

TRIPLET ENERGY SENSITIZATION OF A CRYSTALLINE PHASE PHOTOREARRANGEMENT

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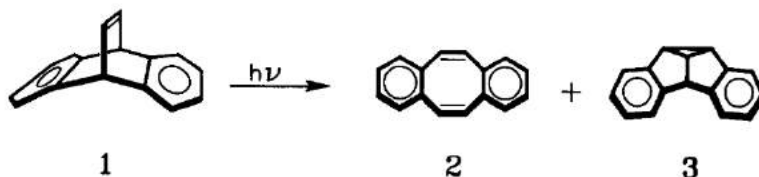
Abstract. Direct irradiation of crystals of dibenzobarrelene leads mainly to dibenzocyclooctatetraene, the singlet product, whereas photolysis of solid solutions of dibenzobarrelene with various crystalline triplet energy sensitizers leads exclusively to dibenzosemibullvalene, the triplet photoproduct. Graphical analysis of the extent of maximum conversion in the sensitized runs versus the sensitizer (xanthone) concentration indicates that one xanthone molecule can photosensitize the formation of up to 24 product molecules.

Chemical reactions of organic crystals frequently differ both qualitatively and quantitatively from their solution phase counterparts as a result of the physical restraints to motion present in the crystal lattice.¹ Both bimolecular² and unimolecular³ processes are affected, and many new reactions and structure-reactivity correlations have been elucidated through solid state chemical studies coupled with the technique of X-ray crystallography.

One difficulty with chemical studies involving organic crystals is that several classical techniques for investigating mechanism, such as competition experiments and chemical trapping of reactive intermediates, are difficult because the addition of extra components to the crystalline medium necessarily disrupts the lattice regularity that is responsible for the unique reactivity in the first place. Similar considerations apply in the field of organic photochemistry where, despite their widespread use in solution, such techniques as sensitization and quenching have not been employed to control crystalline phase photochemical reactivity. This is somewhat surprising in view of the fact that energy transfer in doped crystals is a well documented occurrence, particularly between aromatic molecules, and has been used widely in various studies in photophysics and spectroscopy.⁴

In this communication we report that triplet sensitization can be used to direct the course of a multiplicity-dependent photorearrangement in the solid state. We believe this to be the first demonstration of such a process.⁵ The reaction chosen for study is the well known photorearrangement of dibenzobarrelene (1) into dibenzocyclooctatetraene (2) and dibenzosemibullvalene (3) (Scheme).⁶ Direct irradiation (254 nm) of dibenzobarrelene in cyclohexane or THF solutions affords predominantly dibenzocyclooctatetraene (singlet product),^{6b} whereas photolysis in acetone (Pyrex filter) leads exclusively to dibenzosemibullvalene (triplet product).^{6a} This latter process is recognizable as an example of the general class of photorearrangements known as the di- π -methane reaction.⁷

Before attempting solid state sensitization studies, it was necessary to demonstrate that crystals of dibenzobarrelene (mp 119-120 °C) react upon direct irradiation. They do. Both single crystal and powder samples of dibenzobarrelene afford approximately 80:20 mixtures of photoproducts 2 and 3 when irradiated (< 5% conversion under nitrogen) with the unfiltered



output from a 450 W Hanovia lamp at room temperature. The samples showed no visible trace of melting.

For the sensitized runs, three different sensitizers and two different methods of sample preparation were investigated. The sensitizers tested were benzophenone (mp 48.5 °C), xanthone (mp 174 °C) and γ -phenylbutyrophenone (mp 55-56 °C).⁸ γ -Phenylbutyrophenone was chosen because we had demonstrated earlier that it is photochemically inert in the solid state, but undergoes Norrish type II cleavage to styrene and acetophenone when irradiated in the melt.⁹ It is therefore a potential sensitizer and liquid phase indicator. The sample preparations employed were (1) powdered reactant/sensitizer mixtures prepared by grinding the components in a mortar and pestle, and (2) samples prepared by co-crystallizing the reactant and sensitizer from the melt.

In order to ensure that only the sensitizers absorb light under the photolysis conditions, the sensitizer-dibenzobarrelene mixtures were irradiated with a nitrogen laser (337 nm). Dibenzobarrelene does not absorb at this wavelength, and this was confirmed by control photolyses on crystalline dibenzobarrelene alone. The sensitized photolyses, on the other hand, gave exclusively dibenzosemibullvalene (3), the triplet photoproduct. The possibility that energy transfer was occurring in liquid regions of the sensitizer-reactant phase diagram was ruled out in the case of benzophenone by working at -10 °C, well below the eutectic temperature of ca. 30 °C. For γ -phenylbutyrophenone, the possibility of melting during photolysis was eliminated by finding that no trace of acetophenone was present in the reaction mixture. Finally, the relatively high melting point of xanthone (174 °C) makes it unlikely that melting is responsible for energy transfer in this case. Most of the more detailed studies described below were carried out with xanthone as the photosensitizer.

