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Photochemistry and photophysics of small heterocyclic molecules: III. Continuous wave CO_2 laser chemistry of ethylene oxide

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ABSTRACT: The gas-phase continuous wave IR laser photolysis of ethylene oxide (oxirane) was examined in the presence of SiF_4 as a sensitizer molecule. Acetaldehyde, ethylene, acetylene, methane and carbon monoxide are the resultant gaseous products detected by IR spectroscopy. No significant reaction occurs in the absence of this sensitizing agent or at laser frequencies not resonant with transitions of both oxirane and SiF_4. The dependence of the photolysis on laser fluence, gas (total and/or sensitizer) pressure and laser wavelength was examined. The data are consistent with the involvement of highly vibrationally excited oxirane molecules produced by a combination of collisional and radiative processes. The product distribution is consistent with recent *ab initio* predictions. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: ethylene oxide; laser photolysis; sensitizer

INTRODUCTION

The thermal reactivity of oxirane has been examined under a number of different experimental conditions and several different primary reaction mechanisms have been proposed. Among the earliest studies, Mueller and Walters[1] reported on the thermal reaction of several hundred torr of oxirane at temperatures up to 700 K. These authors speculated that hydrogen abstraction by methyl radicals was responsible for a large fraction of the decomposition of the starting material. Crocco *et al.*[2] employed temperatures as high as 1200 K and suggested that the critical reaction, initiating the chain decomposition of oxirane, was the formation of formaldehyde and methylene radicals directly from a ring-opened oxirane. Neufeld and Blades[3] used approximately 1 atm of oxirane and temperatures up to 750 K. They reported that the observations were consistent with the initial formation of an excited acetaldehyde molecule via thermally induced isomerization, followed by either stabilization of the primary product or subsequent decomposition to methyl and formyl radicals. Benson[4] also reported kinetic data consistent with the initial formation of a hot acetaldehyde intermediate and proposed a complex reaction scheme to account for all of the remaining products. Finally, Lifshitz and Ben-Hamou[5] used a shock tube to study high-pressure reactions of ethylene oxide at temperatures up to 1200 K. These studies produced, in addition to acetaldehyde and alkenes, methane and carbon monoxide. The authors proposed that the last two products result from the direct rearrangement/dissociation of the intermediate acetaldehyde.

Our high-level *ab initio* results[6] indicate that the primary step in the dissociation of oxirane is isomerization along the ground-state potential surface to acetaldehyde. Reaction products are predicted to derive from decomposition along either the singlet or, after intersystem crossing, triplet acetaldehyde surfaces. The former leads to production of CH_4 and CO, while the primary products of the latter would be the CH_3 and HCO radicals which would undergo secondary chemistry. Relative rates, as a function of total oxirane energy, were also predicted.

The use of CO_2 lasers in the initiation of unimolecular processes is well known. While both pulsed and continuous wave (cw) lasers have been employed, relatively few cw examples are known. Tardieu de Maleissye and co-workers[7] reported on the SF_6-sensitized reaction of ethane and in a series of experiments[8–10] Pola and co-workers employed SF_6 sensitization to the decomposition of small fluoro-substituted molecules. The use of sensitizers in IR laser photochemistry typically results in a loss of molecular specificity in the deposition of the laser energy. The chemistry often becomes indistinguishable from that of (homogeneous) high-temperature pyrolysis.[11]

Typically, IR lasers are viewed as initiating photochemistry via the excitation of vibrational degrees of

