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Gas–solid reactions of single crystals: A study of the reaction of bromine with single crystals of *trans*-cinnamic acid and a range of its derivatives by infrared and Raman microspectroscopy†

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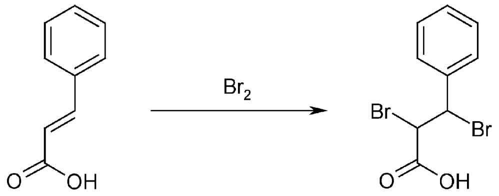
Single crystals of *trans*-cinnamic acid and of a range of derivatives of this compound containing halogen substituents on the aromatic ring have been reacted with 165 Torr pressure of bromine vapour in a sealed desiccator at 20 °C for 1 week. Infrared and Raman microspectroscopic examination of the crystals shows that bromination of the aliphatic double bond, but not of the aromatic ring, has occurred. It is demonstrated also that the reaction is truly gas–solid in nature. A time-dependent study of these reactions shows that they do not follow a smooth diffusion-controlled pathway. Rather the reactions appear to be inhomogeneous and to occur at defects within the crystal. The reaction products are seen to flake from the surface of the crystal. It is shown, therefore, that these are not single crystal to single crystal transitions, as have been observed previously for the photodimerisation of *trans*-cinnamic acid and several of its derivatives. It is shown that there are no by-products of the reaction and that finely ground samples react to form the same products as single crystals.

Introduction

In recent years there has been a strong renewal of interest in the reactions of solid crystalline organic substrates.[1–5] Reactions of this type are desirable from an environmental point of view in that they obviate the need for large quantities of solvent as the reaction medium.[4,6] At the same time it has become increasingly recognised that such reactions give considerable stereochemical control, as the form of the reaction product may be directed by the arrangement of reactant molecules within the crystal.[2,3,7–11] Performing reactions in the solid state has been found in many examples to improve specificity.[12] The explosion of interest in *combinatorial chemistry* where a wide range of reagents are tested on solid beads of substrates provides a further impetus to research in this area.

We have utilised the techniques of infrared and Raman microspectroscopy to monitor reactions of this type and to characterise reaction products.[1–3] The principal advantages of vibrational microspectroscopy in this context are that single crystals may be monitored *in situ* and that the spectra give considerable structural information about reactants and products. Such structural information is much less readily forthcoming from an alternative approach, which has been used elsewhere,[4,6,13,14] in which atomic force microscopy is employed. Here morphological changes to the crystals are seen upon reaction, but it is difficult to relate these changes to the chemical processes ongoing within the crystal. Diffraction methods have, of course, also been used[8,9,15] but are still undergoing development for use in time-resolved monitoring of solid state reactions.[16] Single crystal methods may present difficulties if the crystals under investigation degrade during the experiment.[17] In this context, however, it is interesting to note a very recent single crystal diffraction study of the photodimerisation of the α′-polymorph of *ortho*-ethoxy-*trans*-cinnamic acid in the solid state.[18] Until now we have focused our attention upon photochemical dimerisation reactions of single crystals of *trans*-cinnamic acid and its derivatives.[1–3] An integrated approach using infrared and Raman microspectroscopy clearly demonstrates the *topotactic* nature of these reactions where the form of the dimer obtained is dependent upon the orientation of the monomer molecules within the starting compound.[2,3] We have also extended our studies to investigate the time-dependency of the dimerisation of molecules of α-2,4-dichloro-*trans*-cinnamic acid within a single crystal.[1] The reaction is shown to follow strictly first order kinetics, rather than the zeroth order kinetics predicted by some theoretical models.[1]

We have now turned our attention to the reactions of single crystalline organic substrates with gaseous reagents. Such reactions are considered to be relatively environmentally friendly and often they give yields at least as high as those obtained by analogous solution reactions.[4–6] Their full exploitation, however, in synthesis is held back because of uncertainty as to how controllable are the reactions and as to how the products of the reactions relate to products formed by analogous reactions in solution. As an example of such reactions we selected for study the bromination of *trans*-cinnamic acid:



and some of its halogenated derivatives.

