With allene, the two gas phase products are CO and C_2H_4. Their ratio is not constant, and the primary process in allene is more complex than for C_2H_2. The CO yields increase slightly with allene pressure to an upper limiting value of $\sim$0.015, but the C_2H_4 yield passes through a maximum of $\sim$0.01. The addition of excess CO_2 reduces the C_2H_4 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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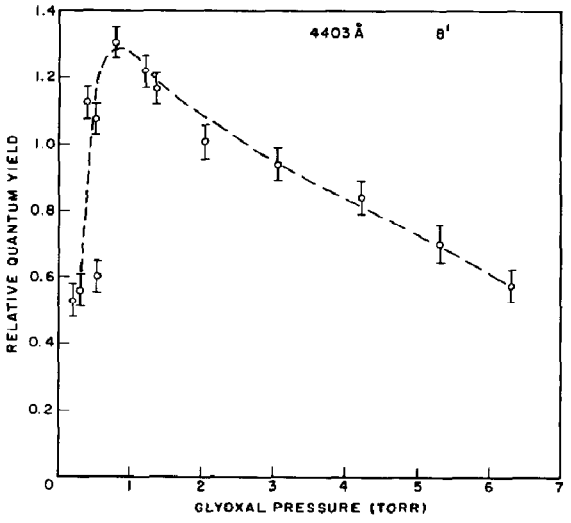
Interest in controlling the course and rate of a photochemical reaction through the selective population of an excited state (usually *via* laser radiation) has permeated the recent literature. Since photochemistry procedes in many polyatomic molecules only after several sequential or competitive excited-state 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 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 Φ_{CO} with pressures below 1 Torr originates at least in part from collisionally-induced $S_1 \rightarrow T_1$ 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