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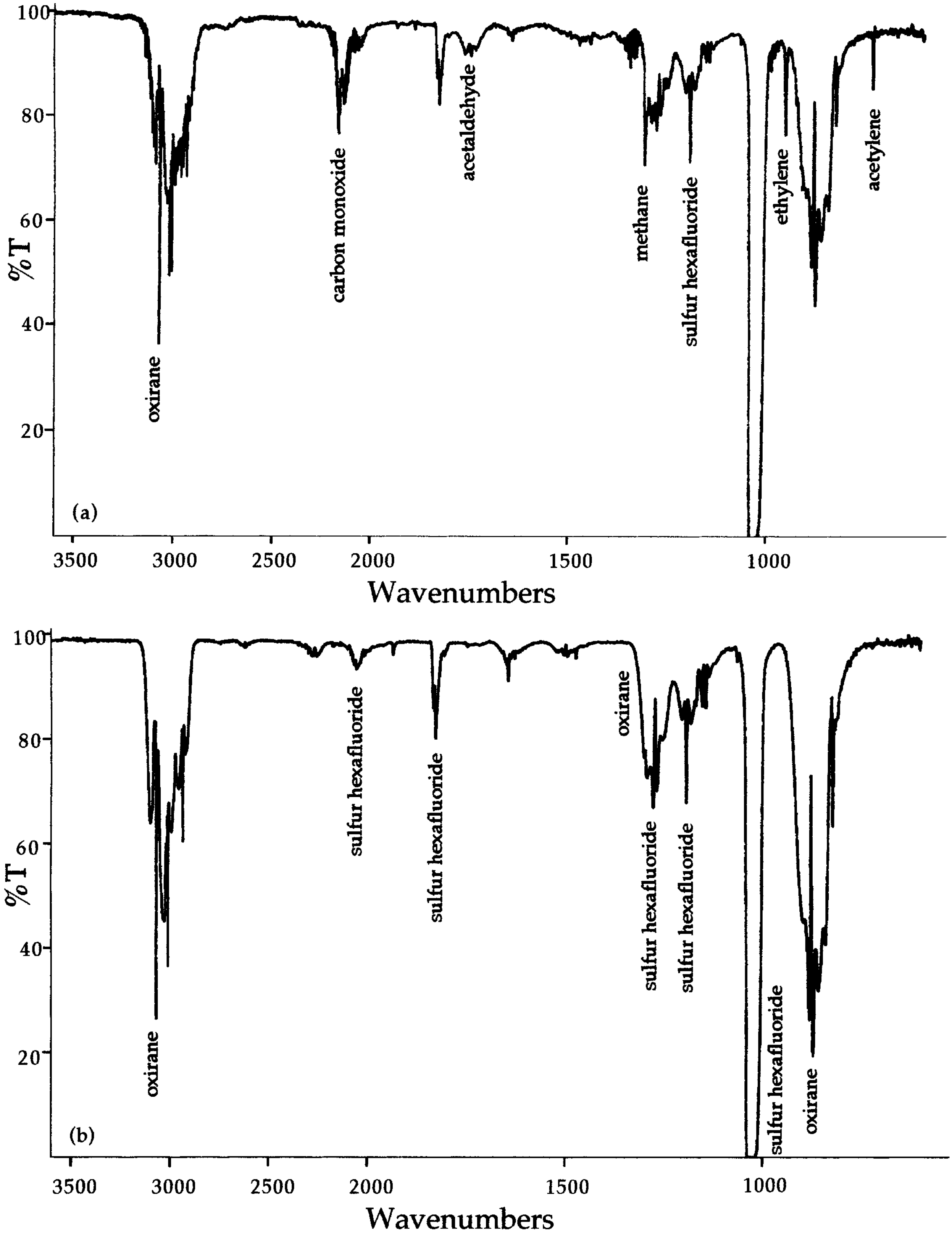

Figure 1. FTIR spectrum of the mixture of SiF_4 and oxirane: (a) after and (b) prior to irradiation at 1032 cm^{-1}. The reactants and products are identified in both spectra

freedom. One suggestion for improving the prospects of IR laser-induced chemistry[12] is to use the excitation of translational in addition to internal modes to permit passage over the reaction barrier. We have reported[13] the CO_2 laser-induced, SF_6-sensitized reaction of ethylene sulfide to yield CS_2, CH_4 and C_2H_4. Both the sensitizer[12] and the reactant molecule[14] had significant absorption coefficients at the P(20) line of the CO_2 laser (944 cm^{-1}). Therefore, irradiation of a cell containing both SF_6 and thiirane caused direct excitation of both molecules. The rapid equilibration of the sample mixture via the many collisions occurring during the course of irradiation resulted in the efficient production of vibrationally excited thiirane via resonant V–V (SF_6–*thiirane*) energy transfer collisions. In this type of process, the vibrationally hot organic molecule may absorb additional laser photons, leading to the formation of products not readily accessible by thermal activation alone. The same technique was used in the current work and provided a means of verifying the *ab initio* predictions.

