Spectroscopic Studies of Photochemical Reactions in Organic Solids. Photodimerization of *p*-Formylcinnamic Acid

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Raman phonon spectroscopy and electronic absorption and emission spectroscopy have been used to study the mechanism of reaction and the role of electron-phonon coupling in determining the photoreactivity of *p*-formylcinnamic acid (*p*-FCA) in the crystalline state. Raman and infrared spectroscopy in the internal vibration region have been used to characterize the reactant *p*-FCA and the dimeric product *t*-3,*t*-4-bis(*p*-formylphenyl)-*v*-1,*c*-2-cyclobutanedicarboxylic acid. Phonon spectroscopy reveals that the reaction proceeds principally by a heterogeneous mechanism though a homogeneous mechanism in the initial stage of short time domain can not be ruled out. The electronic spectroscopy suggests a strong electron-phonon coupling in the monomer crystal.

Recently Raman phonon spectroscopy has been successfully used to study the mechanism and the kinetics of solid state photoreaction in organic crystals.[1–4] Phonon participation and strong electron-phonon coupling have been shown to be involved in solid state photodimerization reaction of 2,6-dimethyl-*p*-benzoquinone.[3] The study revealed that the reaction is homogeneous in the initial stage but becomes heterogeneous in the later stage.

A new type of crystalline state photodimerization has recently been reported by Nakanishi *et al.*[5,6] in case of some cinnamic acid derivatives. In *p*-FCA, for example, it has been shown that a molecule of water is incorporated in dimer during the photodimerization process. We have used the phonon spectra, sampled as a function of reaction progress, to study this photoreaction to see if the reaction is homogeneous or heterogeneous in the molecular level. The electronic absorption and emission spectroscopy on dimerization reaction progress have been studied. The electronic absorption spectroscopy has also been used to determine the extent of reaction progress. The laser Raman spectroscopy and infrared spectroscopy have been used to obtain intramolecular vibrations of the reactants and the products as well as the partially converted samples. These intramolecular

