Spectroscopic study of photoreaction dynamics in *p*-bromo cinnamic acid

MANASH GHOSH, A K MAITY, SUBHASIS CHAKRABARTI and
T N MISRA*

Department of Spectroscopy, Indian Association for the Cultivation of Science
Jadavpur, Calcutta 700 032, India

MS received 21 April 1994; revised 19 September 1994

Abstract. The photodimerization reaction in *p*-bromocinnamic acid (*p*-BCA) in the crystalline state has been probed by Raman phonon spectroscopy. Monotonic redshift of the phonon bands and nonappearance of any new phonon bands on reaction progress suggest that the reaction is homogeneous and the reactant and the product form a solid solution. It is further observed that a low frequency phonon at 18.6 cm^{-1} softens on photoexcitation and progress of reaction. The photoreaction in *p*-BCA crystal therefore seems to be mediated by the lattice phonon. In the IR spectrum disappearance of the aliphatic $>\text{C}=\text{C}<$ stretching frequency and appearance of cyclobutane ring deformation and ring stretching modes on reaction confirm photodimerization by cyclobutane ring formation. Considerable overlap between the absorption and emission bands shows that the exciton-phonon coupling is not very strong in the monomer crystal.

Keywords. Solid state photoreaction; phonon mediated reaction; mode softening; exciton-phonon coupling; *p*-bromocinnamic acid crystal.

1. Introduction

Photoreaction in organic crystals has attracted considerable attention since the detailed investigation of cinnamic acids by Schmidt and co-workers (Schmidt 1976). *p*-Bromocinnamic acid (*p*-BCA), like many other cinnamic acid derivatives, also undergoes photodimerization when irradiated in the crystalline state and gives 4,4-dibromo- β -truxinic acid, a mirror-symmetric cyclobutane derivative (Cohen *et al* 1964) as the photo product. This reaction is considered to be topochemically controlled and the reactivity and the structure of the product are governed by the geometry and the proximity of the reaction sites of the precursors in the lattice (Wegner 1977). Photodimerization occurs in some cases where reacting double bonds are either nonparallel (Patel *et al* 1980; Bhadbhade *et al* 1984; Hasegawa *et al* 1984; Theocaris *et al* 1984; Gnanaguru *et al* 1985) or the centre-to-centre distance between them is beyond the accepted topochemical limit (Gnanaguru *et al* 1984; Nakanishi *et al* 1985). It has now been established (Misra and Prasad 1982; Murthy *et al* 1984; Ghosh and Misra 1985, 1987, 1988) that molecular motion has a significant role in their photoreactivity. Murthy *et al* (1984) also considered the influence of orientational flexibility of the

* For correspondence

molecules and their environment in the crystal in the solid state photoreaction. Laser Raman phonon spectroscopy has successfully been used earlier (Misra and Prasad 1982; Ghosh and Misra 1987; Chakrabarti *et al* 1990) to show that many solid state photoreactions are mediated by lattice phonons. Earlier (Ghosh and Misra 1985, 1988) we have shown that the photodimerization reaction in *o*-methoxy cinnamic acid crystal is mediated by softening of a specific phonon mode in the excited state of the crystal. Photoreaction in *p*-chloro cinnamic acid crystal, on the other hand is also phonon-mediated but not through softening of a phonon mode but by strong exciton-phonon coupling (Chakrabarti *et al* 1990). In this paper we have used the Raman phonon and electronic absorption and emission spectroscopic techniques to characterize the reaction mechanism in *p*-BCA crystal and show that in this case also crystalline state reaction is mediated by softening of a low frequency phonon mode.

2. Experimental

p-BCA was purchased from Aldrich Chemical Company (USA) and further purification was done by repeated crystallization from spec-grade ethanol (E Merck, Germany). White needle-type crystals were obtained from ethanol water mixture (9:1).

Purified *p*-BCA crystals were taken in a petri dish covered with a quartz plate and was irradiated using 200 W high pressure mercury lamp. Samples were taken at different stages of reaction progress and studied. The UV absorption and emission spectra were run on a Shimadzu UV-VIS 210A spectrophotometer and Perkin-Elmer MPF 44A spectrofluorimeter respectively. The infrared spectra were recorded on a Perkin-Elmer 783 IR spectrophotometer. Raman spectra were obtained using a Spex double monochromator with gratings having 1800 grooves/cm, model 1403. For sharp bands, in such cases measurement is thought to be accurate within 0.5 cm^{-1} . For normal width bands the measurement is thought to be correct to $\pm 1\text{ cm}^{-1}$ (Misra and Prasad 1982). We used 5145 Å line of Spectra Physics, model 2020-5 argon ion laser as the Raman excitation source. Spex Datamate IB was used for spectrometer control, data acquisition and analysis.