As may be seen from the discussion above, the previous studies of the gas-phase pyrolysis of ethylene oxide have been complicated by the possibility of reaction at the cell walls. The use of sensitizers in conjunction with cw CO_2 radiation provides an environment in which the chemistry is homogeneous. The technique also offers the advantage of a ‘steady-state’ method by employing cw rather than pulsed lasers. The goals of the work described in this paper were twofold: first, to provide a test of the homogeneous dissociation mechanism of oxirane and our *ab initio* results, and second, to explore further the utility of the sensitizer technique, which has been limited to only a handful of chemical systems.

EXPERIMENTAL

An Apollo Lasers Model 122 CO_2 laser was employed. The beam, ~8 mm in diameter, was passed unfocused through the photolysis cell. For most of the reported experiments, the laser was tuned to the P(40) line, although photolysis at other frequencies was attempted and noted in the results. The laser output was measured with a surface calorimeter and ranged from 4 to 12 W. The laser was operated in an electronically chopped mode such that a single cycle of the output was obtained. In this mode, the irradiation time is adjustable and was determined with a storage oscilloscope and a pyroelectric detector.

The photolysis cells were constructed of 316-type stainless steel and fitted with KBr windows for both photolysis and analysis. The data reported in the tables and figures were collected with a cell 8.25 cm in length and 3.8 cm in diameter. The cell was evacuated by a rotary pump prior to sample introduction and was filled from a stainless-steel vacuum line. Oxirane was purchased as a gaseous sample of research purity from Fluka Chemical and used as received. The sensitizers (SiF_4 and SF_6) and background gas (N_2) were purchased from Matheson Gas Products and used as received. Sample pressures were measured via capacitance manometers (Baratron).

Reactions were typically run using a single exposure of 3 s to the laser output. This time represents an experimental compromise and was chosen in order to minimize the effects of secondary processes while obtaining accurately measurable yields of products. In studies involving variables other than laser fluence, the laser output was set to 12 W. Initial concentrations and products were determined using quantitative IR absorption spectroscopy on a Perkin-Elmer 1600 Series Fourier transform (FT) IR instrument. All FTIR spectra were recorded using 16 scans and maximum resolution (2 cm^{-1}) over the range 400–4000 cm^{-1}. Spectra were recorded prior and subsequent to laser exposure and the composition of the sample was determined, using difference spectra, from calibration data. The characteristic peaks for acetaldehyde, acetylene and ethylene were easily distinguished from all other absorption bands. Some spectral overlap occurs for the CO and CH_4 bands. The difference spectra permit quantitative measurements.

RESULTS

Most of the data discussed in this paper were obtained by irradiation of the SiF_4–oxirane mixture at 1027 cm^{-1}. Unless noted otherwise, all experimental data refer to irradiation at this frequency. This frequency overlaps[15a] the ν_3 triply degenerate Si–F stretching mode of SiF_4, which is centered at 1032 cm^{-1}. Oxirane also exhibits a weak absorption[15b] at this frequency assigned to the ν_8 CH_2 rocking motion. Therefore, for excitation with the P(40) line of the laser, both the target molecule and the sensitizer transitions were resonant or nearly resonant with the laser wavelength. However, owing to the relative absorption coefficients and pressures, most of the input energy was initially deposited into the SiF_4 manifold. Figure 1 shows the IR spectrum of the photolysis mixture after (a) and prior to (b) irradiation. The spectral region 4000–400 cm^{-1} is included in this figure so that the products may be assigned. Absorbances due to CO, C_2H_4, CH_4, C_2H_2, acetaldehyde, unreacted oxirane and SiF_4 are noted on the spectrum. These bands were identified from the IR spectra of the pure materials. The nature of the products and their relative ratios were invariant with changing experimental conditions. The typical product distribution is given in Table 1. The results in the table are based on the fraction of the total carbon reacted (as oxirane). The most significant product is CO, the yield of which is approximately equal to that of all other carbon-containing products. There is a small, difficult to quantify, yield of acetaldehyde estimated as <5%, and also involatile solid product. We conclude that, with these constraints and within the experimental errors (~5%), that all of the reaction products have been identified.