The reaction of solid aryl alkenes with bromine vapour has been known for almost 150 years.[19] While these conditions are thought to give the same products as those formed in solution by an ionic mechanism there is still uncertainty regarding the course of the reaction. In the first place it has been proposed[20] that bromination of the *para*-position of the aromatic ring as

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† Electronic supplementary information (ESI) available: Tables S1–S6. See http://www.rsc.org/suppdata/cp/b5/b501427c/

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well as of the aliphatic double bond will occur. Secondly, there has been some controversy as to whether the reaction is truly gas–solid in nature.[21,22] It has been suggested[22] that the reaction actually occurs in an adsorbed phase on the surface of the crystal or in a film of solution formed by the aromatic compound dissolved in liquid.

It is of interest to mention two studies which are related to the work reported here.[23,24] Garcia-Garibay and his co-workers[23] found that bromine gas induced an enantioselective carbocation rearrangement upon reaction with crystalline bibenzobarrelene. The products were identified by GC and NMR spectroscopy. When powders were reacted, yields of 85–90% of one dibrominated product were obtained; by contrast reaction of large single crystals (20–100 mg) gave a large number of by-products. Reaction of moist chlorine gas with crystals of 4-phenylthiazole-2(1*H*)-thione over a period of several weeks[24] led to complete destruction of the starting material and the formation of two products. The major product (as identified by single crystal X-ray diffraction and NMR spectroscopy) was chlorinated at the *para* position of the phenyl rings and oxidation and ring-opening had led to the formation of (4-chloro) phenacyl disufide in which two molecular units were linked by an S–S bond.

It is thus apparent that there remain uncertainties in the interpretation of these gas–solid reactions and that, with the exception of a number of studies by single crystal X-ray diffraction[25] and by atomic force microscopy,[26] few investigations of single crystals have been made. Vibrational microspectroscopy has not, to our knowledge, previously been employed to investigate the reaction of any organic single crystal with a gaseous reagent. Given the current general interest in such reactions and our previous success in utilising vibrational microspectroscopy to monitor photodimerisation reactions in single crystals we felt that the study reported here was very timely. We felt, moreover, that our approach could usefully address specific questions regarding these particular reactions such as: (i) Are the aromatic and aliphatic bonds of aryl alkenes brominated? (ii) Are the reactions homogeneous or inhomogeneous, are they truly single crystal to single crystal processes? (iii) Are they diffusion controlled?

Experimental section

Samples of all organic solids were used as supplied by Aldrich. The stated purities of the reagents used were as follows: *trans*-cinnamic acid (99+%), 4-bromo-*trans*-cinnamic acid (98%), 4-chloro-*trans*-cinnamic acid (99%), 4-fluoro-*trans*-cinnamic acid (99%), 2-fluoro-*trans*-cinnamic acid (98%), 3-fluoro-*trans*-cinnamic acid (98%), 9-methylanthracene (98%) and hydantoin (99%). Bromine (99.5%+ purity) was used as supplied by Aldrich.

Reactions of bromine vapour with organic substrates were carried out in a sealed desiccator in which an open reservoir of bromine and a watch glass with a single crystal of the reagent under investigation were placed. The temperature of the system was held at 20 °C at which Br_2 has a vapour pressure of 165 Torr. After a period of 1 week the single crystal was extracted and examined by infrared and Raman microspectroscopies. For 'bulk' reactions a finely ground sample was reacted under identical conditions and IR spectra were recorded on the product in a KBr disc. NMR spectra were also recorded on DMSO-d_6 solutions.

The infrared (Brucker IRscope II attached to a Brucker Equinox 55 FT interferometer) and Raman (Renishaw model 1000) microscopes which were used to record vibrational spectra of single crystals have been described elsewhere.[2,3,27] Infrared spectra of bulk samples were recorded using a Perkin Elmer 1720-X FTIR, NMR spectra were measured on a Bruker DPX 250 MHz spectrometer at 250 Hz.

