

Laser Raman spectroscopic study of photoreaction dynamics in o-chlorocinnamic acid polycrystals

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Abstract : Raman phonon spectroscopy has been used to study photodimerization reaction in o-chlorocinnamic acid (o-CCA) crystal which yield 2,2'-dichloro β -truxinic acid dimer. Five distinct and intense low frequency phonon bands are observed in the monomer crystal. With reaction progress, the low frequency phonon bands show a monotonic shift in frequency which suggests that the reaction is homogeneous in the initial stages. On further reaction progress, the phonon bands broaden appreciably and in the final stages only one broad phonon band persists indicating that the dimer lattice is highly disordered. Disappearance of the aliphatic C-C double bond stretching frequency and appearance of cyclobutane ring deformation and breathing vibrations after reaction in the infrared spectrum confirm photodimerization by cyclobutane ring formation. The large Stokes' shift between the absorption and emission band suggests strong exciton-phonon coupling in the monomer crystal. This solid state photodimerization reaction, therefore, seems to be phonon mediated.

Keywords : Solid state photoreaction, phonon assisted reaction, photodimerization of cinnamic acid derivatives, Raman spectroscopic study of photoreaction, o-chlorocinnamic acid.

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1. Introduction

o-Chlorocinnamic acid (o-CCA) is known to undergo photodimerization in the crystalline state (Cohen *et al* 1964). This reaction is thought to be topochemically controlled, the reactivity and the stereo chemistry of the product depend on the molecular arrangement in the monomer lattice. In some earlier works (Ghosh and Misra 1987, Misra and Prasad 1982) it is shown that many solid state photoreactions are mediated by lattice phonons. Phonon participation in solid state photoreaction occurs generally through strong exciton-phonon coupling (Misra and Prasad 1982, Ghosh and Misra 1985) though in some cases softing of a phonon mode leads to photoreaction (Ghosh and Misra 1986).

It was therefore thought worthwhile to investigate if the photodimerization reaction in *o*-CCA crystal is also phonon mediated. For this purpose we have used Raman phonon spectroscopy and electronic absorption and emission spectroscopy. Infrared spectroscopy has been used to characterize the reactant and the product. In this paper we report our experimental results which suggest that the photoreaction in *o*-CCA crystal is also phonon mediated. These results further show that the reaction mechanism is homogeneous in the initial stages and the product lattice is highly disordered.

2. Experimental

o-CCA sample purchased from Aldrich, U.S.A. was purified by repeated crystallization from spectro-grade ethanol (Merck) and water (triple distilled) mixture. Purified *o*-CCA was taken in a petri-dish covered with a quartz plate and was irradiated by 200 W high pressure Hg lamp. Polycrystalline samples were taken out at different stages of reaction progress and studied. The UV absorption spectra were run in a Shimadzu UV-VIS 210A spectrophotometer. The emission spectra were run in a Perkin-Elmer MPF 44A spectrofluorimeter. The infra-red spectra were recorded in a Perkin-Elmer 783 IR spectrophotometer. 5145 Å line of a 5W Ar⁺ ion laser (Spectra Physics Model 2020-05) was used as the Raman excitation source and the spectra were recorded in a Spex 1403 double monochromator coupled with a Spex Datamate IB for monochromator control, data acquisition and data analysis. Laser power falling on the sample was 70 mW. 5145 Å radiation energetically being far below the photoreactive lowest excited single state of *o*-CCA, does not induce any reaction.

3. Results and discussion

o-CCA when crystallised from ethanol solution yield β -form of the crystal in which

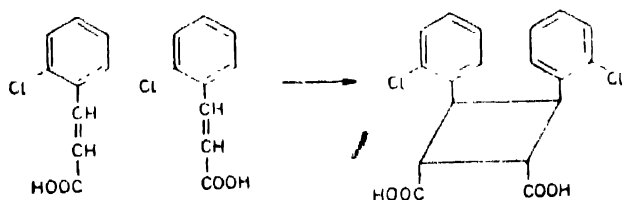


Figure 1. Chemical structure of the monomer molecular pair of *o*-CCA and of the photoproduct 2,2'-dichloro β -truxinic acid.

two molecules of the nearest neighbour molecular pair is related to one another by mirror symmetric relationship. Cohen *et al* (1964) have shown that this form of the crystal, when photoirradiated, yield mirror symmetric dimer 2,2'-dichloro β -truxinic acid. The structures of the monomer and dimer molecules are shown in Figure 1.