A reasonable measure of the reactivity of oxirane under these experimental conditions is the per cent

Table 1. Typical product distribution[a]

Product	Yield (%)	Relative yield (%)
CH_3CHO	<5	<0.1
CH_4	19	0.45
CO	42	1.0
C_2H_4	19	0.45
C_2H_2	7	0.17

[a] As fraction of the total carbon lost as oxirane. Involatile and unanalyzed solid material is assumed to account for the remaining carbon.

Table 2. Oxirane reactivity[a] as a function of cw-laser power

Nominal laser power (W)	Maximum temperature[b] (K)	Per cent depletion (s^{-1})
12.5	950	23.9
9.3	890	21.4
7.7	875	22.7
6.8	870	11.0
4.4	850	3.6

[a] Reaction conditions: 25 Torr oxirane with 60 Torr SiF_4; irradiation for a total of 3 s.
[b] Ref. 17.

depletion (per second) of the starting material for a given set of conditions; a quantity analogous to the conversion per flash (CPF) in pulsed CO_2 photolysis. This is defined as 100% × $(\Delta P/P_{\text{initial}})_{\text{oxirane}}$/photolysis time, where ΔP is the quantity of starting material reacted under the experimental conditions. The per cent depletion is, in effect, a rate, since the exposure time has been kept constant. It is critical to keep in mind that the depletion yield is averaged over the entire volume of the reaction vessel (that is, we measure the total change in oxirane or product concentration in the cell), while the reaction itself mainly occurs along the path of the CO_2 laser whose beam diamter is much smaller than that of the cell. Figure 2 presents data on reactivity as a function of the initial concentration of oxirane. Each point represents a separate experiment and multiple runs at nearly identical pressures indicate an estimated error of 10% at pressures greater than 10 Torr. Using 60 Torr of sensitizer gas, the rate of depletion is seen to increase approximately linearly with increasing initial concentration of reactant at pressures less than 25 Torr, but to decrease at higher pressures. The effect of increasing laser fluence on reactivity is shown in Table 2. At laser powers greater than the threshold, the reactivity increases sharply, but levels off at laser powers greater than ~8 W.

Increasing the sensitizer gas pressure served to decrease the oxirane reactivity. The experimental results are shown in Fig. 3. In these experiments, the irradiation time was 3 s, the laser power was 12 W and the oxirane pressure was 25 Torr. In order to test whether the effect evident in Fig. 3 was dependent on the nature of the gases present, two additional experiments were run using identical experimental conditions, but in the presence of N_2 (pressures of 30 Torr N_2 with 30 Torr SiF_4 and 40 Torr N_2 with 60 Torr SiF_4). There was no significant difference between the results of these experiments and those expected for reaction in the presence of 30 and 60 Torr SiF_4 alone. That is, only the pressure of sensitizer gas was important. The results shown in Figs 2 and 3 indicate that only species capable of absorbing the incident radiation affect the rate of depletion of oxirane.

SiF_4-sensitized CO_2 laser photochemistry of pure samples of the product species was examined. With the exception of acetaldehyde and ethylene, all of the

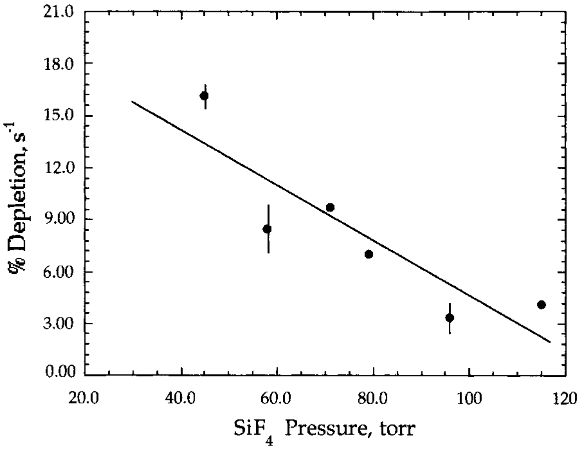

Figure 2. Depletion of the starting material as a function of the initial concentration of oxirane. The estimated uncertainty in the higher pressure points is 10%, but the error in the points representing lower pressure experiments is greater owing to the smaller net conversion. The line is intended only to guide the eye through the data points. Experimental points were obtained with 3 s exposures at a laser power of 12 W and 60 T added SiF_4