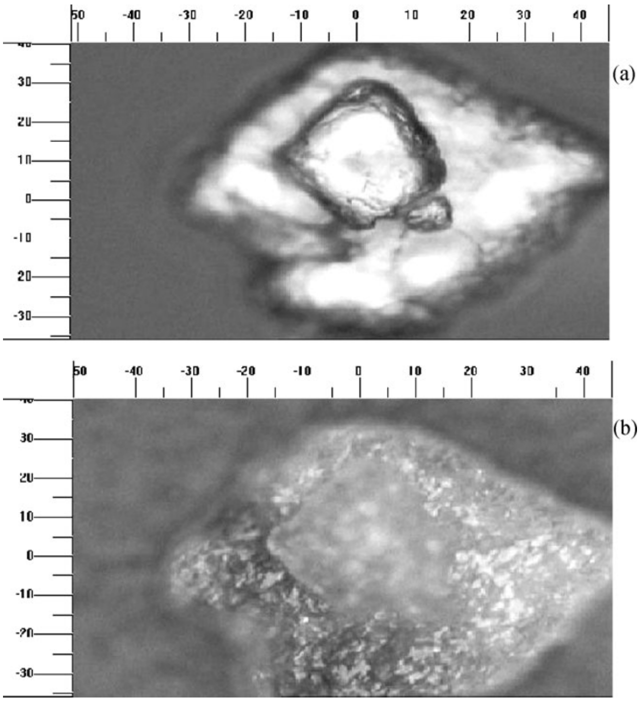

Fig. 1 A single crystal of *trans*-cinnamic acid before (a) and after (b) exposure to 165 Torr of bromine vapour for a period of 1 day. The scale shows distance measured in μm.

Results and discussion

Reaction of *trans*-cinnamic acid with Br_2 vapour

Single crystals of *trans*-cinnamic acid, whose infrared spectra had previously been recorded were exposed in a sealed desiccator to a pressure of 165 Torr of Br_2 vapour for a period of 1 week. At the end of that time the crystals were examined by optical microscopy. It may be seen from the photographs in Fig. 1 that the surface of the crystal has begun to disintegrate upon exposure to Br_2; it has become cracked and pitted. This disintegration of the crystal may be contrasted with the photodimerisation reactions of *trans*-cinnamic acid and several of its derivatives where the crystals remain intact.[1,2] Infrared spectra recorded on a single crystal before and after exposure to Br_2 vapour (Fig. 2) show clearly that a chemical reaction has occurred. The wavenumbers of the observed bands are listed in Table 1, and the principal changes may be summarised as follows.

(1) The band assigned to ν(C=C) aliphatic at 1627 cm^{-1} [28] has disappeared, indicating reaction across the double bond.

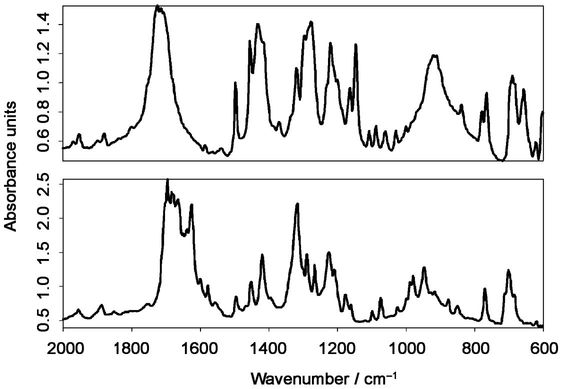

Fig. 2 The infrared spectra of a single crystal of *trans*-cinnamic acid before (below) and after (above) exposure to 165 Torr pressure of bromine vapour for 1 week.

Table 1 Positions of infrared absorptions (cm^{-1}) of a single crystal of *trans*-cinnamic acid before and after exposure to 165 Torr pressure of bromine vapour for 1 week

Assignment	Infrared: *trans*-cinnamic acid/cm^{-1}	Infrared: *trans*-cinnamic acid after exposure to bromine vapour/cm^{-1}
ν(C–H) unsaturated (aliphatic and aromatic)	3025 br	3009 br
ν(C=O) (carboxyl)	1682	1722 vs
ν(C=C) (aliphatic)	1627	
ν(C=C) (aromatic)		
C–H deformation (unsaturated)^a	1494, 1450 s, 1422 s	1496 s, 1432 s
ν(C–O) (carboxyl)^a	1316, 1209, 1205	1280, 1220 s
δ(C–H) (aliphatic and aromatic)^a	1177, 1068, 1027, 935, 872 s	1147 s, 1108, 1088, 1060, 913 vs
Ring vibration (aromatic)^a	770 s, 702 s, 677	767, 693 s
ν(C–Br)^a		658

[a] Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

(2) The band assigned to ν(C=O) of the carboxyl group at 1682 cm^{-1} in *trans*-cinnamic acid[28] has disappeared and has been replaced by a band at 1722 cm^{-1} in the brominated product.

