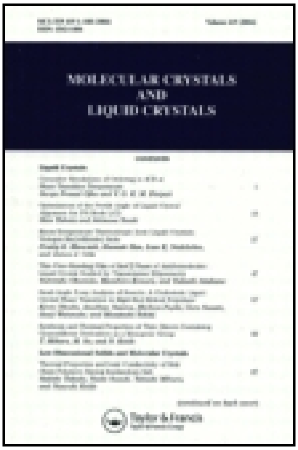

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Kinetic and Mechanistic Aspects of a Crystal-to-Crystal Photoreaction: Effective use of Single Crystal X-ray Diffraction

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Kinetic and Mechanistic Aspects of a Crystal-to-Crystal Photoreaction: Effective use of Single Crystal X-ray Diffraction

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X-ray diffraction has been used to reveal precise kinetic data, ***in situ***, for the photodimerisation reaction of a 2-benzyl-5-benzylidenecyclopentanone (BBCP) single crystal. The reaction obeys first order kinetics over a wide temperature range, is a one photon process and likely to be phonon assisted. Below a threshold temperature of ~173 K the rate constant decreases and an Arrhenius type plot reveals that the activation energy for the reaction is ~13.2 kJ mol^{-1}. The rate constant is slightly reduced at higher temperatures, possibly due to increased thermal motion of the olefin bonds.

Keywords crystal-to-crystal; reaction kinetics; X-ray diffraction

INTRODUCTION

Kinetic studies of topochemical reactions are often performed by a time resolved composition analysis of a bulk sample.[1] Such an approach, however, informs only on an 'average' extent of reaction. Specific study of rare crystal-to-crystal topochemical reactions presents the tantalising possibility of making measurements ***in situ*** for an individual crystal. Such data can the be used to understand topochemical reactions in general. Using the example of the photodimerisation of 2-benzyl-5-benzylidenecyclopentanone (BBCP)[2] (Figure 1) we demonstrate here that precise ***in situ*** kinetic measurements can be made by simply monitoring the change in diffracted X-ray intensities from a reacting single crystal. Using this information we present some insight into the mechanism of the reaction.

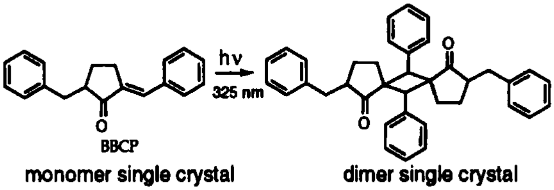

FIGURE 1 The dimeristaion reaction of BBCP

THEORY

During a crystal-to-crystal reaction, the single crystal is a two component mixed crystal of unreacted and product molecules. This is evident from numerous studies of crystal structures of partially reacted crystals. For example, the mixed crystal structures of α-trans cinnamic acid and it's photodimer have been determined at various compositions after different degrees of reaction.[3] Similar experiments have been performed for the photodimerisation reaction of BBCP.[2] As can be seen from Table I, the variation in the unit cell parameters between a pure BBCP monomer crystal, a 50/50 mixed monomer/dimer crystal and a pure dimer crystal is very small. Hence during reaction, the reference lattice that contains both types of molecule remains approximately constant. Monomer and dimer molecules occupy different sites within this lattice, however.

TABLE I Unit cell parameters at 295 K, orthorhombic, Pbca.

	a (/Å)	b (/Å)	c (/Å)
BBCP monomer	31.318(2)	10.795(2)	8.688(2)
BBCP 50/50 mixed crystal	31.378(6)	10.761(2)	8.672(2)
BBCP dimer	31.354(6)	10.816(4)	8.631(3)

The redistribution of electron density as BBCP molecules move from unreacted monomer to dimer sites can be quantified by a change in diffracted X-ray intensity of certain reflections. This can be understood by considering the simulated X-ray diffraction patterns presented in Figure 2. Moving from the monomer to 50/50 mixed crystal to dimer diffraction patterns, it can be seen that all the reflections remain at the same 2θ angle, yet their intensities change, e.g. the intensity of the 111 reflections increases.

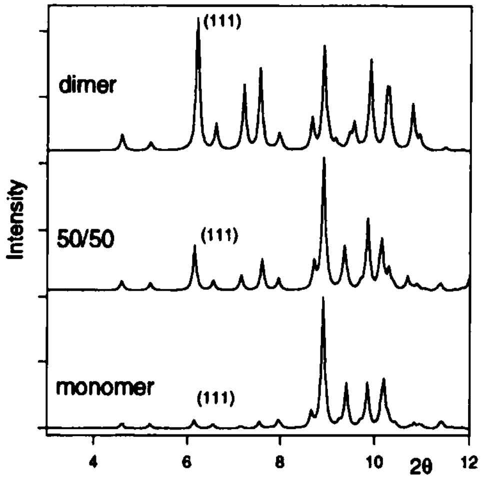

FIGURE 2 Simulated powder X-ray diffraction patterns.