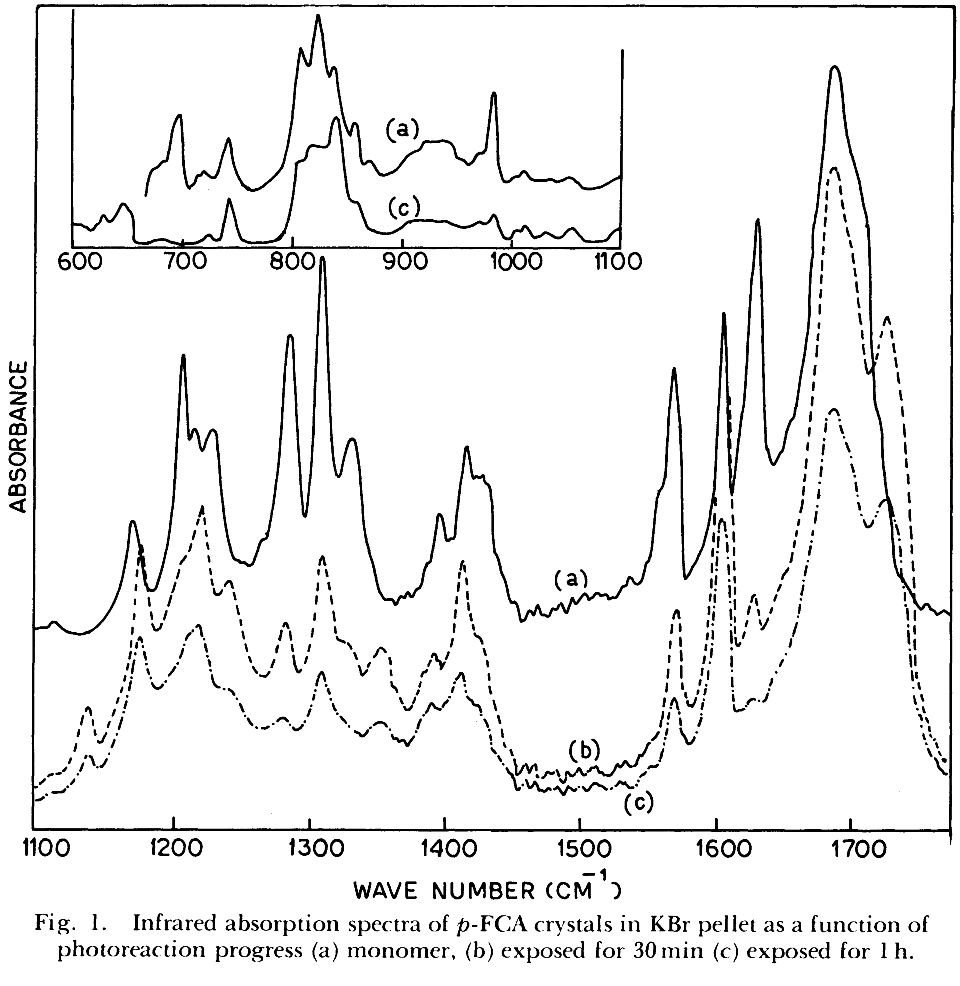

Fig. 1. Infrared absorption spectra of *p*-FCA crystals in KBr pellet as a function of photoreaction progress (a) monomer, (b) exposed for 30 min (c) exposed for 1 h.

vibrations have also been used to characterize the materials as well as to study the mechanism of the reaction. In this paper we report our results.

Experimental

p-FCA prepared as described earlier[6)] was further purified by repeated crystallization from ethanol. Crystals were finally grown from ethanol and acetone. Photodimerization was carried out by using a 750 W Xe lamp with the *p*-FCA crystallites dispersed in water in a quartz vessel at room temperature. For the specific set up, almost complete photodimerization was obtained in one hour. The experimental set up was the same as reported earlier.[3)] The electronic absorption spectra were run in Shimadzu UV-Vis 210 A Spectrophotometer. The emission spectra were run in Perkin-Elmer MPF 44 A Spectrofluorimeter. The infrared spectra were run in a KBr pellet on a Beckman Spectrophotometer (Model 4240).

Results and Discussion

Two crystalline modifications of *p*-FCA crystals are known. Crystals grown from ethanol solution are photoreactive and belong to the β-form while γ-form of crystals, obtained from acetone solution, are photostable. The phonon spectra of the two forms are distinctly different as are their reported X-ray diffraction patterns.[6)] Nakanishi[6)] *et al.* have not observed any phase transition point.

The extent of photodimerization has been monitored by studying the electronic absorption spectra. Monomer *p*-FCA has its absorption maximum at 295 nm in ethanol solution at room temperature whereas the photodimer under similar condition has its maximum at 257 nm.

Table 1. Infrared bands (in KBr) of *p*-FCA crystal before and after photodimerization

Monomer bands/cm^{-1}	Dimer bands/cm^{-1} (After extensive dimerization)$^{a)}$	Inference
698 (ms)		
	720 (w)	D: cyclobutane ring deformation
738 (w)	738 (m)	D
808 (ms)	808 (vw)	M
825 (s)	825 (vw)	M
	843 (s)	D: C–C Skeletal stretch
860 (mw)	860 (vw)	M
875 (w)		M
941 (s, br)	941 (w, vbr)	M
986 (s)	986 (w)	M
1015 (w)	1015 (w)	D
	1036 (w)	D: cyclobutane ring deformation
	1052 (w)	D
1111 (w)		M
	1135 (m)	D
1167 (m)		M
	1170 (m)	D
1202 (s)		M
1214 (ms)		M
	1216 (s)	D
1225 (ms)		M
	1240 (ms)	D: O–H in-plane bending
1282 (vs)	1282 (w)	M
1305 (vs)	1305 (s)	M
1329 (s)		M
	1355 (ms)	D: aliphatic C–H deformation
1393 (s)	1393 (w)	M
	1410 (s)	D
1424 (ms)		M
1564 (vs)	1564 (ms)	M
1599 (ms)	1599 (s)	D
1624 (vvs)		M: aliphatic C=C stretch
1682 (vvs)	1685 (vvs)	D: C=O carboxylic
	1722 (s)	D: C=O formyl

a) m: medium, s: strong, ms: medium strong, w: weak, vw: very weak, vs: very strong, br: broad, mw: medium weak, vbr: very broad, vvs: very very strong. b) M: monomer, D: dimer.