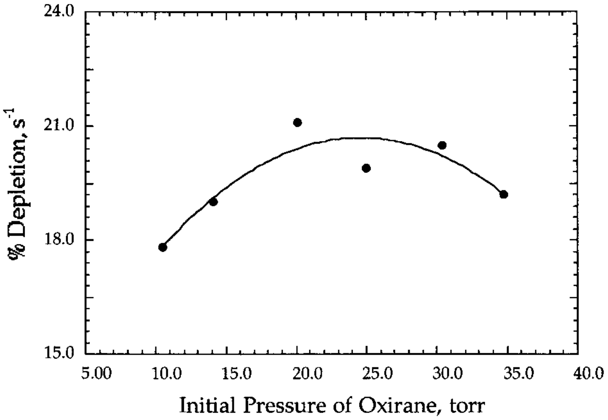

Figure 3. Effect of sensitizer pressure on the reactivity of oxirane. The solid line is intended only to guide the eye through the data points. Experimental conditions include irradiation time 5 s, laser power 12 W and oxirane initial pressure 25 Torr

products are stable to irradiation under the conditions of this experiment. Acetaldehyde was observed to decompose with an overall depletion rate approximately twice as large as that of oxirane and to produce methane and carbon monoxide as final products. This is a rapid decomposition rate and we attribute the observation of only minute traces of acetaldehyde in the photolysis to this reactivity. Based upon these control experiments, all of the methane observed in these experiments is assumed to reflect the initial production levels of acetaldehyde. Similarly, all of the observed acetylene is assumed to result from the decomposition of ethylene based on our observations of the reaction of the latter under conditions identical with those in the oxirane studies.

Attempts to react pure oxirane were unsuccessful even though the molecule exhibits weak absorption at 1032 cm^{-1}. SiF_4 was essential to the initiation of the reactive process. Other attempts to drive the reaction thermally,[11] that is, without the possibility of resonant V–V energy transfer, did not meet with any success. A laser frequency of 935 cm^{-1} falls within an absorption band of SF_6, which was substituted for SiF_4 as the sensitizer. For SF_6 pressures of 60 Torr and approximately 5 W of cw laser power (up to 3 s irradiation) the pressure of oxirane changed only slightly from the initial value. Preliminary experiments indicate that the overall, cell-averaged depletion rate for sensitization with SF_6 at 935 cm^{-1} is $\sim$100 times slower than with SiF_4 sensitization and irradiation at 1032 cm^{-1}.

DISCUSSION

The products observed in this study included only two oxygen-containing molecules. In addition, no gaseous alkanes other than methane are directly observed. The *relative* product yields are essentially invariant with reactant/sensitizer pressure and laser fluence, although the *extent* of reaction is affected by all of these parameters. These results contrast with reported studies of the pyrolysis of oxirane.[1–5] In those studies a number of alkanes were observed and conflicting reports on the number of different oxygen-containing molecules were made.

The effect of increasing laser fluence, shown in Table 2, indicates that the efficiency of increasing fluence is less as the total fluence increases. The rate of increase in oxirane depletion is not constant and decreases at higher fluence. This same behavior was observed in the SF_6-sensitized reaction of ethylene sulfide. It is attributed to changes in the effective absorption length of the absorber gas, in this case, SiF_4. We estimate, using the high fluence measurements reported in the literature,[16] that the laser was >99% attenuated after a pathlength of 2.75 cm for 5 W input power. The maximum temperature over this excitation region, along the laser axis, is estimated by the formulation of Zhu and Yeung[17] and is noted in Table 2 for each set of conditions. Increasing reactivity with increasing laser fluence is indicative of the greater number of activated oxirane molecules as the heated volume increases. The fact that the heating process becomes less efficient in promoting reactivity as the laser fluence increases results from the bleaching of the absorption coefficient at the highest laser intensities. The relative fraction of absorbed energy per unit length is lower at high laser fluence.[16]

