3, (I)-(IV). Although X-ray diffraction patterns of three kinds of crystalline dimers (I)-(III) resemble each other, there are some distinct differences between two dimers of them, (I) and (III). The peaks at 16.1°, 25.0° and 26.9° (2θ) are characteristic to the dimer (I) and those at 16.9° and 26.5° (2θ) to the dimer (III). From the diffraction, the dimer (II) seems to be a mixture of (I) and (III). As shown in Fig. 3, (III) and (IV), the dimer prepared at -45°C is considerably crystalline whereas the dimer prepared at 35°C is amorphous. Amorphous dimer (IV) is also obtainable by heating the dimer (II) at 100 °C for additional 5 hours.

From the observation of the morphology of resulted dimers, it was observed that both water-free crystalline and amorphous dimers could be produced from the p-FCA crystal in non-aqueous dispersant and that the degree of crystallinity became higher with decreasing the reaction temperature in the range of 0°C to -45°C. When the reaction is carried out at room temperature, the presence of water appeared to be a determining factor for the formation of crystalline p-FCA dimer. However, by the present study it was demonstrated that crystallinity of the product obtained by the reaction in non-aqueous dispersant was controlled by the reaction temperature as is well known in the topochemical reaction of several olefin crystals.$^{3)}$ It should be emphasized that the temperature for the maximal rate in non-aqueous dispersant was observed in the temperature range where the crystal-to-amorphous transformation occurred.

The steric configuration was studied by ^{13}C-NMR and concluded to be identical of all the dimers. By the heat-treatment of (I) and the treatment of (III) and (IV) in aqueous medium, p-FCA dimers (I)-(IV) were confirmed to be essentially interconvertible as shown in Scheme I, if the question as to the degree of crystallinity was put aside. For example, the amorphous water-free p-FCA dimer was converted into the crystalline p-FCA dimer•H_2O when suspended in water at room temperature for 20 days, of which the crystallinity was not so high as the p-FCA dimer•H_2O produced directly by the photoirradiation of p-FCA crystal in water.

Scheme. I.



In conclusion the photodimerization behavior of p-FCA depends upon the dispersant to a great extent. In water the dimer obtained was highly crystalline, and the yield was quantitative below 35°C, and gradually decreased above 35°C. In non-aqueous dispersant, the amorphous dimer was obtained above 0°C, and the fairly crystalline dimer was obtained below 0°C, the degree of crystallinity increasing with decreasing the reaction temperature. The dimer yield was quantitative below 55°C, and gradually decreased above 55°C.

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