We propose that the composition of the reacting crystal can be expressed as a function of the intensity of certain reflections (equations 1 and 2):

$$I_{(t)} = (1 - p_{(t)})I_{(m)} + p_{(t)}I_{(d)} \tag{1}$$

and therefore:

$$p_{(t)} = \frac{I_{(t)} - I_{(m)}}{I_{(d)} - I_{(m)}} \tag{2}$$

where $p_{(t)}$ is the mole fraction of dimer in the crystal after irradiation time t, $I_{(t)}$ is the intensity of a reflection at time t, $I_{(m)}$ is the intensity for that reflection from the pure monomer crystal (i.e. t = 0) and $I_{(d)}$ is the intensity for that reflection from the pure dimer crystal (i.e. t = ∞). The values of $p_{(t)}$ can then be used to determine kinetic parameters.

EXPERIMENTAL

BBCP crystals were prepared by the literature method[4] and re-crystallised from a methanol/chloroform solution.

Typical Photodimerisation Experiment

Photodimerisation experiments were carried out by irradiating a BBCP single crystal with a 325 nm UV line emitted from a helium-cadmium (He-Cd) laser (Omnichrome Inc., Series 74). The He-Cd laser emits lines at 442 nm and 325 nm and a suitable band-path filter was employed to remove the 442 nm line. The crystal was mounted on an Enraf-Nonius CAD4 four-circle diffractometer and the UV light was introduced with a multimode optical fibre, with a fibre tip-to-crystal distance of 4 mm and a spot diameter of approximately 2 mm. The UV light intensity was measured through a 1 mm diameter pinhole set at the crystal position using a PM-311-A90 Optical Laser Power Meter (Nihon Kagaku Engineering). The beam power was 1.3 mW (1.69 mW/mm^2)

The crystal was rotated about the diffractometer phi axis during UV irradiation. At regular time intervals, UV irradiation was halted to allow the measurement of selected diffracted X-ray intensities. These measurements were made by an ω-scan method. In one set of experiments, the orientation matrix was redetermined after every UV irradiation period by centring 15 strong high 2θ reflections, before the other intensity measurements were performed. However, it was found that the change in orientation matrix was very small each time and in all other experiments it was redetermined only occasionally during the reaction. UV irradiation and X-ray diffraction measurement were both performed at 295 K.

Reaction Rate Dependence on UV Intensity

It was found that the reaction rate for two individual crystals may be quite different at the same apparent incident UV intensity. This was thought to be mainly due to the precise positioning of the crystal in the UV beam, which may not be of uniform flux. To quantify the rate dependence on UV intensity, it was necessary to devise an experiment whereby the reaction could be performed at different intensities but on the *same* crystal. This was achieved by irradiating the crystal with UV light attenuated with a soda-lime glass plate such that the intensity of the incident radiation was approximately half that of normal operation [0.68 mW (0.87 mW/mm^2)]. X-ray reflection intensities were measured as before until the reaction was approximately 50% complete. At this point the UV attenuator was removed and the irradiation and X-ray reflection intensity measurements continued until the reaction had reached completion. Again, UV irradiation and X-ray diffraction measurement were both performed at 295 K.

Reaction Rate Dependence on Temperature

To overcome the influence of the precise placement of the crystal in the UV beam on reaction rate, experiments were performed at different temperatures for the *same* crystal. For the first crystal, the reaction rate was determined as before and at a constant temperature, T_1, until the reaction was estimated to be ~30% complete. The temperature was then cooled to T_2 and the reaction rate determined over the ~30-60% conversion range. The temperature was cooled again, to T_3, and the reaction rate determined over the final ~60-100% conversion range. The same experiment was then performed for the next crystal but starting at temperature T_3 and cooling to T_4 and T_5. The ratio between the two values of the rate at T_3 was then used to determine the rates at T_4 and T_5 relative to T_1. This procedure was repeated for a total of ten crystals over a temperature range of 353-117 K at 15-30 K increments. Crystal cooling and heating was achieved with a liquid nitrogen gas-stream cryostat (Nonius FR558-S). The temperature of the crystal was estimated later by placing a very-fine copper-constantan thermocouple at the crystal position.

RESULTS and DISCUSSION

Although the change of intensity for many different reflections were measured to determine the composition of the BBCP crystals during reaction, only data based upon the 111 reflection is presented here. Full data with a detailed statistical analysis will be published elsewhere.