(3) The appearance of the spectrum in the region associated with vibrations of the aromatic ring (650–1050 cm^{-1})[29] is somewhat changed in appearance although the basic profile of bands is similar.

(4) New bands are seen around 600 cm^{-1} which may arise from C–Br stretching vibrations.[31]

The Raman spectra (Fig. 3) show perhaps more striking changes. Once again, the band arising from ν(C=C) aliphatic has disappeared and a new strong band at 666 cm^{-1} which may be assigned to ν(C–Br) has appeared. The observed Raman bands of a single crystal of *trans*-cinnamic acid before and after exposure to Br_2 vapour are listed in Table 2.

One of the questions which we wished to address is: has bromination occurred only at the aliphatic C=C bond or has bromination of the aromatic ring occurred also? The vibrational spectra, which we have obtained allow us to explore this point. Empirical observation has allowed the positions of attachment at a benzene ring to be determined by inspection of the pattern of Raman bands resulting from vibrations of the ring.[29] The spectra of *trans*-cinnamic acid before and after exposure to Br_2 vapour show bands (*before* bromination 1032, 1006, and 625 cm^{-1}, *after* bromination 1030, 1008, 627 cm^{-1}) in the regions 1015–1035, 990–1010 and 605–630 cm^{-1} which are indicative of a monosubstituted ring. Moreover, such a ring is expected to show strong infrared bands in the regions 690–710 and 730–770 cm^{-1}. Bands are seen *before* bromination at 702 and 770 cm^{-1} and *after* bromination at 693 and 767 cm^{-1}. Thus the vibrational spectra confirm that bromination has occurred at the aliphatic double bond only and that the aromatic ring remains unchanged. Identification of the ring vibrations as above allows us to assign the infrared band of the brominated product at 658 cm^{-1} to ν(C–Br). This corresponds to the Raman band at 666 cm^{-1}. In addition to this we note the correspondence between our product spectra and that of an authentic sample of α,β-dibromohydrocinnamic acid (Fig. 4). It is possible to make some further observations from these vibrational spectra regarding the shift in the position of ν(C=O) to high frequency. This shift demonstrates that the C=C aliphatic bond has been converted to a C–C single bond, resulting in loss of conjugation to, and hence a strengthening of, the C=O bond. The magnitude of this shift (40 cm^{-1}) may be compared with the corresponding shift in band position when *trans*-cinnamic acid is photodimerised to the corresponding dimer[3] of 8 cm^{-1} (from 1680 cm^{-1} to 1688 cm^{-1}). The much greater shift which occurs during the bromination reaction is caused by the electron withdrawing –I effect of the Br atom in the α-position to the C=O bond.

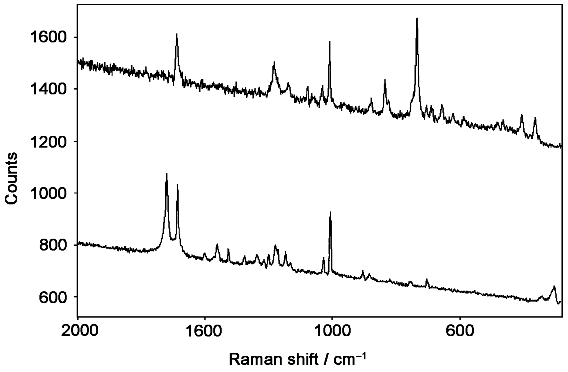

Fig. 3 The Raman spectra of a single crystal of *trans*-cinnamic acid before (below) and after (above) exposure to 165 Torr pressure of bromine vapour for 1 week.

We have carried out time-dependent studies of the reaction by extracting crystals, which had been exposed to 165 Torr of bromine vapour under identical conditions for periods ranging from 24 h to 1 week. These studies show that the reactions do not follow diffusion control. Rather they proceed very slowly in the early stages, with no discernable spectral changes in the first 24 h of reaction, but much more rapidly once the crystal starts to fragment. Under these circumstances it was not possible to obtain any meaningful kinetic plots from these data.

