

With allene, the two gas phase products are CO and C<sub>2</sub>H<sub>4</sub>. Their ratio is not constant, and the primary process in allene is more complex than for C<sub>2</sub>H<sub>2</sub>. The CO yields increase slightly with allene pressure to an upper limiting value of  $\sim 0.015$ , but the C<sub>2</sub>H<sub>4</sub> yield passes through a maximum of  $\sim 0.01$ . The addition of excess CO<sub>2</sub> reduces the C<sub>2</sub>H<sub>4</sub> 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

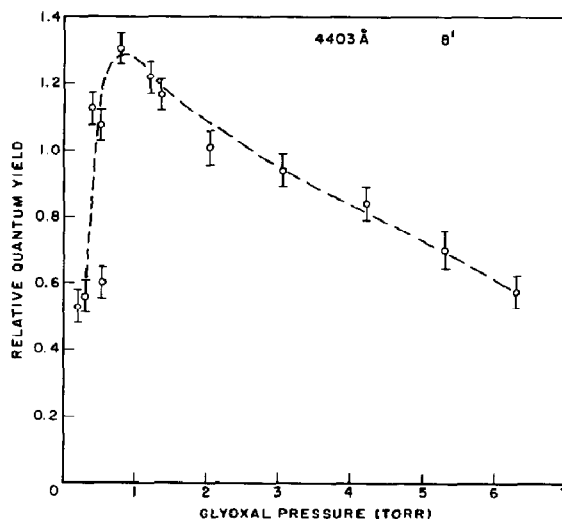
### Single Vibronic Level Photochemistry of Glyoxal

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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 ( $\Phi_{CO}$ ) 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  $\mu\text{m}$  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  $\Phi_{CO}$  versus pressure following population of the  $8^1$  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  $\Phi_{CO}$  with pressures below 1 Torr originates at least in part from collisionally-induced  $S_1 \rightarrow T_1$  intersystem crossing. The decrease of  $\Phi_{CO}$  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.

## $\alpha 2$

### 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

region from 350 - 1000 nm, yet their temporal widths are the same as the picosecond pulses which generate them. Thus these continuum pulses constitute excellent light sources for the measurement of time resolved absorption spectra of transient intermediates produced in photochemical reactions. Experimental configurations which generate and utilize picosecond continua will be described and the results of recent experiments employing them will be presented and discussed.

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

- 1 T. L. Netzel, W. S. Struve, and P. M. Rentzepis, *Ann. Rev. Phys. Chem.*, **24** (1973) 473.
- 2 R. R. Alfano and S. L. Shapiro, *Phys. Rev. Letters*, **24** (1970) 584.
- 3 G. E. Busch, R. P. Jones and P. M. Rentzepis, *Chem. Phys. Letters*, **18** (1973) 178.

#### α9

##### Picosecond Resolution of Intersystem Crossing and Measurement of Quantum Yields in Rose Bengal

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Through the use of picosecond time resolved absorption spectroscopy, we have been able to determine the first excited singlet state lifetime of Rose Bengal, an iodinated analogue of Rhodamine 6G. We also measured the rate of ground-state repopulation. By combining these data with a literature value of the radiative lifetime, the quantum yields of intersystem crossing, internal conversion and fluorescence could be obtained without recourse to triplet quenching techniques or other secondary techniques. We suggest that this important development could find general applicability in measuring quantum yields of intersystem crossing and internal conversion.

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#### α10

##### Laser Photolysis in Globular Proteins

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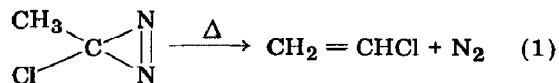
Pyrene and several derivations of pyrene are solubilized in aqueous systems by using globular proteins such as serum albumin. The pyrene atmosphere resides in various parts of the protein, but not in the aqueous phase. Laser excitation of the pyrene leads to the excited singlet and triplet state. The lifetime of the excited singlet states is dependent on the pH and temperature of the system. The changes in the lifetime reflect structural changes in the protein. Several quenchers such as O<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub>, I<sup>-</sup>, Ti<sup>+</sup> quench the excited states of pyrene in the protein. These quenchers reside mainly in the aqueous phase. The experiments thus measure the factors that affect the permeability of the protein to these quenchers. The data also give information on the nature of the protein site containing pyrene.

#### β4

##### The Photochemistry of 3-Chloro-3-Methyldiazirine

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The mechanism of thermolysis of methyl diazirines has been elucidated [1]. In the ground state the decomposition products of 3-chloro-3-methyldiazirine (I) are nitrogen and vinyl chloride.



Bridge, Frey and Liu did not detect any other products [2].

The photolysis of I is known to produce [3] the products of reaction (1) as well as the fragmentation products, acetylene and hydrogen chloride [4].