It can be seen from Figure 3(a) that an exponential increase in the intensity of the 111 reflection was observed during irradiation, and that the intensity reaches some maximum value. Using this intensity data, values for

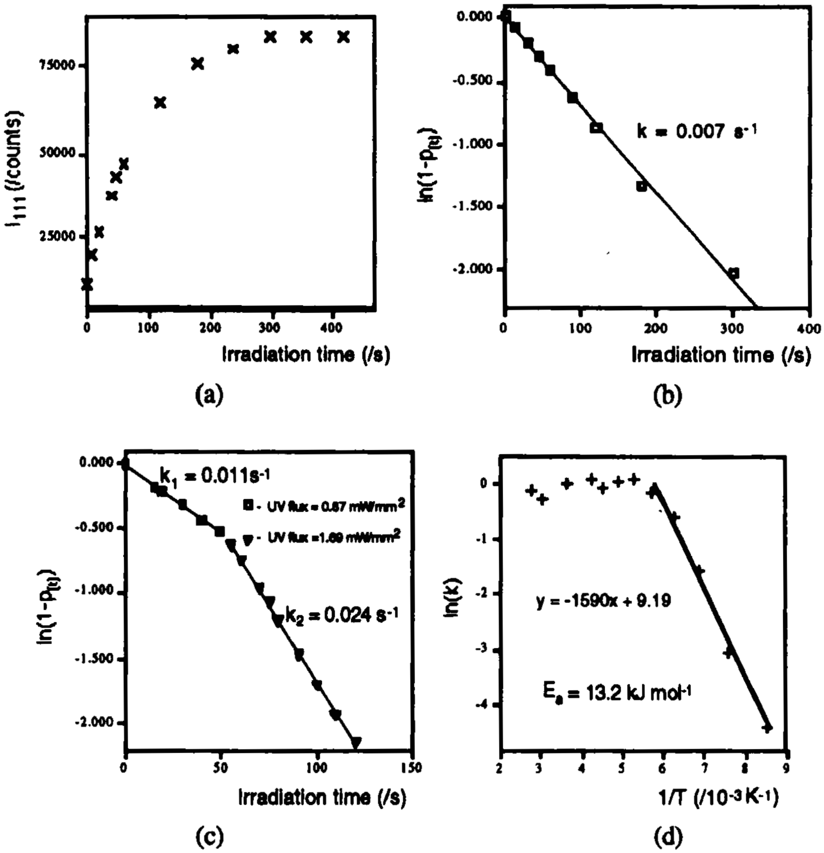

FIGURE 3 (a) Plot of the intensity of the 111 reflection *vs* t for a reacting crystal of BBCP; (b) linear plot of $\ln(1-p_{(t)})$ *vs* t for a BBCP crystal at 295 K; (c) plot of $\ln(1-p_{(t)})$ *vs* t at two different UV intensities; (d) Plot of ln(k) *vs* 1/T over the temperature range of 353-117 K.

$1-p_{(t)}$ (the monomer mole fraction) are easily calculated from equation 2. A plot of $\ln(1-p_{(t)})$ *vs* time is linear (Figure 3(b)) and hence demonstrates the reaction exhibits first order kinetics. The rate constant (k) is given by the slope of this plot, which for this crystal at 295 K is 0.007 s^{-1}.

Figure 3(c) indicates that when the intensity of UV radiation is doubled, the reaction continues to obey first order kinetics yet the rate constant is approximately doubled. Hence the reaction is likely to be a one-photon process.

The reaction was also found to obey first order reaction kinetics over the whole 373-117 K temperature range. In the ~273-173 K range it was found hat k was almost constant. However, a marked decrease in k was observed over the ~173-117 K range. Figure 3(d) is a plot of ln(k) *vs* 1/T and it can be seen that the plot is linear over the ~173-117 K range. The activation energy (E_a) for the reaction can be estimated from the slope of this Arrhenius type plot as ~13.2 kJ mol^{-1}. This small value probably equates to the energy required for reaction between one excited and one ground state molecule. This is a similar value to that reported for the photodimerisation reaction of a styrylpyrylium triflate[5]. The BBCP dimerisation reaction has been reported to be phonon assisted[6]. The measured decrease in k below the threshold temperature of ~173 K provides more strong evidence that this is the case.

The k was found to decrease very slightly at the high temperature range of the measurement (~353-273 K). Such an observation has also been reported for the photopolymerisation reaction of *p*-phenelenediacylic acid diethyl ester.[7] It is thought that the reaction rate is dependent on the potential deviation of two olefin bonds from the optimal position for reaction. At higher temperatures this deviation is larger because of increased thermal motion and so k is smaller.

CONCLUSION

The results indicate that X-ray diffraction can be used to reveal precise kinetic data, *in situ*, for the reaction of a single crystal. Using this technique it was demonstrated that the photodimerisation reaction of BBCP obeys first order kinetics over a wide temperature range. The reaction is a one photon process and likely to be phonon assisted. Below a threshold temperature of ~173 K the rate constant decreases and an Arrhenius type plot reveals that the activation energy for the reaction is ~13.2 kJ mol^{-1}. The rate constant was found to be slightly reduced at higher temperatures, possibly due to increased thermal motion of the olefin bonds.

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