3. Results and discussions

When crystallised from water and ethanol mixture *p*-BCA yield β form of the crystal and belongs to the space group $P2_1/a$ having four molecules per unit cell. The lattice parameters are $a = 33.0\text{ Å}$, $b = 3.97\text{ Å}$, $c = 6.66\text{ Å}$ and $d = 1.739\text{ Å}$ (Schmidt 1964).

Figure 1. Chemical structure of the monomer molecular pair of *p*-BCA and the photoproduct 4,4'-dibromo- β -truxinic acid.

The distance between the two nearest aliphatic C=C bonds is the *b*-axis distance of 3.97 Å. After photodimerization this form of monomer crystal yields cyclobutane derivatives. The structures of the monomer and the dimer molecules are shown in figure 1.

3.1 Study of internal vibrations of the reactant and the product by infrared and Raman spectroscopy

The positions of the IR absorption bands of a molecule are in general extremely sensitive to the molecular structure. We have recorded the infrared absorption as well as the Raman spectra to characterise the monomer and the dimer molecules.

The IR spectra of *p*-BCA monomer and dimer crystals are shown in figure 2. The vibrational IR and Raman (monomer only) bands and their tentative assignments are given in table 1. The aliphatic C=C stretching mode at 1619 cm^{-1} which is strong in the monomer decreases in intensity on reaction progress and it becomes a weak shoulder in the *as*-dimerized sample. This weak intensity of the shoulder is due to C=C stretching of some unreacted monomer still present in the dimer crystal. This observation is in conformity with the assumption that dimerization occurs through cyclobutane ring formation by the $>\text{C}=\text{C}<$ bond. Also new bands appear at 670 cm^{-1} and 1140 cm^{-1} . The first one has been assigned to the cyclobutane ring-deformation and the other to cyclobutane ring-stretching vibration. All these observations confirm that photodimerization occurs by cyclobutane ring formation. The 1675 cm^{-1} monomer band is, by all the above, the C=O stretching mode. In the

Figure 2. Infrared spectra of (a) monomer and (b) dimer of *p*-BCA in KBr pellet at 300 K.

Table 1. Infrared (in KBr pellet) bands of monomer and photodimer and Raman bands (monomer only) of *p*-BCA.

Monomer		Photodimer	Tentative assignment
IR (cm ⁻¹)	Raman (cm ⁻¹)	IR (cm ⁻¹)	
—	237(w)	—	M:
—	—	290(w)	D:
—	—	310(vw)	
342(s)	340(vw)	337(s)	
411(s)	—	405(s)	
—	—	461(w)	D:
488(vs)	—	480(vw)	
—	—	498(w)	
544(ms)	—	555(ms)	
—	—	590(w)	D:
—	—	610(w)	D:
630(s)	631(s)	630(vw)	D: cyclobutane ring deformation
—	—	670(s)	
709(ms)	696(s)	700(w)	
732(s)	738(vw)	722(s)	
—	770(s)	770(s)	D:
818(vs)	—	818(vs)	
850(w)	851(vw)	—	M:
870(s)	872(vw)	865(s)	
920(sh)	—	920(w)	
940(s)	—	940(w)	
958(w)	—	—	
980(ms)	—	—	M: CH=CH <i>trans</i>
1008(vs)	1009(w)	1012(vs)	
1070(vs)	1074(ms)	1077(vs)	
1108(s)	—	1110(vw)	
—	—	1120(vw)	
—	—	1140(s)	D: cyclobutane ring stretching
1175(s)	1180(vs)	1182(sh)	
1201(s)	1207(s)	—	
1225(ms)	—	—	M:
—	—	1238(vs)	D:
1280(ms)	1289(s)	1275(s)	
1300(ms)	—	1300(vw)	
1310(sh)	—	1310(s)	Carboxyl O–H out-of-plane bending
1328(s)	—	—	M: C–H deformation (aliphatic)
—	—	1345(sh)	
1391(s)	—	1395(sh)	
—	1402(s)	1405(sh)	
1418(vs)	—	1428(vs)	Aromatic ring stretching
—	1448(vw)	—	
1480(vw)	—	1487(vs)	Aromatic ring stretching
1558(s)	—	1568(w)	
1577(ms)	1588(vw)	1587(w)	Aromatic skeletal breathing
1619(vs)	—	1620(sh)	C=C stretching (aliphatic)
—	1639(vs)	—	Aromatic ring stretching
1675(vs)	—	1695(vs)	C=O stretching

photodimer this frequency increases to 1695 cm^{-1} possibly due to the disruption of strong hydrogen bonds in the monomer crystal (Cohen *et al* 1964; Joesten and Schaad 1974; Swiatkiewicz and Prasad 1982) on reaction and their replacement by a weaker association (Bellamy 1975).