3.1. Study of internal vibrations of reactant and product by infra-red spectroscopy :

The infrared spectra of *o*-CCA monomer and dimer crystals in KBr pellet are shown in Figure 2. The aliphatic C=C stretching mode at 1622 cm^{-1} is intense in the monomer. With the extent of dimerization, the intensity of the band decreases and in the dimer spectrum the band disappears. Also in the dimer spectrum, cyclobutane ring deformation vibration at 645 cm^{-1} and cyclobutane ring stretching

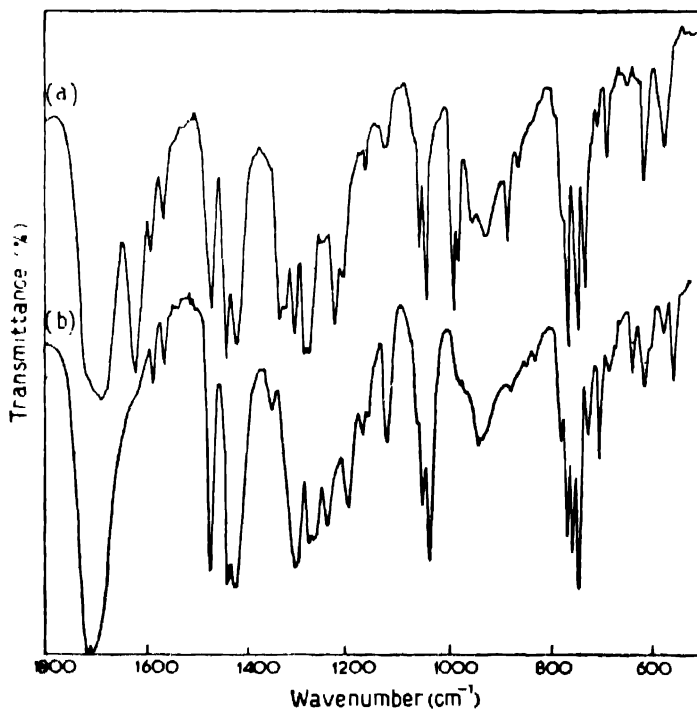


Figure 2. Infrared spectra of (a) monomer (unexposed) and (b) dimer (monomer exposed for 360 min) in the solid state (in KBr pellet) at 300 K.

vibration at 1128 cm^{-1} appear. These observations confirm photodimerization by cyclobutane ring formation in this crystal. The observed infra-red and Raman bands in the monomer and infrared bands in dimer are listed and partial assignment of the bands is presented in Table 1.

3.2. Electronic spectral change with reaction progress :

The progress of the photodimerization reaction in *o*-CCA crystal was monitored by electronic absorption spectroscopy. In the solid film, two broad absorption bands are observed at 198 nm and 276 nm in the monomer. With reaction progress, the intensity of the 276 nm band decreases and finally disappears in the dimer spectrum. The high energy band shows slight shift towards red in the dimer

Table I. Raman (polycrystals) and infra-red (KBr pellet) bands of monomer and infra-red (in KBr pellet) bands of dimer crystals of o-CCA.

Monomer		Dimer infrared (3)	Assignments (4)
Infrared (1)	Raman (2)		
	247 (w)		M
		285	D
300	295 (w)		M
		345	D
415	419 (ms)	410	
435			M
450		460	
		485	D
	546 (w)		
565 (ms)		560 (ms)	
		580 (w)	
605 (ms)	599 (w)	605 (sh.v.w.)	M
		620	
640 (vw)		645 (ms)	
		665 (vw)	D : cyclobutane ring deformation
680 (ms)	672 (ms)	675 (ww)	
698 (w)		693 (w)	
		710 (ms)	
		732 (ms)	D : cyclobutane ring deformation
730 (s)		750 (s)	
745 (s)		760 (s)	
765 (s)		772 (s)	
		785 (w)	D : C-C skeletal stretching
		835 (w)	
860	860 (w)		
880 (ms)	883 (w)	880 (vw)	
928 (w)			
950 (vw)		948	
		962 (vw)	
		970 (ww)	
980 (w)	981 (w)		
990 (ms)	991 (w)		M : HC - CH trans
1045 (s)	1044 (ms)	1040 (s)	
1055 (ms)		1055 (ms)	
1125 (w)	1124 (w)	1128 (ms)	D : cyclobutane ring stretching
	1138 (w)		
1165 (w)	1164 (ms)	1165 (vw)	
		1175 (w)	
1210 (w)		1205	
1228 (s)	1220 (ms)		

Table I. (Contd.)

Monomer		Dimer	Assignments
Infrared (1)	Raman (2)	Infrared (3)	
1278 (sh, s)	1280 (sh)	1280 (s)	
1305 (ms)	1293 (s)	1310 (ms)	carboxyl O - H out-of-plane bending
1335 (ms)	1321 (sh)	1335 (w) 1355 (w)	D : aliphatic C - H deformation
1425 (s)		1425 (s)	carboxyl O - H in-plane bending
1440 (s)	1440 (ms)	1440 (s)	C = C skeletal in-plane vibration (aromatic)
1470 (s)	1475 (ms)	1470 (s)	Aromatic C - C stretching
1565 (ms)		1570 (ms)	
1590 (ms)	1595 (vs)	1590 (ms)	C - C symmetric stretch (benzene ring)
1622 (vs)			C = C stretch (aliphatic)
	1641 (vs)		
1685 (vs)		1705 (vs)	C - O stretch

sh - shoulder ; s- strong ; ms medium strong ; vs very strong ;
w- weak ; vw very weak ; M Monomer ; D - Dimer,

