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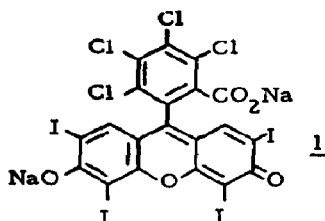
Photooxygenations with Heterogeneous Sensitizers

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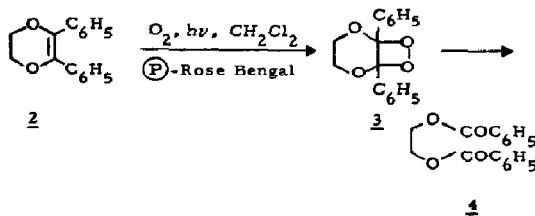
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Although many sources of singlet oxygen are now available, the photosensitized formation of singlet oxygen using various dyestuffs remains the method of choice for most synthetic and mechanistic applications. However, there have been several limitations to the photooxidation method: (1) the sensitizer (dye) must be soluble in the reaction solvent limiting the dye/solvent combinations which can be used; (2) the dye is often bleached over long reaction times; (3) the dye can interact with the substrates and/or the products; and (4) the separation of the dye from the products can be difficult.

We have prepared several insoluble polymer-bound dyes and found these heterogeneous sensitizers useful for the photochemical generation of singlet molecular oxygen. Polymer-bound sensitizers have several advantages over the free sensitizers in solution. They can be used in solvents in which the unbound dye is insoluble and therefore unable to sensitize singlet oxygen formation efficiently. They are significantly more stable toward bleaching than are the free sensitizers. The polymer-bound sensitizers can be easily removed at the end of the reaction by filtration, and can be reused with little or no loss in efficiency.



Reaction of Rose Bengal **1** with chloromethylated styrene-divinyl-benzene copolymer beads (200 - 400 mesh, 1.11 meq Cl/g polymer) gave **1** chemically bound to the polymer beads, designated P-Rose Bengal. Photooxidation of 2,3-diphenyl-p-dioxene (**2**) with P-Rose Bengal in methylene chloride gave **4** in 95% yield. Absorp-



tion spectra of the reaction solution before and after photolysis indicated that no Rose Bengal had leached into the solution during the reaction. The results of several control experiments indicate this to be an authentic singlet oxygen reaction sensitized by the heterogeneous sensitizer (P)-Rose Bengal. The quantum yield for the production of $^1\text{O}_2$ in CH_2Cl_2 with (P)-Rose Bengal is 0.46.

Other sensitizers that have been attached to the polymer beads include eosin-Y, fluorescein, chlorophyllin and hematoporphyrin. Experiments utilizing these (P)-sens will be described.

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Z3

The Reactions of Photoexcited SO_2 with Polyunsaturated Olefins

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The reactions of SO_2 , photoexcited at 3130Å and 25 °C, with C_2H_2 and C_3H_4 (allene) have been studied. With C_2H_2 , the sole gas phase product is CO. Its quantum yield, $\Phi\{\text{CO}\}$, increases with the ratio $[\text{C}_2\text{H}_2]/[\text{SO}_2]$ to an upper limiting value of 0.04. In the presence of excess CO_2 or H_2O vapor, $\Phi\{\text{CO}\}$ is reduced at low values of the ratio $[\text{C}_2\text{H}_2]/[\text{SO}_2]$, but remains unchanged or increases slightly at high values of the ratio. As NO is added it first increases $\Phi\{\text{CO}\}$, but then reduces it to zero. The results are consistent with the interpretation that the SO_2 electronic states responsible for the chemistry are the triplet states.

With allene, the two gas phase products are CO and C₂H₄. Their ratio is not constant, and the primary process in allene is more complex than for C₂H₂. The CO yields increase slightly with allene pressure to an upper limiting value of ~ 0.015 , but the C₂H₄ yield passes through a maximum of ~ 0.01 . The addition of excess CO₂ reduces the C₂H₄ yield to zero, but only partially depresses the CO yield. The inference is that different electronic states may be involved for the products. Possibly all accessible electronic states contribute to the chemistry.

Z6

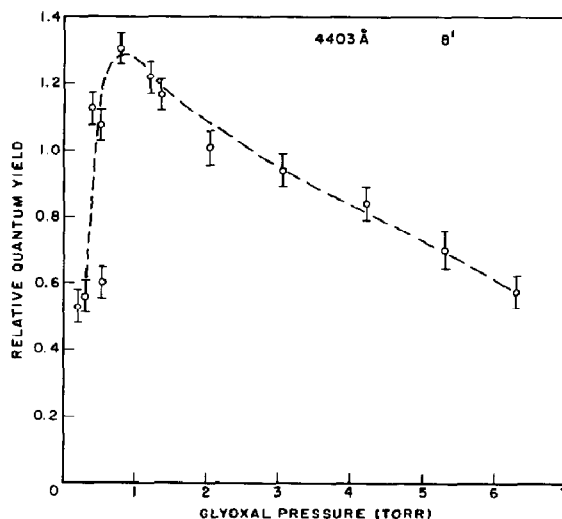
Single Vibronic Level Photochemistry of Glyoxal

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Interest in controlling the course and rate of a photochemical reaction through the selective population of an excited state (usually *via* laser radiation) has permeated the recent literature. Since photochemistry proceeds in many polyatomic molecules only after several sequential or competitive excited-state processes, it is clear the "laser-controlled" photochemistry must rely on a detailed understanding of the molecular mechanisms by which photochemistry occurs.

We describe here a new experimental technique capable of examining photodissociation mechanisms as a function of both pressure and excitation wavelength and the first results on the dissociation of glyoxal into CO. A pulse, tunable laser (0.1 Å bandpass) is used to populate single vibronic levels in glyoxal at pressures between 0.1 and 6 Torr. The relative quantum yields of CO (Φ_{CO}) are obtained by resonance emission methods. The output from an electrodeless rare gas lamp excites emission from CO which is then measured quantitatively by a solar blind photomultiplier. Carbon monoxide concentrations below 0.5 μm are easily measured. Low pressure extinction coefficients for each 0.1 Å bandpass of excitation are measured in a separate multiple pass cell.

Figure 1 shows Φ_{CO} versus pressure following population of the 8¹ level in the ¹A_u



state of glyoxal (several other vibronic levels have also been studied with similar results). These data reveal that at least two separate excited-state processes precede photodissociation. The increase of Φ_{CO} with pressures below 1 Torr originates at least in part from collisionally-induced S₁ → T₁ intersystem crossing. The decrease of Φ_{CO} with pressures above 1 Torr appears to result from a collisionally-induced process destroying the intermediate which is the precursor to CO formation. The nature of this intermediate remains unknown.

α2

Picosecond Continua for Time Resolved Absorption Spectroscopy

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Picosecond spectroscopy [1] has been applied to the study of numerous ultrafast processes in recent years, however, most of the applications to date have been more photophysical than photochemical. This circumstance has been, in part, due to the fact that only a discrete set of laser frequencies has been available for probing a system. The recent development of picosecond continuum pulses generated in glasses and liquids [2, 3] constitutes a significant improvement in the versatility of picosecond techniques. The spectral widths of these pulses span the entire wave-length