Characterization of the Reactant and the Product by Infrared and Raman Spectroscopy. The infrared spectra of *p*-FCA crystal before and after photodimerization to different extent are shown in Fig. 1 and the results are summarized in Table 1. The infrared bands observed in partially dimerized crystals were attributed to the monomer if it appeared relatively weaker. Bands present in monomer if appeared in the partially dimerized crystal without losing intensity were attributed to the dimer as existence of some dimer in the monomer crystal can not be ruled out. New bands, of course, were the dimer bands. In monomer crystal, the band at 1624 cm^{-1} which is due to the aliphatic C=C stretching mode is very intense but decreases with the increase of the extent of photodimerization and almost disappears in near complete photodimer crystal. This, indeed, suggests cyclobutane ring formation. The cyclobutane ring breathing vibration around 1000 cm^{-1}, however, has not been observed in the Raman spectrum. Observation of such a Raman active mode has usually been attributed to the confirmation of four center type photopolymerization with cyclobutane ring formation.[4)] Absence of such a vibration in the Raman spectrum is however consistent with the structure of the dimer as suggested by Hasegawa *et al.*[6)] which is trans, head to head type like β-truxinic acid.

The other infrared features also suggest such a structure of four center type photodimerization in the crystalline state. The bands observed in the dimer at 720, 1035, and 1052 cm^{-1} are possibly the ring deformation vibrations. In such structure of the dimer, the C=O stretching frequency in the carboxyl group and in the formyl group are distinctly resolved, the former possibly is 1722 cm^{-1} and the latter 1685 cm^{-1}. Due to the loss of conjugation through the aliphatic C=C bond, some of the bands are shifted on dimerization. C–C skeletal stretching mode at 825 cm^{-1}, O–H in-plane bending at 1225 cm^{-1} and aliphatic

C-H deformation at 1329 cm^{-1} in monomer shift to 843, 1240, and 1355 cm^{-1} respectively in the dimer.

The Raman spectrum of the dimer is very weak, possibly due to the low value of the polarizability tensor. Intense Raman bands of the monomer are only observed in the partially dimerized sample without any significant change in the band positions.

Electronic Spectral Change on Dimerization Reaction Progress. *p*-FCA in the polycrystalline film at 25 °C show a broad absorption band with λ_{max} at 300 nm. Another band is also observed with λ_{max} at 200 nm. On photoreaction the product dimer in the solid film at 25 °C also shows two broad absorption bands, the 300 nm band is now shifted to 260 nm, the second band at λ_{max} 200 nm does not show any appreciable shift. This band shows a red shift to 210 nm on cooling at 77 K, 260 nm band, however, does not show any appreciable shift on cooling. The solid state absorption spectra are shown in Fig. 2.

Cinnamic acid molecule like benzoic acid is nonfluorescent and only strong phosphorescence emission is observed[7] which, as in benzoic acid, is possibly a $^3\pi,\pi^* \rightarrow S_0$ transition. *p*-Formylcinnamic acid in ethanol solution, on the other hand, is only fluorescent and no phosphorescence emission is observed. The emission spectra of *p*-FCA are shown in Fig. 3, (solid film). In monomer crystal a strong broad fluorescence emission in the 430—550 nm region with λ_{max} at 470 nm is observed at 77 K. This emissive property of *p*-FCA molecule evidently arises because the carbonyl oxygen in the formyl group contributes an additional set of $n\pi^*$ states. Relative energetic position of such states may make the singlet triplet intersystem crossing inefficient. The broad structureless absorption and emission spectra in the crystal at 77 K and the large Stokes' shift (12057 cm^{-1}) between the absorption and emission maxima provide a clear evidence for a strong lattice distortion in the excited state and thus a strong electron phonon coupling. On dimerization reaction progress, the monomer emission