Our experiments demonstrate, beyond any reasonable doubt, that bromination of the aliphatic double bond, but not of the aromatic ring, has occurred upon exposure of *trans*-cinnamic acid to Br_2 vapour. In order to demonstrate that the same reaction occurs in finely-ground bulk samples as in single crystals we measured infrared spectra of a bulk sample (as a KBr disc) and ^{1}H and ^{13}C NMR spectra [δ_H(DMSO-d_6) 7.65–7.33 (m, 5 H), 5.56–5.51 (d, 1 H), 5.34–5.30 (d, 1 H). δ_C(DMSO-d_6) 129.42, 129.03, 128.76, 52.25, 47.52, 31.06]. The infrared spectra are identical, within experimental error, in band position to the corresponding spectra of single crystals and are also identical to the spectrum of an authentic sample of α,β-dibromohydrocinnamic acid. The ^{1}H NMR spectra serve to confirm the findings. The position of the peak arising from the aliphatic H atoms shifts from *ca.* $\delta = 6.6$ to *ca.* $\delta = 5.5$ ppm upon bromination. The signal from the brominated sample appears as a doublet of doublets with a 1 : 1 intensity ratio, indicating coupling between the two H atoms which are non-equivalent, but showing that coupling to the quadrupolar ^{79}Br and ^{81}Br nuclei is not resolved. ^{13}C NMR shows peaks arising from the aliphatic carbon atoms of the brominated product at 52.25 and 47.52 ppm. These have shifted from around 120 ppm in the starting material indicating the attachment of the electronegative Br atoms. Spectra in the aromatic region are more difficult to interpret fully, with a cluster of peaks being seen between 7 and 8 ppm. We note, however, that the ^{1}H and ^{13}C NMR spectra of our product are identical to those of an authentic sample of α,β-dibromohydrocinnamic acid.

Examination of these infrared and NMR spectra demonstrates two important points. First, that the yield must be 100% (or very close to this figure) as all infrared and NMR bands of the starting material have disappeared upon reaction. At the same time all of the infrared and NMR bands that appear and grow during reaction may be assigned to the product α,β-dibromohydrocinnamic acid, showing that a clean

Table 2 Positions of Raman bands (cm^{-1}) of a single crystal of *trans*-cinnamic acid before and after exposure to 165 Torr pressure of bromine vapour for 1 week

Assignment	Raman: *trans*-cinnamic acid/cm^{-1}	Raman: *trans*-cinnamic acid after exposure to bromine vapour/cm^{-1}
ν(C–H) unsaturated (aliphatic and aromatic)		
ν(C=O) (carboxyl)		
ν(C=C) (aliphatic)	1643 s	
ν(C=C) (aromatic)	1605 s	1611
C–H deformation (unsaturated)^{a}	1501, 1450	
ν(C–O) (carboxyl)^{a}	1331, 1298, 1273, 1217	1229 br
δ(C–H) (aliphatic and aromatic)^{a}	1183, 1032, 1006, 882, 855	1171, 1095, 1030, 1008 s, 844
Ring vibration (aromatic)^{a}	689 w, 625	791, 627 w
ν(C–Br)^{a}		666 vs

^{a} Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

addition reaction has taken place. In some cases the crystals were a little discoloured after reaction, suggesting the presence of some dissolved bromine. However, this was at a level too low to be detected by Raman spectroscopy. Upon exposure to bromine vapour for periods in excess of 1 week (up to 1 month) no new products were observed, indicating that the primary products are unreactive towards bromine and that the reaction stops at this point.

