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# Evidence for the primary decomposition of propylene oxide to singlet methylene

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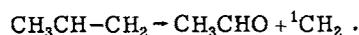
Using laser-induced fluorescence as a probe for  $^1\text{CH}_2$ , we have determined that infrared multiphoton dissociation of propylene oxide yields singlet methylene as a primary product. Experiments with specifically labeled 1- $d_2$  propylene oxide confirm, by showing only  $^1\text{CD}_2$ , that the carbene is ejected exclusively from the terminal position of the heterocycle and that fragmentation is faster than any competing hydrogen migration process.

## I. INTRODUCTION

The technique of infrared laser-induced multiphoton dissociation combined with the time-resolved product detection by laser-induced fluorescence has provided a substantial new store of detailed information about the dynamics of primary processes in the unimolecular decompositions of a large number of systems.<sup>1-7</sup> An interesting subset of these consists of oxygen containing hydrocarbons that decompose to yield singlet methylene  $^1\text{CH}_2$ . Extensively characterized examples include ketene, acetic anhydride, and acetic acid,<sup>6,7</sup> all of which, as suggested by recent work, dissociate to methylene through the same intermediate—highly excited ketene.<sup>6</sup>

In this paper we wish to report a new unimolecular dissociative source of methylene that we believe does not involve the intermediacy of ketene. The subject of our investigation is propylene oxide, a prototypical alkyl epoxide important for its relevance in air pollution and stratospheric systems as an oxygen atom olefin-addition product. Our findings on the mechanism of its decomposition are worthy of particular note in light of the fact that carbene elimination has not previously been associated with hydrocarbon epoxide decomposition. Earlier studies of propylene oxide, involving both pyrolysis<sup>8-10</sup> and chemical activation by oxygen atom addition,<sup>11-13</sup> list isomerization to propanal and acetone followed by fragmentation as the major pathways for decomposition.

We find substantial evidence for primary elimination from the terminal position in the epoxide heterocycle to form  $^1\text{CH}_2$  and acetaldehyde:



Our conclusion is based on the observation of strong, prompt laser-induced fluorescence signals: from  $^1\text{CH}_2$  for multiphoton dissociation of  $\text{CH}_3\text{CHCH}_2\text{O}$ , and from  $^1\text{CD}_2$  (and only  $^1\text{CD}_2$ ) for multiphoton dissociation of specifically labeled  $\text{CH}_3\text{CHCD}_2\text{O}$ .

## II. EXPERIMENTAL

Figure 1 shows a schematic of our experimental set-up for laser-induced fluorescence detection. Propylene epoxide is admitted in a low pressure controlled flow through a Granville-Phillips variable leak valve. Pressure, typically 5–20 mTorr, is monitored in the cell

by means of a MKS Baratron capacitance manometer.

Dissociation of the sample is produced by the pulse from a grating tuned  $\text{CO}_2$  TEA laser, set to the region of the  $\text{CH}_3$  rocking mode of propylene epoxide at  $944\text{ cm}^{-1}$ , and focused at the viewing region of the apparatus by a 10 in. focal length germanium lens. The intensity of infrared light is controlled by using extracavity NaCl and  $\text{CaF}_2$  attenuators.

The  $^1\text{CH}_2$  dissociation products are detected by laser-induced fluorescence using the visible pulse from a Quanta-Ray DCR 1A/PDL1 Nd:YAG pumped dye laser. This pulse passes through an iris before entering the cell and on exciting is deflected by a Ge flat.

The fluorescence cell is configured around a glass cross. Its long arms are fitted with internal baffles, brewster angle NaCl windows, and Wood's horns to minimize scattered light. Laser-induced fluorescence is gathered by a 25 mm focal length concave mirror and, after passing through a 550 nm cutoff filter, focused by a 38 mm focal length quartz lens onto the face of an EMI 9558 QB photomultiplier tube.