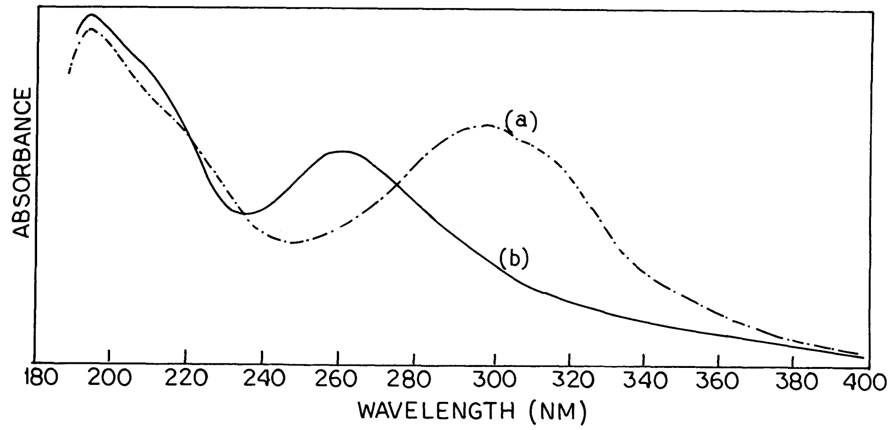

Fig. 2. Solid state absorption spectra at room temperature (a) monomer (b) dimer.

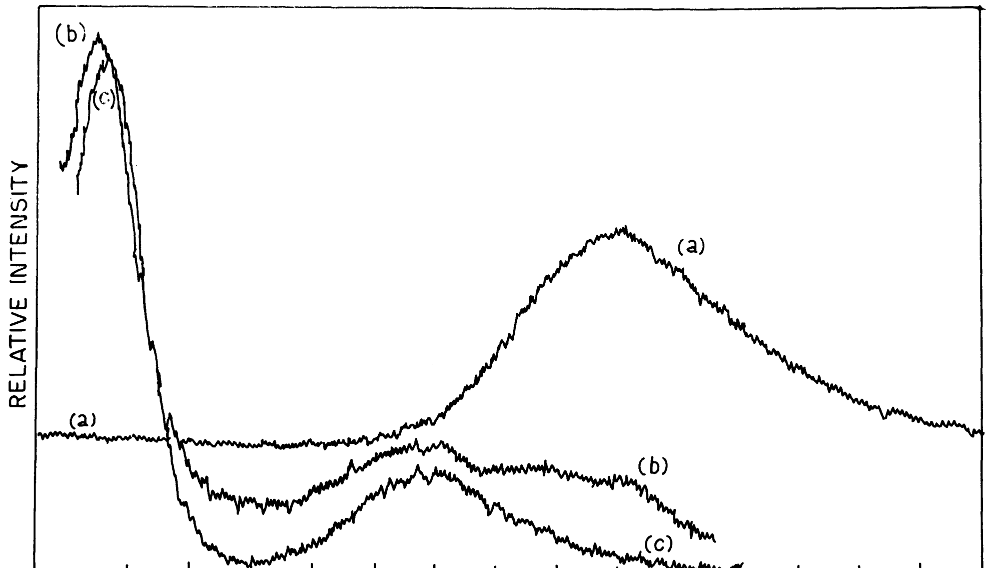

Fig. 3. Emission spectra of solid film of *p*-FCA at 77 K (a) monomer (b) partially dimerized (c) dimer.

