Crystal Lattice Photochemistry Often Proceeds in Discrete Stages. Mechanistic and Exploratory Organic Photochemistry[1,2]
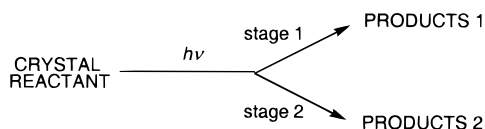
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ABSTRACT

While the solid-state photochemistry of crystals has been assumed to proceed to some critical point beyond which the crystal is destroyed, it has now been found that crystal lattice photochemistry often occurs in stages or regimes. In each regime different chemistry generally results. The reaction in different stages may be followed kinetically.

Solid state photochemistry provides a powerful synthetic tool of particular mechanistic interest. Often products, otherwise not accessible, may be obtained. The one question most often posed relative to a solid-state photochemical reaction, is to what conversion the reaction is practical. Thus, it is usually assumed that crystal-lattice reactions proceed consistently only to a given point followed by ill-defined results.[3]

We now report that for a large fraction of crystal lattice photochemical reactions, reactivity occurs in definite stages with each regime having its own characteristic course and that this is a general phenomenon. Additionally, we have succeeded in analyzing the kinetics involved. There are several important consequences of our findings. Perhaps the most important is that in a stage beyond the initial one, a reaction can often be obtained which is not accessible initially from any ordinary crystal reactant. Another consequence is that for solid-state photochemical processes which do not

proceed with one reaction to very high conversions, the process can still be quite practical.

This investigation was prompted by our observations in a study of dimorphs.[4] A discontinuity was observed in the reactivity as the reaction proceeded and it proved possible to deal with the reaction kinetics. It now has been found that the phenomenon extends beyond dimorphs and is common, and we have generalized the kinetic treatment.

For the present study we selected the Type B Enone Rearrangement[5] since both stereo- and regioselectivity are involved, and thus several products are possible in each case. Thus, in the first reaction, that of α-naphthyl-β-naphthyl enone **1**, four stereoisomers are observed in solution photolyses[6] and three in the solid-state reaction. In the second reaction studied, that of 2-methyl enone **2**, while one photoproduct results in solution, in the early stage of the

(1) This is Paper 255 of our general series.

(2) For Paper 254 see Zimmerman, H. E.; Alabugin, I. V. *J. Am. Chem. Soc.* **2000**, *121*, 952−953.

(3) (a) Hitherto, there have been literature examples where a reaction has been described as proceeding with continuous product variation. (b) For example, note Teng, M.; Lauber, J. W.; Fowler, F. W. *J. Org. Chem.* **1991**, *56*, 6840−6845.

(4) Zimmerman, H. E.; Alabugin, I. V.; Chen, W.-C, Zhu, Z. *J. Am. Chem. Soc.* **1999**, *121*, 11930−11931.

(5) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036−4042. (b) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749−3760. (c) For a review, see: Schuster, D. I. In *Rearrangements in Ground and Excited States*; P. DeMayo, Ed.; Academic Press: New York, 1980; Vol. 3.

(6) Zimmerman, H. E.; St. Clair, J. D. *J. Org. Chem.* **1989**, *54*, 2125−2137.

crystal photolysis an additional product also results.[7a] In more extended photolysis, the solution product appears.[7b] In a third example, that of phenyl α-naphthyl enone **3**, again the solid-state chemistry contrasts with that observed in solution.[8]

The examples we report presently are those with two regimes. In two cases, regime two affords a single product while regime one gives two products. In the third case, both regimes afford several photoproducts but with different distributions. We also anticipate reactions where further regimes occur.

In Schemes 1, 2, and 3 we show the behavior of (a) 4-α-naphthyl-4-β-naphthylcyclohex-2-enone **1**, (b) 2-methyl-4,4-diphenylcyclohex-2-enone **2**, and (c) 4-α-naphthyl-4-phenylcyclohex-2-enone **3**.

In a general treatment, if one plots separately the amounts of two photoproducts, **A** and **B**, versus the conversion, it can be shown that at any point with A_o and B_o concentrations, the ratio of slopes is given by eq 1. Here the slope of the plot of **A** is α, and that of **B** is β. The conversion is C and R gives the ratio of **A** to **B**. A_0, B_0, C, and R are variables.[9]
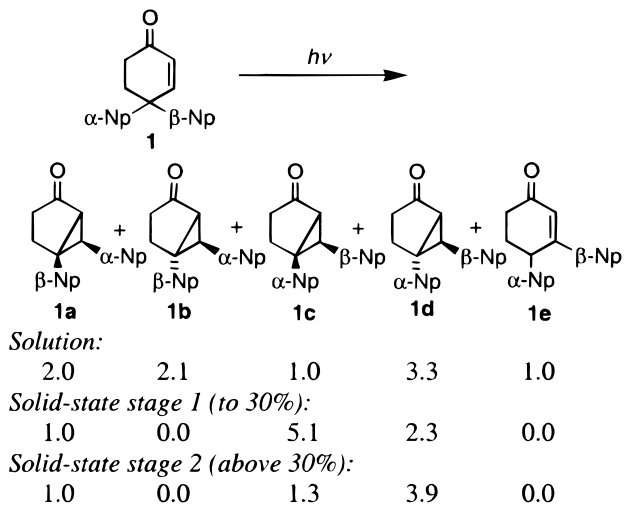
$$\alpha/\beta = [CR - A_0(R + 1)]/[C - B_0(R + 1)] \qquad (1)$$