Figure 2 shows a diagram of the timing and signal processing electronics. A master oscillator triggers the Q-switch relay in the Nd:YAG laser. After an internal delay of 3 ms it starts each of two channels in an Evans Products dual channel gate and delay generator. One channel, triggered at 10 Hz, fires the YAG laser Q switch. The second, divided down to 1 Hz, fires the  $\text{CO}_2$  laser. The time jitter between pump and probe pulses with this arrangement is typically 40–80 ns, due principally to the command jitter in the spark-gap fired  $\text{CO}_2$  laser.

To precisely determine the time interval for each pair of pulses we place fast detectors on the outputs of each laser. To monitor the dye laser we use a Hewlett Packard 5082-4203 PIN photodiode, for the  $\text{CO}_2$  laser a Laser Precision KT-1510 fast pyroelectric detector amplified by an Avantek UFC15-128, 28 dB wideband preamplifier. The output of the  $\text{CO}_2$  laser detector is used to start, and that of the dye laser detector to stop a Hewlett Packard 5370A Fast Time Interval Counter (TIC). This device is controlled through a IEEE-488 interface by a home-built laboratory microprocessor.

The fluorescence signal at the photomultiplier is amplified by an EMI VA.02 preamplifier, and passed to an

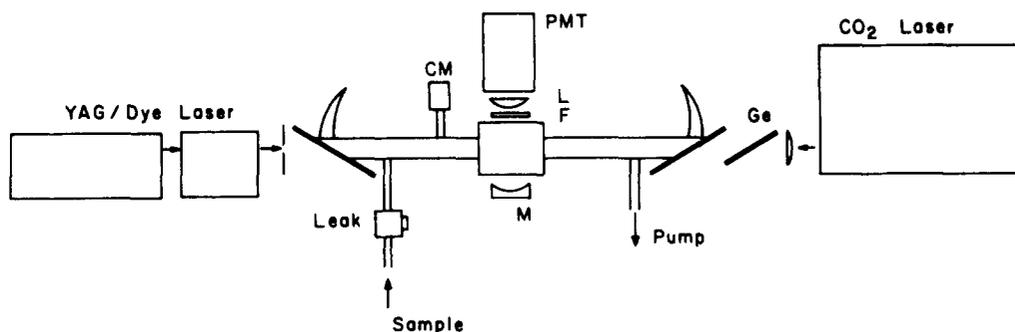


FIG. 1. Schematic view of the experimental set-up: CM, capacitance manometer; M, mirror; F, filter; L, lens; PMT, photomultiplier; Ge, germanium flat.

Evans Products boxcar used as a single shot gated integrator. Under computer control the gated integrator collects an appropriate portion of the fluorescence waveform and supplies the integrated voltage to the computer's on-board 12 bit ADC. At the same time the computer reads the time interval for that shot from the TIC, storing the two pieces of information together for the off-line reconstruction of the  $^1\text{CH}_2$  rise time. The computer also controls the dye laser wavelength, so that the above time discrimination facility can be used in conjunction with scanning to produce a constant delay-time spectrum.

The fluorescence signal at 70 mTorr has a lifetime of about  $1 \mu\text{s}$ . At 3 mTorr its lifetime grows to about  $4 \mu\text{s}$ . These values are in reasonable agreement with earlier observations of  $^1\text{CH}_2 \bar{b}^1B_1$  decay rates.<sup>6,7</sup>

Propylene oxide was obtained from Aldrich Chemical Co. Following trap-to-trap distillation, the purity of this reagent, tested by flame-ionization GC, was found to be greater than 99%. Propylene oxide- $d_2$  was prepared by reduction of  $\alpha$ -chloromethyl propionate by  $\text{LiAlD}_4$  to the  $d_2$ -chlorohydrin. The substituted alcohol was then epoxidized over concentrated KOH.