Reactions of derivatives of *trans*-cinnamic acid with Br_2 vapour

In the next stage of our work we extended our studies to a number of derivatives of *trans*-cinnamic acid. The first derivative that we studied was 4-bromo-*trans*-cinnamic acid. In this case a bromine atom is already present at the 4-position on the aromatic ring. Thus if bromination of *trans*-cinnamic acid itself did proceed by addition across the aliphatic double bond *and* by substitution of the 4-position of the benzene ring we would expect the products of reaction of 4-bromo-*trans*-cinnamic acid and of *trans*-cinnamic acid itself to be identical. Inspection of the infrared spectra shown in Fig. 5 demonstrates clearly that the products are not identical. This observation confirms that reaction of *trans*-cinnamic acid only occurs at the aliphatic double bond. Observed infrared and Raman band positions of 4-bromo-*trans*-cinnamic acid before and after exposure to Br_2 vapour are listed in Table S1 which is available as supplementary material.† The main observations are:

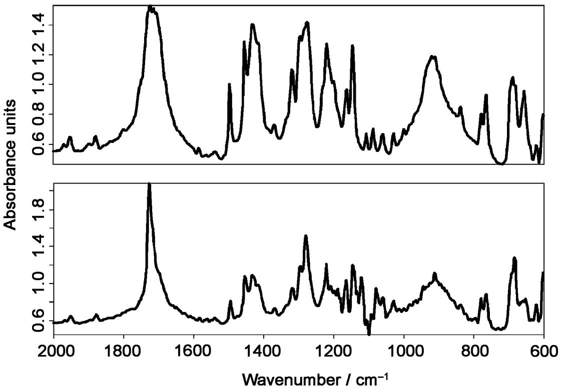

Fig. 4 Comparison of the infrared spectrum of a single crystal of *trans*-cinnamic acid after exposure to 165 Torr pressure of bromine vapour for 1 week (above) and of a single crystal of an authentic sample of α,β-dibromohydrocinnamic acid (below). Small differences between the two spectra arise from (i) the greater intensity of the upper spectrum leading to saturation of the detector, especially around 1700 cm^{-1}, and (ii) slight differences in the structures of the two crystals leading to solid-state effects. The crystal of α,β-dibromohydrocinnamic acid is an authentic sample which has been recrystallised after preparation while the crystal of the reaction product of *trans*-cinnamic acid with bromine has been formed by a gas–solid reaction and has not been recrystallised.

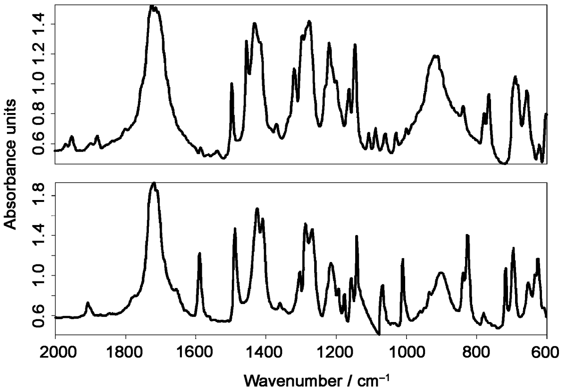

Fig. 5 Comparison of the infrared spectra of single crystals of *trans*-cinnamic (above) and 4-bromo-*trans*-cinnamic acid (below) after exposure to 165 Torr pressure of bromine vapour for 1 week.

(1) That the infrared (1627 cm^{-1}) and Raman (1652 cm^{-1})‡ bands assigned to ν(C=C) aliphatic disappear.

(2) That the infrared band assigned to ν(C=O) (1688 cm^{-1}) disappears and is replaced by a band at 1725 cm^{-1}.

(3) That a band assigned to ν(C–Br) appears at 654 cm^{-1} (infrared) and 659 cm^{-1} (Raman).

We have also investigated the 4-chloro and 4-fluoro derivatives. These derivatives were selected as having groups attached to the 4-position on the benzene ring which are unlikely to be replaced by Br as the enthalpies of reaction would be unfavourable.[30]

The positions of infrared and Raman bands of 4-chloro-*trans*-cinnamic acid and 4-fluoro-*trans*-cinnamic acid before and after exposure to bromine vapour are listed in Tables S2 and S3 which are given as supplementary material.† The principal changes observed are as follows. Firstly, the disappearance of the band arising from ν(C=C), aliphatic (4-fluoro-*trans*-cinnamic acid: 1650 cm^{-1} infrared, 1663 cm^{-1} Raman‡; 4-chloro-*trans*-cinnamic acid: 1630 cm^{-1} infrared, 1640 cm^{-1} Raman). Secondly, the shift of the band arising from ν(C=O) (4-fluoro-*trans*-cinnamic acid 1680 cm^{-1} replaced by 1721 cm^{-1}; 4-chloro-*trans*-cinnamic acid 1700 cm^{-1} replaced by 1725 cm^{-1}). Thirdly the appearance of bands resulting from ν(C–Br) (4-fluoro-*trans*-cinnamic acid 665 cm^{-1} infrared, 668 cm^{-1} Raman; 4-chloro-*trans*-cinnamic acid 646 cm^{-1} infrared, 659 cm^{-1} Raman).