If we have, for example, several regimes, each with its own selectivity, then within a given regime as product concentrations increase, the incremental ratio, R_{inc}, of product **A** to **B** becomes constant and is given by the ratio of slopes. Note eq 2.[9]

$$\alpha/\beta = R_{inc} \qquad (2)$$

The first of the three examples is depicted in Scheme 1. This example is that of 4-α-naphthyl-4-β-naphthyl enone **1** whose reactivity in solution and in the crystal lattice differs markedly. The second example is that of the 2-methyl-4,4-diphenylcyclohexenone **2** whose chemistry is dealt with in

Scheme 1. The Solution and Solid State Rearrangement of 4-α-Naphthyl-4-β-naphthylcyclohexenone **1**.


	1a	1b	1c	1d	1e
Solution:	2.0	2.1	1.0	3.3	1.0
Solid-state stage 1 (to 30%):	1.0	0.0	5.1	2.3	0.0
Solid-state stage 2 (above 30%):	1.0	0.0	1.3	3.9	0.0

Scheme 2. The Solution and Solid State Rearrangement of 2-Methyl-4,4-diphenylcyclohexenone **2**.
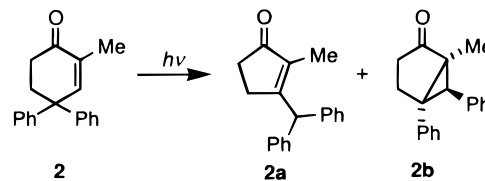
	2a	2b
Solution:	0.0	1.0
Solid-state stage 1 (to 10%):	1.0	1.0
Solid-state stage 2 (above 10%):	0.0	1.0

Scheme 2. The last example, presented in Scheme 3, involves the competition between phenyl and α-naphthyl migration.[10]

Scheme 3. The Solution and Solid State Rearrangement of 4-α-Naphthyl-4-phenylcyclohexenone **3**.
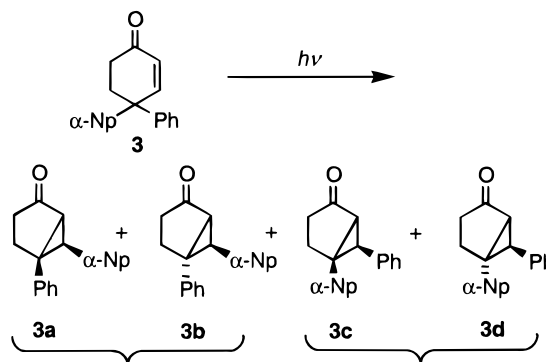
	3a	3b	3c	3d
Solution:	8.9		1.0	
Solid-state stage 1 (to 28%):	1.0		1.0	
Solid-state stage 2 (above 28%):	0.0		1.0	

In each of the three examples, the observed multistage reactivity is depicted quantitatively in Figures 1, 2, and 3. The most remarkable facet is the linearity seen for each product within each stage of the reaction and the different rates of formation of these products in the first and second regimes. A particularly striking further observation was made in the reaction of the dinaphthyl enone **1**. Within each of

(7) (a) Zimmerman, H. E.; Zhu, Z., *J. Am. Chem. Soc.* **1995**, *117*, 5245−5262. (b) It is clear that this did not result from melting as evidenced by monitoring the crystal shape and melting point throughout the photolysis. The minimum melting point was 80 °C while the run was at 0 °C.

(8) Interestingly, in the case of the enone **3**, two polymorphs, $P2_1/n$ and $P2_12_12_1$ were found, and only the latter, that described here, was found to be reactive.

(9) This is derived in the Supporting Information.

(10) Regime 2 is more complex than in the first two examples in that cis−trans isomerization of the product of stage 1 occurs. This does not affect the interpretation.
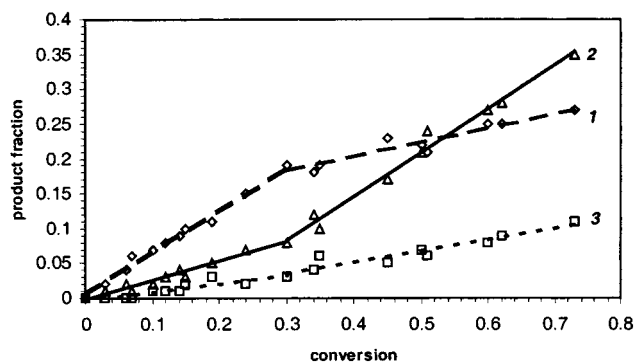
Figure 1. Stages and changes in reactivity with extent conversion of reactant **1**. Plot *1* corresponds to *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]hexan-2-one **1c**, plot *2* corresponds to *trans*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]hexan-2-one **1d**, plot *3* corresponds to *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **1a**.