### III. RESULTS

The laser-induced fluorescence spectrum of  $^1\text{CH}_2$  obtained from multiphoton dissociation of propylene oxide using an incident  $\text{CO}_2$  laser energy of 1 J, focused to a

cross sectional area of approximately  $10^{-3} \text{ cm}^2$ , is shown in Fig. 3. This spectrum was taken at a constant pump-probe laser delay time of 400 ns. The propylene oxide pressure was 5 mTorr. For these conditions essentially the same spectrum was obtained with a delay time of 600 ns.

We observed the rise time for the formation of  $^1\text{CH}_2$  to depend weakly on laser fluence. Figure 4 shows the time dependence of the rising population of  $^1\text{CH}_2 \bar{a}^1A_1(0, 0, 0)$  for three  $\text{CO}_2$  laser fluences, 0.8, 1.0, and 1.1 J/pulse. The relative conversion efficiencies corresponding to these fluences, as determined by the maximum amplitude of the Q-branch bandhead signal for each case, are given in Fig. 5.

The laser-induced fluorescence spectrum obtained following MPD of specifically labeled propylene oxide- $d_2$  is given in Fig. 6(a). This spectrum is the characteristic  $\bar{b}^1B_1(0, 18, 0) \rightarrow \bar{a}^1A_1(0, 0, 0)$  band of  $^1\text{CD}_2$ ,<sup>14</sup> obtained in our experiment with a probe delay of 600 ns.

Figure 6(b) gives the results of a search for  $^1\text{CH}_2$ . It is a high sensitivity scan of the region of the  $(0, 16, 0)$  band of  $^1\text{CH}_2$  taken using the deuterated compound as reactant. The pressure of  $\text{CH}_3\overline{\text{CH}}\text{CD}_2\text{O}$  for this scan was 60 mTorr. Comparison with Fig. 3, obtained with 12 times less sample density and 20 times less gain, places a conservative upper limit on the production of  $^1\text{CH}_2$  from  $\text{CH}_3\overline{\text{CH}}\text{CD}_2\text{O}$  at 0.1%.

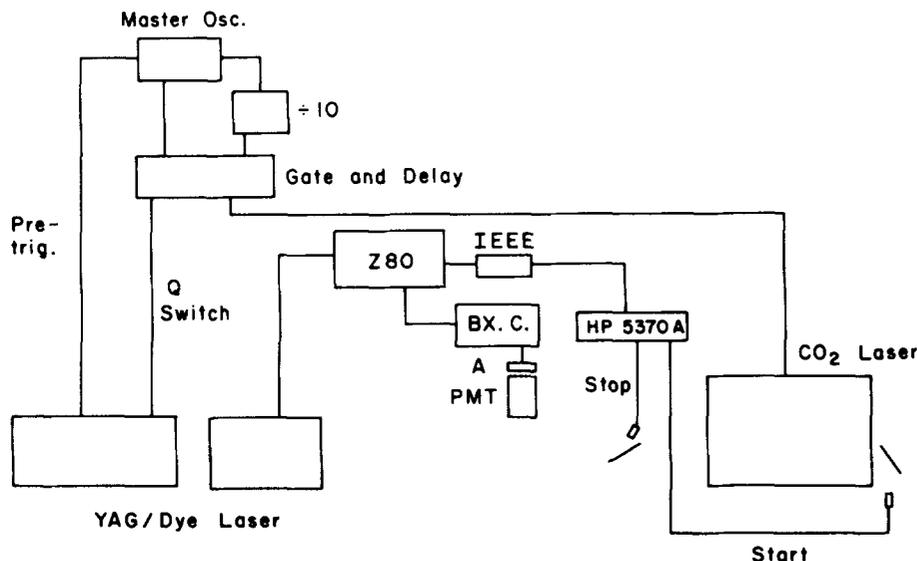


FIG. 2. Timing and signal processing electronics (see the text).