The role of the sensitizer gas may be considered by examination of Fig. 3. The data indicate that increasing the pressure of sensitizer causes a decrease in the rate of reactivity. There are two possible causes for this observation. The first is that the increase in pressure causes an increase in collisional deactivation of the energized oxirane molecules since molecules will experience a larger number of collisions at higher pressure. This is discounted by the observation that reactions run with mixtures of N_2 and SiF_4 yield results which are equivalent to those obtained with the SiF_4 alone. That is, the addition of N_2 and the additional molecular collisions that ensue have no effect on the rate of reaction. The alternative explanation is related to the fact that all of the incident radiation is absorbed within the cell and the optically active region is only a fraction of the entire cell pathlength. An increase in the sensitizer pressure reduces this active length and, therefore, the volume of the active region. The absolute number of activated oxirane molecules and the rate of reaction also decrease proportionately. The observation that the addition of N_2 has no effect is consistent with this hypothesis. The results for increasing P_{oxirane} support this conclusion. An increase in the pressure of the target molecule will also decrease the reaction volume and, hence, the extent of reaction. The depletion of starting material is, therefore, dependent not only upon chemical factors, but also upon physical processes.

The lower reactivity for the SF_6-sensitized reaction is indicative of the need for both direct internal excitation of the oxirane molecule (via efficient V–V energy transfer) and thermal activation. Irradiation at 935 cm^{-1} does not allow for either resonant V–V energy transfer or direct absorption since the oxirane molecule does not have an internal motion at this energy. However, the ν_8 CH_2 rock is observed (weakly) at 1020 cm^{-1} and overlaps the intense SiF_4 absorption band at 1032 cm^{-1}. This allows for nearly resonant V–V transfer, not present in the SF_6-sensitized reaction even at laser powers similar to that used in the SiF_4 sensitized reactions. The vibrationally excited oxirane so created would then be available to absorb additional photons from the laser field. This mode of energization appears to be essential for reactivity in the current experiment as was also observed in the case of the related thiirane molecule.

The information presented in this paper does not necessarily lead to a unique detailed mechanism for the observed reaction. However, one possible, general kinetic pathway is outlined below. Note that many possible secondary reactions have been omitted from this scheme. In particular, we do not address the possibility of a radical-initiated chain reaction decomposition of oxirane. The data do not permit that question to be answered. It is possible that a secondary process, involving radical-initiated decomposition of oxirane, may occur. However, it cannot be a significant fraction of the total decomposition for the following reasons. The observation that, under the experimental conditions of the current work, the relative yields of the products are invariant provides an indication of the nature of the reaction pathway. Statistical theory predicts that the ratio of products should be temperature dependent. The absence of any significant variation is an indication that all of the products are derived from the same primary product and the results of the *ab initio* calculations[6] are consistent with this viewpoint. The *ab initio* calculations indicate that primary reactivity occurs in the acetaldehyde channel populated by sensitized isomerization from oxirane. The decomposition of the resulting acetaldehyde, in either quantum state, may, but need not be, sensitized by the presence of SiF_4. The *ab initio* results show a reaction barrier, but also a significant excess energy to overcome the barrier in this system. An abridged mechanism consistent with both the experimental results and the *ab initio* calculations is as follows:

$$SiF_4 + h\nu \rightarrow SiF_4{}^{\dagger} \tag{1}$$

$$SiF_4{}^{\dagger} + M \rightarrow M + SiF_4 \tag{2}$$

$$SiF_4{}^{\dagger} + C_2H_4O(S_0) \rightarrow SiF_4 + C_2H_4O(S_0)^{\dagger} \tag{3}$$

$$C_2H_4O(S_0)^{\dagger} + h\nu \rightarrow C_2H_4O(S_0)^{\dagger\dagger} \tag{4}$$

$$C_2H_4O(S_0)^{\dagger\dagger} + M \rightarrow C_2H_4O(S_0) + M \tag{5}$$

$$C_2H_4O(S_0)^{\dagger\dagger} \rightarrow CH_3CHO(S_0)^{\dagger\dagger} \tag{6}$$

$$CH_3CHO(S_0)^{\dagger\dagger} \rightarrow CH_4 + CO \tag{7a}$$

$$CH_3CHO(S_0)^{\dagger\dagger} \rightarrow CH_3CHO(T_1)^{\dagger\dagger} \tag{7b}$$

$$CH_3CHO(T_1)^{\dagger\dagger} \rightarrow CH_3 + CHO \tag{8a}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{8b}$$