the two stages broad melting behavior was found. However, at the point where the first stage ended and the second began, a sharp melting point was encountered. Here we know from X-ray analysis that each reactant molecule is surrounded by three neighbors. The point of discontinuity between the two stages occurs just as every reactant molecule has a product
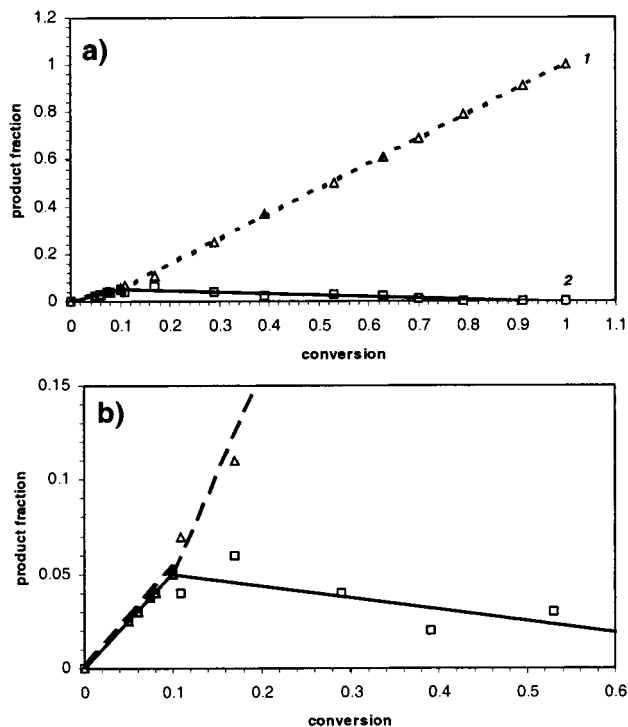

Figure 2. Stages and changes in reactivity with extent conversion of reactant **2**. Graph b shows the area of graph a corresponding to low conversions. Plot *1* corresponds to 1-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexanone **2b**, plot *2* corresponds to 2-methyl-3-(diphenylmethyl)cyclopent-2-enone **2a**.
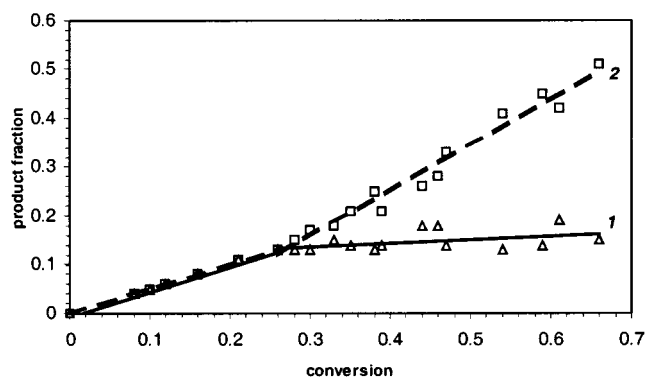

Figure 3. Stages and changes in reactivity with extent conversion of reactant **3**. Plot *1* corresponds to the sum of products of α-naphthyl migration (trans- and cis-bicyclics) **3a** and **3b**; plot *2* corresponds to the sum of products of phenyl migration (trans- and cis-bicyclics) **3c** and **3d**.

molecule adjacent. The occurrence of a sharp melting point at the point of discontinuity strongly supports the interpretation of a newly ordered molecular arrangement at this juncture. In contrast, in the case of the 2-methyl enone **2**, despite our finding two discrete stages, the melting point remained sharp but decreased until 60% reaction and then became broad until the final photoproduct was formed at which point it again was sharp.

We ascribe the existence of stages to the different reactivity of a molecule surrounded by one or more product molecules compared with the original situation where a reactant is in an environment with neighboring reactant molecules. In the dinaphthyl enone **1** reaction, it seems that the presence of one product neighbor diminishes reactivity so that isolated reactant molecules react preferentially. Similarly, in the case of the 2-methyl enone **2**, there are eight molecules surrounding any single one. Thus, as before, if the reactivity is diminished by the presence of one product neighbor, then at ca. 10% conversion, only a slower and different reaction is possible and stage two begins. With the large ratio of unreacted neighbors to reacted molecules, one anticipates a delayed change in melting behavior.

Conclusion. Crystal lattice photochemistry often proceeds in stages, each stage with its own reactivity. A most critical aspect is the chemistry of subsequent stages which by definition cannot be obtained directly in a photolysis but only by utilizing a subsequent stage of solid-state reaction.

Supporting Information Available: Experimental details, and spectroscopic and X-ray data for compounds described. Also, mathematical derivation of eqs 1 and 2, as well as a generalized treatment of stage reactivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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