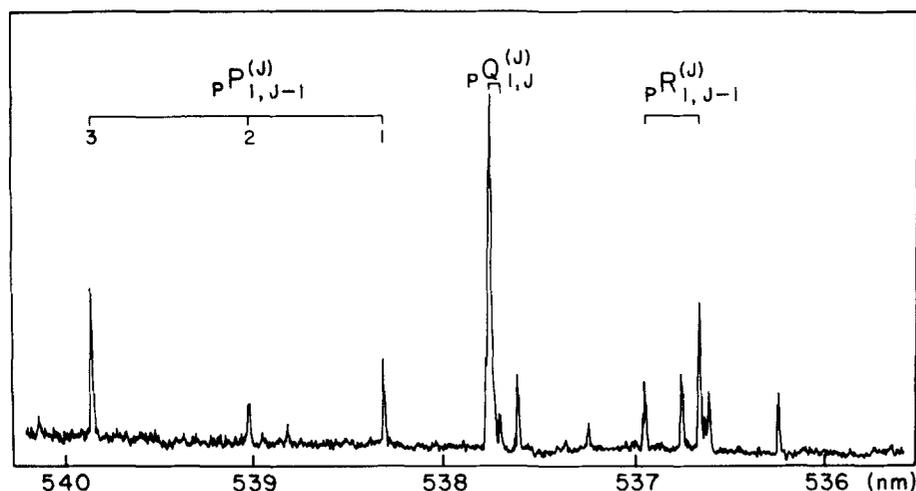


FIG. 3. Laser-induced fluorescence spectrum of  ${}^1\text{CH}_2 \tilde{a}^1A_1(0, 0, 0) - \tilde{b}^1B_1(0, 16, 0)$  from infrared multi-photon dissociation of propylene oxide.

#### IV. DISCUSSION

Conventional studies of propylene epoxide pyrolysis point to hydrogen migration combined with simple C-C bond scission as the principal pathway for the decomposition of this molecule.<sup>8-11</sup> The initial step is seen as fracture of the three-membered ring:

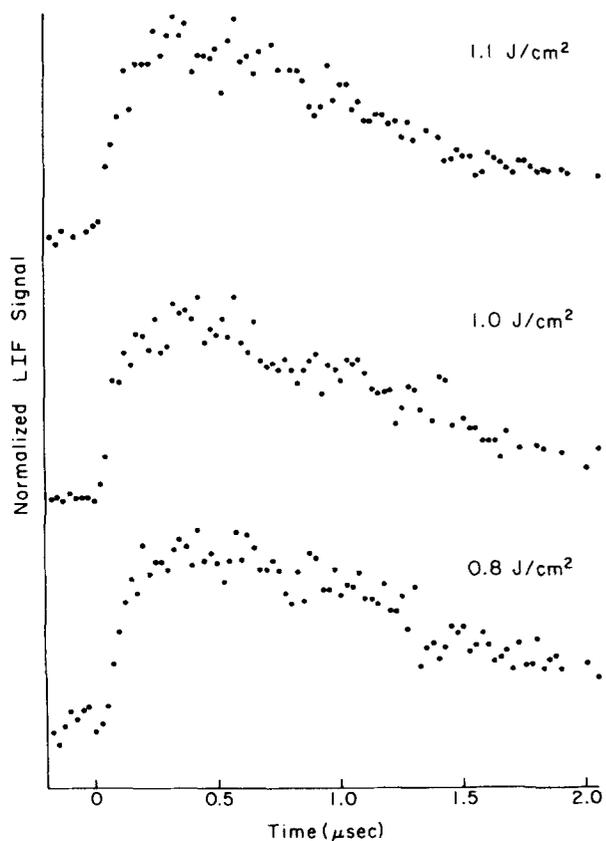
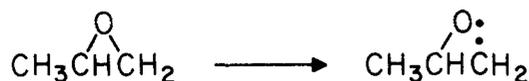


FIG. 4.  $\text{CO}_2$  laser energy dependence of the rise time for  ${}^1\text{CH}_2$  production from MPD of propylene oxide. Sample pressure in all three cases is 6 mTorr.

followed by isomerization. One such path leads to acetone, which, in part decomposes through methyl radicals to yield ethane and CO. Other products assumed to come from isomerization are propanal, methyl vinyl ether, and allyl alcohol. No previous study has associated  ${}^1\text{CH}_2$  with propylene oxide decomposition.