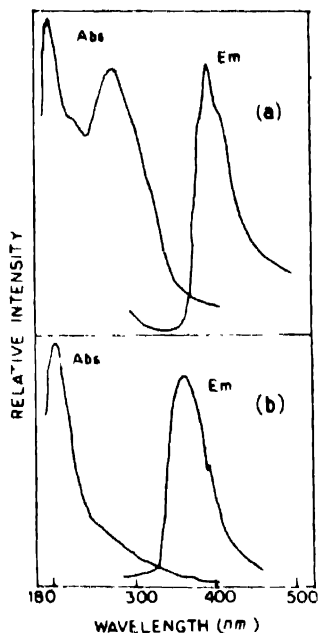


Figure 3. Electronic emission and absorption spectra of (a) monomer (unexposed) and (b) dimer (monomer exposed for 360 min) of o-CCA in polycrystalline state at 300° K.

spectrum. o-CCA shows fluorescence emission in the crystalline state but no phosphorescence is observed. The broad emission band with λ_{max} at 393 nm in

the monomer crystal shifts to higher energy with reaction progress and in the dimer crystal λ_{\max} is observed at 365 nm. In Figure 3, the absorption and emission spectra of the monomer and dimer crystals are shown. The absorption and emission bands of monomer do not overlap and there is a significant Stokes' shift of 10786 cm^{-1} . Such large Stokes' shift and broad absorption and emission bands suggest strong exciton-phonon coupling in *o*-CCA monomer crystal. Such observations are quite general in cinnamic acid derivatives (Ghosh and Misra 1985, 1987).

3.3. Raman phonon spectral change with reaction progress :

It is now well established that if the photoreaction in the crystal is homogeneous i.e. if the reactant and the product form solid solution, the phonon frequencies show a monotonic shift with reaction progress (Misra and Prasad 1982). On the otherhand if the reactant and the product form separate lattices, segregated phonon spectra are obtained. Phonon spectra also reveal if there is any phonon mode softening with reaction progress. Softening of a phonon mode in the excited state may drive the photoreaction in the crystal (Ghosh and Misra 1988). Phonon spectroscopy thus also provide information about the dynamic response of the reaction.

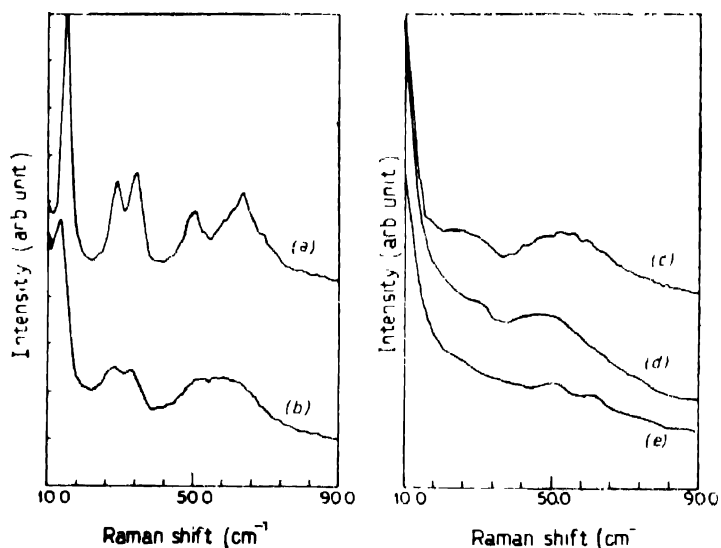


Figure 4. The Raman spectra of *o*-CCA polycrystals with reaction progress at 300 K. a > e are in the increasing order of dimerization (Exposed for a : 0 min, b : 10 min, c : 30 min, d : 60 min, e : 360 min).

We have investigated the Raman phonon spectra of *o*-CCA crystal with photoreaction progress. In Figure 4, the phonon spectra of *o*-CCA crystal at

different stages of reaction progress are shown. In the monomer, five distinct and intense low frequency phonon bands are observed at 15.2, 29.2, 34.2, 50.4 and 63.8 cm^{-1} . In addition four broad and weak bands are observed at 84.5, 99.0, 113.8 and 161.5 cm^{-1} . With reaction progress, the low frequency phonon bands show a monotonic shift in frequency which confirms that the reaction is homogeneous in the initial stages. On further reaction progress, as the product concentration increases, the phonon bands broaden appreciably and 29.2 and 34.2 cm^{-1} and 50.4 and 63.8 cm^{-1} band pairs fuse together to give two broad bands at 28.0 and 56.4 cm^{-1} respectively. This observation is similar to that one makes in order-disorder phase transition (Chakrabarti and Misra 1989). In the final stages, the 28 cm^{-1} phonon band also disappear and only one broad phonon band at 56.4 cm^{-1} persists. This band gradually shifts further with reaction time to lower frequency and finally a structureless broad phonon spectrum is obtained. That no new phonon band is observed with reaction progress suggests that the product does not form any separate lattice but only make the monomer lattice progressively disordered with increase of dimer concentration and a structureless broad phonon spectrum in the extensively dimerized crystal confirm a highly disordered product lattice.

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