Sensitization was much more efficient for the sensitizer-reactant samples prepared from the melt as opposed to grinding. For example, prolonged photolysis of powdered samples containing up to 8% (mol/mol) xanthone in dibenzobarrelene led to <5% conversion to dibenzosemibullvalene. In contrast, the samples prepared by co-crystallization from the melt, which we assume to be solid solutions of xanthone in dibenzobarrelene, gave much higher conversions. Figure 1 shows a typical plot of conversion percentage versus time for a sample containing 1% (mol/mol) of xanthone in dibenzobarrelene. Irradiation was carried out on KBr pellets containing the co-crystallized reactant/sensitizer mixtures, and the points were determined by quantitative gas chromatography. Similar runs were conducted for xanthone concentrations up to 8% (mol/mol). Interestingly, each plot levels off at a limiting conversion that is dependent on

sensitizer concentration. Also interesting is the fact that the solid state reaction is much less efficient than the solution process. Nitrogen laser irradiation of a benzene solution containing 0.1 M dibenzobarrelene and 10^{-3} M xanthone leads to 50% conversion in only five minutes.

By dividing the limiting photoproduct percentage by the xanthone percentage for each solid state run and plotting these data versus the xanthone concentration, we obtain a sensitizer efficiency curve, i.e., a plot of the number of dibenzosemibullvalene molecules formed per molecule of photosensitizer as a function of sensitizer concentration for xanthone (Figure 2). This plot indicates that xanthone's efficiency as a solid state sensitizer decreases with increasing concentration, a circumstance that can be attributed reasonably (if speculatively) to accompanying sensitizer aggregation and self-quenching.¹⁰

Figure 1. Product Saturation Curve, 25°
1% (mol/mol) Xanthone in Dibenzobarrelene

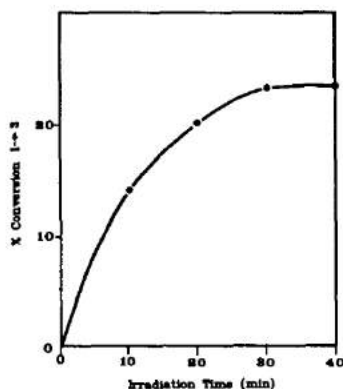
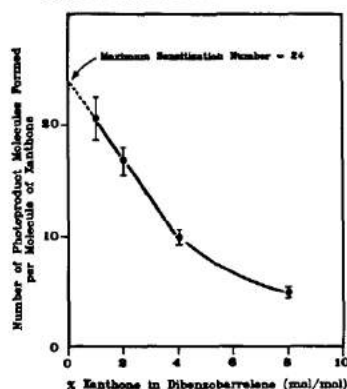


Figure 2. Xanthone Sensitization Efficiency



To the extent that it is justified to extrapolate the sensitizer efficiency curve to 0% sensitizer concentration, Figure 2 indicates that one xanthone molecule can photosensitize the formation of up to 24 product molecules. In order to determine whether this is a reasonable number, X-ray crystal structure studies on dibenzobarrelene were undertaken. Dibenzobarrelene crystallizes in space group C2, $a = 14.4667(7)$, $b = 8.0425(2)$, $c = 11.7337(6)$ Å, $\beta = 126.160(3)^\circ$, $Z = 4$, $R = 0.034$ for 1106 observed reflections with $I \geq 3\sigma(I)$.¹¹ We used the structural data to calculate the number of neighbor molecules within a given (center of mass)-to-(center of mass) distance from a reference molecule in the lattice (assumed to be the sensitizer molecule). This showed that there are 24 neighbors within a distance of 12 Å from the central (sensitizer) molecule; at 15 Å, there are 53. All have a clear line of vision to the sensitizer. Previous studies have suggested an upper limit of 10-15 Å for triplet-triplet energy transfer in rigid media.¹² Our findings are thus consistent with these results. But what prevents xanthone from transferring triplet energy to more than 24 dibenzobarrelene molecules? The answer is that the photoproduct, dibenzosemibullvalene, quenches xanthone triplets.¹³ This is also probably the main reason why the solid state % conversion vs

time curve (Figure 1) rises less steeply and levels off at a lower value than the corresponding solution curve. We are continuing our studies on the use of crystalline sensitizers (and quenchers) in solid state photochemistry.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

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(Received in USA 23 January 1987)