Our experiment establishes by direct observation that  ${}^1\text{CH}_2$  radicals are produced in the dissociation of propylene oxide. Time resolved measurements show that this diradical species is formed promptly, with an appearance rate much faster than the collision frequency. Thus,  ${}^1\text{CH}_2$  must be regarded as a *unimolecular* product of the parent, and not the result of a secondary, *bi-molecular* reaction.

However, rise time alone fails to answer two impor-

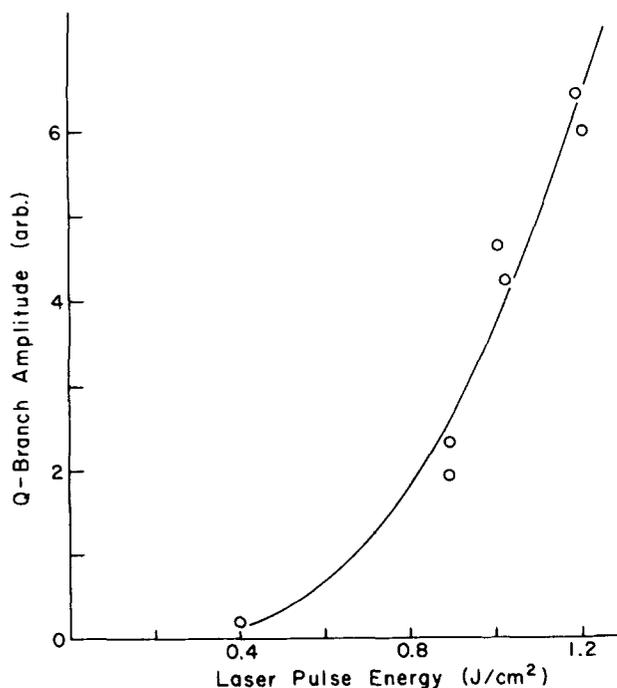


FIG. 5. Relative conversion efficiency as a function of incident laser fluence.