$$C_2H_6 + h\nu \rightarrow C_2H_4 + H_2 \tag{8c}$$

$$CHO + h\nu \rightarrow H + CO \tag{8d}$$

$$H + H + M \rightarrow M + H_2 \tag{8e}$$

$$CH_3CHO(S_0)^{\dagger\dagger} + M \rightarrow CH_3CHO(S_0) + M \tag{9}$$

In this mechanism, initiation of the reaction occurs with excitation of SiF_4. Initial oxirane excitation is by means of near resonant V–V collisions with the excited sensitizer. The vibrationally excited oxirane is further energized both by means of additional collisions and by direct absorption of the infrared photons. The oxirane crosses to the acetaldehyde ground-state potential surface and reaction primarily to CH_4 and CO occurs. Confirmation that, under the experimental conditions of these experiments, acetaldehyde reacts to yield methane and carbon monoxide was obtained by using mixtures of acetaldehyde and SiF_4 as starting materials in a separate reaction. The reaction was observed indeed to produce only these two products.

Note that a number of radical species are generated in the proposed mechanism and these would be expected to exhibit secondary reactivity. The relative importance of radical reactions to this system is a matter of some controversy. The *ab initio* calculations[6] indicated that the primary product is acetaldehyde (S_0), which subsequently undergoes further unimolecular decomposition to produce CH_4 and CO or undergoes intersystem crossing, for which the rate constant is fixed by the experimental conditions. The second set of products (ethylene and acetylene) result indirectly from the unimolecular reactivity of the lowest triplet state of acetaldehyde. The latter produces $CH_3 + HCO$, with subsequent formation of CO and C_2H_6. Secondary decomposition of ethane yields the unsaturated products. This model predicts that the relative yield of CO should equal that of the sum of all other products, as was observed in the experimental results.

The rate constant for removal of oxirane resulting from the mechanism noted above is given by

$$\text{rate} = \frac{-\mathrm{d}[C_2H_4O]}{\mathrm{d}t} = \frac{kI[C_2H_4O]}{k_5[M]+k_6} \tag{10}$$

where I is the photon flux, and, if we assume that reaction (2) is much faster than reaction (3) and that $[M] \approx [SiF_4]$, k is given by

$$k = \frac{k_1k_3k_4k_6}{k_5} \tag{11}$$

This rate law is consistent with the experimental details. In particular, the rate law implies that the process is first order in $[C_2H_4O]$; however, if the oxirane concentration becomes significant, the value of [M] increases and the reaction would be inhibited as observed in Fig. 2. The addition of SiF_4 increases [M] and inhibits the reaction, as observed in Fig. 3. Finally, the rate should increase with increasing laser fluence, where I is fluence dependent, and this behavior is evident in Table 2. The mechanism proposed above is also consistent with the invariance of the relative product ratio. The predicted ratio of CH_3 to CH_4 is given by the ratio of rate constants k_{7b}/k_{7a}. There is no reason to expect any significant temperature dependence for k_{7b}, since it is an intersystem crossing rate constant. The ratio of singlet to triplet acetaldehyde should be approximately independent of temperature. If we consider an RRK-type probability to estimate the relative rate constants for formation of the final products CH_3 and CH_4 from acetaldehyde, there is an excess energy of 31.1 and 27.5 kcal mol^{-1}, respectively, due to the initial excitation to reach the transition state. The temperature range of the experiments, 850–950 K, provides an insignificant addition to the excess energy already available and the product yields are essentially invariant over the temperature range examined, in agreement with the experiment within experimental error.

CONCLUSIONS

The cw infrared laser SiF_4-sensitized chemistry of oxirane has been reported. The major detected products were CH_4, CO, C_2H_4 and C_2H_2. CO is the dominant product with formation of 1 mol for every mole of reacted oxirane. Trace yields of acetaldehyde were observed. The results are consistent with a mechanism in which the majority of the excited oxirane isomerizes to acetaldehyde and reacts as a highly vibrationally excited species along the ground-state potential. The ethylene product is a reflection of the fraction of acetaldehyde-isomerized oxirane undergoing intersystem crossing from the hot ground state to CH_3CHO (T_1).

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