Finally we investigated the reactions of 2-fluoro-*trans*-cinnamic acid and 3-fluoro-*trans*-cinnamic acid. Both of these compounds brominate across the aliphatic double bond. Positions of infrared and Raman bands before and after bromination are listed in Tables S4 and S5 (ESI†). Principal changes observed are as follows. 2-fluoro-*trans*-cinnamic acid: (i) disappearance of ν(C=C) aliphatic (1652 cm^{-1} infrared, 1652 cm^{-1} Raman); (ii) shift of ν(C=O) from 1679 to 1723 cm^{-1} (infrared); and (iii) appearance of ν(C–Br) 661 cm^{-1} (infrared), 668 cm^{-1} (Raman). 3-fluoro-*trans*-cinnamic acid: (i)

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‡ The broadness of the infrared absorption probably accounts for the discrepancy in the position of the infrared and Raman bands arising from these vibrations.

disappearance of ν(C=C) aliphatic 1658 cm^{-1} (infrared), 1654 cm^{-1} (Raman); (ii) shift of ν(C=O) from 1684 cm^{-1} to 1722 cm^{-1} (infrared); and (iii) appearance of ν(C–Br) 699 cm^{-1}, (infrared) 690 cm^{-1} (Raman).

For all of the derivatives mentioned above we recorded ^1H NMR spectra. In each case a pair of doublets arising from the aliphatic protons was seen at around 5.5 ppm together with a more complex set of bands from the aromatic protons between 7 and 8 ppm. The positions of ^1H NMR features observed for all of the derivatives studied are listed in Table S6.†

Discussion

Our experiments have demonstrated a number of important points regarding the reaction of bromine vapour with single crystals of *trans*-cinnamic acid and its derivatives. First the reaction is shown to be quantitative and clean. This may be contrasted with some previously studied halogenations of crystals[23,24] in which rather complex reactions were observed and in which a number of by-products were seen. These reactions included chlorination of the phenyl rings of 4-phenylthiazole-2(1*H*)-thione,[24] oxidation,[23,24] fragmentation,[24] and rearrangement[23] processes. The reactions investigated in the current work presented here proceed by bromination of the aliphatic C=C bond, and once this bond is brominated the reaction stops. There is no sign of any bromination of the aromatic ring and no other by-product is formed even upon prolonged exposure to Br_2 vapour. The procedure may therefore find use in a synthetic context.

However, it is clear that these are not homogeneous single crystal to single crystal transitions. The reactions do not follow any known diffusion-controlled kinetics.[31] Rather bromination appears to occur at crystal defects and is greatly accelerated once the crystal begins to fragment. This behaviour may be contrasted with the photodimerisation reactions of the 2-chloro-, 4-chloro- and 2,4-dichloro- derivatives of *trans*-cinnamic acid.[1] Here the crystals remain intact upon photolysis, the reactions are topotactic and they follow a smooth conversion from monomer to dimer, which may be modelled kinetically.

The crucial difference between these processes is that upon bromination a large amount of additional matter is being added. This clearly causes too large a distortion to the crystal to be accommodated and leads to disintegration. It has been reported elsewhere[27] that where intermolecular spacing between monomers of *trans*-cinnamic acid derivatives are too large, photodimerisation will either not proceed or leads to fragmentation. In the bromination of an aliphatic double bond, the highly exothermic nature of the reaction (*ca.* -280 kJ mol^{-1})[30] presumably drives the reaction to completion, even at the expense of fragmentation of the crystal.

Our experiments show the usefulness of infrared and Raman microspectroscopies in monitoring reactions of this type. This approach is especially useful in a situation where the single crystal fragments upon reaction, making single crystal X-ray diffraction studies impossible.

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