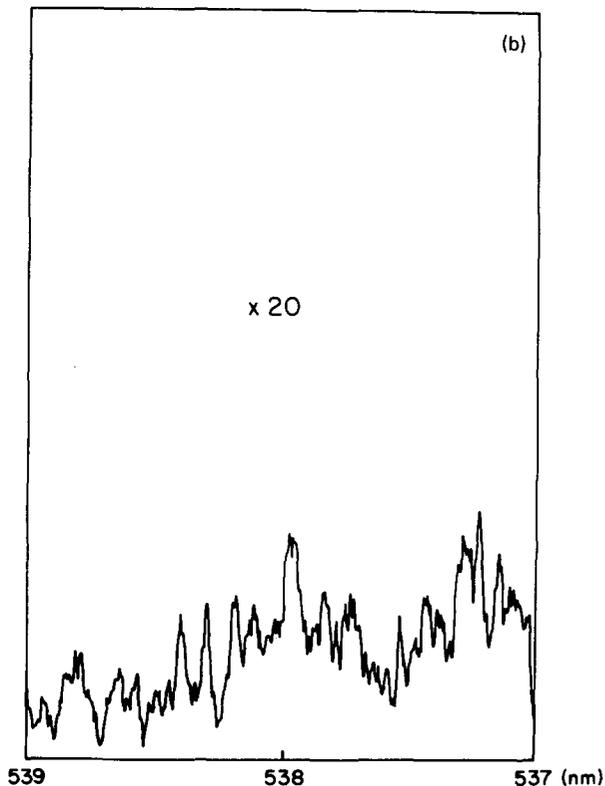
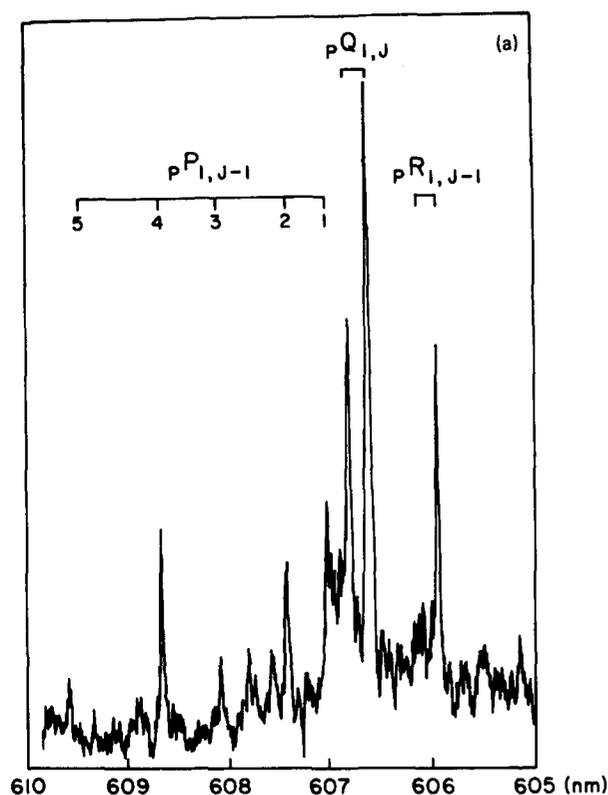


FIG. 6. Upper frame: Laser-induced fluorescence spectrum of  ${}^1\text{CD}_2 \tilde{a}^1\text{A}_1(0, 0, 0) \rightarrow \tilde{b}^1\text{B}_1(0, 18, 0)$  from infrared multiphoton dissociation of  $1-d_2$  propylene oxide. Lower frame: Scan for  ${}^1\text{CH}_2$  from the multiphoton dissociation of  $1-d_2$  propylene oxide (compare with Fig. 3).

tant questions that remain. Sequential decompositions are common in MPD. Is methylene in this case a primary product formed directly from the parent or is it a secondary product of some fragment or isomer formed during the laser pulse? Laser-induced fluorescence is a sensitive technique. If  ${}^1\text{CH}_2$  is the product of a primary pathway, how important is this channel in relation to other decomposition routes?

Preliminary answers to these questions are indicated by the results of isotopic substitution. The production of only  ${}^1\text{CD}_2$  from  $\text{CH}_3\text{CH}(\text{CD}_2)\text{O}$  proves that the formation of methylene is site specific with respect to the parent compound. This means that fragmentation or isomerization products with scrambled hydrogens cannot be intermediates in the formation of methylene.

The importance of this channel in relation to possible competing processes is not as clearly established. The isotopic specificity of the elimination proves that isomerization back and forth between propylene oxide and acetone cannot be occurring on the time scale of pumping and  ${}^1\text{CD}_2$  loss. However, specific elimination does not rule out the possibility of unidirectional rearrangement. For example, near the thermochemical threshold for methylene elimination, any acetone formed by isomerization will likely dissociate by loss of  $\text{CH}_3$  before reforming scrambled propylene oxide. Such a process would diminish the signal from  ${}^1\text{CD}_2$  but not contaminate it. Thus even though the strong LIF signal in all of these experiments proves that isomerization does not dominate, determination of its absolute contribution to the decomposition of propylene oxide will require a detection method that is sensitive to all products. Such experiments, which apply the technique of scavenged product analysis to MPD,<sup>15</sup> are presently underway.<sup>16</sup>

#### ACKNOWLEDGMENTS

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