3.2 Electronic spectroscopic study

The electronic absorption spectra of the monomer and the dimer crystals are shown in figure 3. The emission spectrum of the monomer crystal is also included in the figure. The monomer has three broad absorption bands with maxima at 198, 220 and 300 nm. With progress of the reaction, the intensity of 300 nm band decreases and finally disappears in the extensively dimerized crystal whereas the 198 nm band shifts to 208 nm in such crystal.

p-BCA shows fluorescence emission in the crystalline state at room temperature but no phosphorescence is observed even at 77 K. The fluorescence band is broad and structureless and has its maxima at 377 nm. Even though both the long wavelength absorption and fluorescence band in the monomer crystals are broad and structureless, they show considerable overlap near the electronic origin. This suggests that exciton-phonon coupling is not very strong in the monomer lattice (Misra 1989).

3.3 Raman phonon spectral change during reaction progress

In solid state photoreactions, the phonon probe is a useful technique to study the reaction dynamics, i.e. whether the reaction is homogeneous or heterogeneous (Misra and Prasad 1982). If there is any phonon mode softening it can also be revealed by the phonon spectra (Ghosh and Misra 1988).

Figure 3. Electronic absorption spectra. (a) Monomer (b) dimer and (c) electronic emission spectra of monomer of *p*-BCA crystals at 300 K.

Acknowledgement

The authors express their thanks to the Department of Science and Technology, Government of India, for financial support.

References

- Bellamy L J 1975 *Infrared spectra of complex molecules* (London: Chapman and Hall) p. 190
- Bhadbhade M M, Murthy G S, Venkatesan K and Ramamurthy V 1984 *Chem. Phys. Lett.* **109** 259
- Chakrabarti, Gantait M and Misra T N 1990a *Proc. Indian Acad. Sci. (Chem. Sci.)* **102** 165
- Chakrabarti, Gantait M and Misra T N 1990b *Indian J. Phys.* **B64** 99
- Cohen M D, Schmidt G M J and Sonntag F I 1964 *J. Chem. Soc.* 2000
- Ghosh U and Misra T N 1985 *Bull. Chem. Soc. Jpn.* **58** 2403
- Ghosh U and Misra T N 1987 *Indian J. Phys.* **B61** 530
- Ghosh U and Misra T N 1988 *Proc. Indian Acad. Sci. (Chem. Sci.)* **100** 337
- Gnanaguru K, Ramasubbu N, Venkatesan K and Ramamurthy V 1984 *J. Photochem.* **27** 35
- Gnanaguru K, Ramasubbu N, Venkatesan K and Ramamurthy V 1985 *J. Org. Chem.* **50** 2337
- Hasegawa M, Nohara M, Saigo K, Mori T and Nakanishi H 1984 *Tetrahedron Lett* **25** 561
- Joesten M D and Schaad L J 1974 *Hydrogen bonding* (New York: Marcel Dekker)
- Misra T N. 1989 *Raman spectroscopy: Sixty years on vibrational spectra and structure* (eds) H D Bist, J R Durig and J F Sullivan (Amsterdam: Elsevier Science) 17 137–166
- Misra T N and Prasad P N 1982 *Chem. Phys. Lett.* **85** 381
- Murthy G S, Arjunan P, Venkatesan K and Ramamurthy V 1984 *Tetrahedron* **43** 1225
- Nakanishi H and Hasegawa M 1985 *Acta Crystallogr.* **C41** 70
- Patel G N, Duahler E N, Curtui D Y and Paul I C 1980 *J. Am. Chem. Soc.* **102** 46
- Schmidt G M J 1964 *J. Chem. Soc.* 2014
- Schmidt G M J 1976 *Solid state chemistry* (ed.) D Ginsburg (Weinhein, Germany: Verlag Chemie) p. 2
- Swiatkiewicz J and Prasad P N 1982 *J. Am. Chem. Soc.* **104** 6913
- Theocharis C R, Jones W, Thomas J M, Motevalli M and Hruthouse M B 1984 *J. Am. Chem. Soc. Perkin Trans.* **2** 71
- Wegner G 1977 *Pure Appl. Chem.* **49** 443