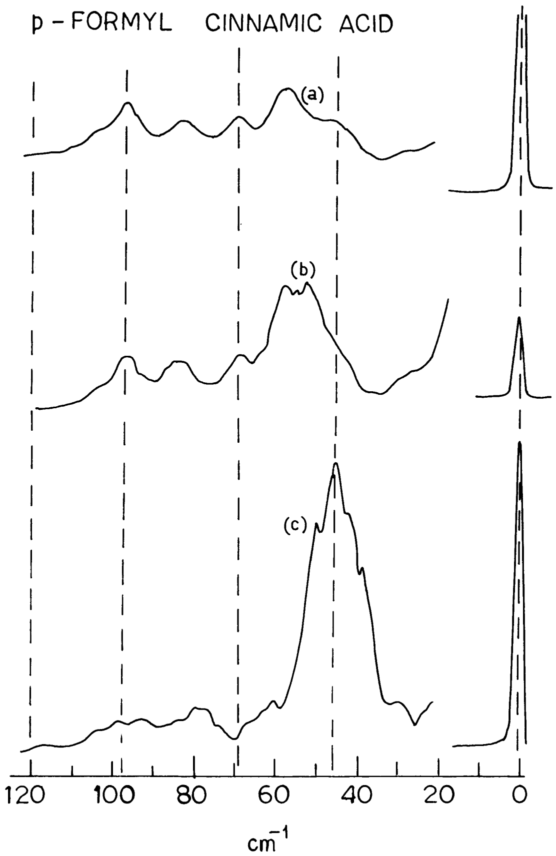

Fig. 4. Raman phonon spectra of *p*-FCA crystal monitored as a function of the photoreaction progress in order of a→c, a being the phonon spectra of the monomer and c that of an extensively dimerized crystal.

intensity decreases and a new emission band system appears on the higher energy side of the monomer crystal emission. This structureless emission band has its λ_{max} at 390 nm. On complete dimerization, only the new emission band, characteristic of the dimer is observed. One interesting feature of the photoproduct emission is that in addition to the emission discussed above another prompt high energy emission is observed with λ_{max} at 290 nm. At this point it is not certain if this double emission arises from the product *t*-3,*t*-4-bis(*p*-formylphenyl)-*ν*-1,c-2-cyclobutanedicarboxylic acid molecule or it is some other secondary photoproduct emission.

Phonon Spectral Change on Dimerization Reaction Progress. *β*-Form of the *p*-FCA crystal is photoreactive. The change in the phonon spectra as the dimerization reaction progress is shown in Fig. 4. The phonon spectrum of the monomer crystal of the *β*-form obtained from ethanol solution (top) show five distinct phonon bands at 45, 57, 69, 83, and 98 cm^{-1}. In addition two weak phonon bands are observed at 29 and 104 cm^{-1}. On photoirradiation for few minutes slight photodimerization occurs and the phonon spectrum of such crystal (middle) shows some new phonon bands at 31, 52, 55, 63, 87, and 92 cm^{-1}. The monomer phonon bands appear more broad and their intensity is slightly diminished. The broadening of monomer phonon bands may indicate slight shift in frequency of monomer phonons suggesting an amalgamation of phonons in this initial stage of reaction. Appearence of new phonon bands indicates initiation of seggregation of the reaction product. On extensive photodimerization (bottom), the monomer phonon bands appear very weak and new phonon spectrum arise with phonon bands at 29, 39, 43, 45, 50, 60, 63, 67, 74, 77, 87, 92, and 117 cm^{-1}, the 45 cm^{-1} phonon band being most intense in the dimer lattice. Thus the phonon spectrum of the dimerized crystal shows seggregated phonon spectra of the monomer and the dimer lattice. These results suggest that the solid state photoreaction in this crystal is homogeneous in the initial stage but becomes heterogeneous as the concentration of the product increases with reaction progress. The lattice distortion introduced by the product becomes too strong and the product seggregates out, the reactant and the product form their own lattices and no solid solution results.[1,8,9] Further, the existence of the 45 cm^{-1} monomer lattice phonon throughout the reaction progress and its enhanced intensity in the photodimer lattice suggests thet the lattice topology along this phonon coordinate is preserved during the reaction.

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