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CO_2 Laser Induced Sensitized Dissociation of Ethylene Oxide

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Ethylene Oxide (C_2H_4O), when excited by energy transfer from SF_6 using a pulsed CO_2 laser, undergoes isomerization to CH_3CHO followed by dissociation. The intermediate isomerized product, acetaldehyde, is formed with excess internal eergy sufficient to decompose into CH_3 and CHO radicals. CH_3 radicals could be trapped by their reaction with chlorine, forming CH_3Cl as a stable product. Also, the intermediate acetaldehyde could be partially stabilized in the presence of argon. An average excitation energy of C_2H_4O molecule was found to be 65 kcal mol^{-1}. Average number of photons absorbed per SF_6 molecule, $\langle n \rangle$, was calculated to be 13 from the direct measurement of absorbed energy. The product distribution indicates that radical chain mechanism does not play a significant role in the present laser induced reaction.

The vibrational excitation of a polyatomic molecule which can exist in different isomeric forms, often leads to isomerization at low excitation energies which are below the dissociation limit of the molecule. Studies related to such isomerization processes are of basic interest since they can give valuable insight into the energetics and dynamics of structural changes in the process of isomerization. Earlier work on strained molecules has shown that a nearly complete conversion of perfluorocyclobutene to the thermodynamically less stable perfluorobutadiene can be induced by CO_2 laser irradiation.[1] The reverse reaction occurs when an intermediate butadiene has excess energy associated with it.[2] Unstable fulvene isomers are formed in the multiphoton CO_2 laser excitation of perfluoropyridine and they decay to the parent isomer with millisecond life times.[3]

A product isomer can become highly excited and thereby undergo decomposition, when the exit barrier energy in the isomerization process is released into the internal degrees of freedom of product molecule. An interesting example of such a product isomer excitation is the structural isomerization of ethylene oxide (C_2H_4O) to acetaldehyde (CH_3CHO). In this case the the activation energy for isomerization (57.2 kcal mol^{-1}) and the exothermicity of the reaction (27 kcal mol^{-1}) goes into the product to give excited acetaldehyde. Earlier we observed that vibrationally excited perfluoropyridine molecules in the ground electronic state cross over to electronic excited state and thereby emit light.[3] Since acetaldehyde is also produced in highly excited state, it would have been interesting to observe if light emission occurs from this molecule. However, no UV-vis light emission could be observed during the irradiation.

Ethylene oxide is a strained molecule and numerous studies are reported on pyrolysis, shock wave and VUV photolysis.[4—9] It has been found that though the nature of products remains similar but their relative yields change significantly depending on temperature, pressure, and the excitation source used. The role of chain mechanism is also not well understood. To our knowledge the dissociation of ethylene oxide under purely vibrational excitation condition has not been studied. This molecule has no IR absorption in the region of CO_2 laser emission. In the present work we have employed SF_6 as vibrational energy transfer reagent for C_2H_4O excitation and thereby investigated the sensitized dissociation of ethylene oxide under conditions where intermolecular V–V energy transfer activates this strained molecule. Subsequently, isomerization and decomposition processes are governed by vibrational temperature of the system. Under these conditions, the life time of excited acetaldehyde intermediate is as large as 30 ns, such that about 43% of isomer could be stabilized by addition of as little as 15 Torr (1 Torr=133.322 Pa) argon.

Experimental

The decomposition of C_2H_4O is studied in a stainless steel cell 4.7 cm long and 2.8 cm in diameter fitted with two polished KCl windows. A 1 : 3 mixture of C_2H_4O and SF_6 was made in a stock bulb from which known amounts were transferred into the IR cell and irradiated. Since C_2H_4O dimerizes at room temperature, its partial pressure was kept low (1 to 3 Torr) in the mixture and the integrity of the sample was checked by GC analysis and IR spectrophotometry prior to laser irradiation. Ethylene oxide and acetaldehyde were obtained from Fluka Chemicals (Switzerland) whereas SF_6 was from Matheson (U.S.A).

A transversely excited atmospheric pulsed CO_2 laser (Lambda-Physik EMG 201) tuned to 10P(20) line with a repetition rate of 2 Hz was employed to pump the ν_3 mode of SF_6. The laser pulse had a 100 ns spike with 2/3 of its energy and a broad 2 μs tail. A factory calibrated pyroelectric detector (Lumonics, model 20D) was used to measure the pulse energy. Specific laser lines were tuned by means of a spectrum analyzer (Optical Engineering Co.). A Ge lens (focal length 200 cm) was used to focus the laser beam. The cell was positioned at different locations in the condensing portion of the laser beam to achieve different levels of fluence under nearly parallel beam geometry at each fluence. The fluence was varied in the range 0.4 to 1.2 J cm^{-2}.

The reaction products after irradiation were monitored by gas chromatography. A method for quantitative gas transfer under vacuum, compression, and gas chromatographic analysis for the individual components of the gas mixture as described by Rao and Iyer[10] was adapted using the gas handling apparatus. For syringe injection, a sampling adapter with septum arrangement was used (Fig. 1b of Ref. 10). An additional septum seal attachment was provided between this apparatus and the cell for direct injection of inert gas to the irradiation cell. A known amount of argon was added to the cell to facilitate quantitative transfer of the sample. For analysis, the sample was kept under positive pressure by the mercury column. Known amounts were withdrawn with the help of gas tight syringes and injected into three gas chromatographs operated simultaneously for monitoring different components from the same experimental sample.

A silica gel column (152 cm i.d. 0.3 cm) gave well separated peaks for a mixture of hydrocarbons containing CH_4, C_2H_6, C_2H_4, C_3H_8, C_2H_2, and C_3H_6 in the order mentioned. A carbowax column (183 cm, i.d. 0.5 cm) was capable of separating hydrocarbons from chlorohydrocarbons. Both these columns were operated at room temperature. Satisfactory separation between ethylene oxide and acetaldehyde was observed on Porapak-T column (152 cm, i.d. 0.3 cm) operating at 120 °C only when the concentration of the latter was at least 3%. This column had the advantage of separating formaldehyde from ethylene oxide and/or acetaldehyde. In all the above cases a flame ionization detector was employed with nitrogen as the carrier gas. The hydrocarbons were calibrated daily against a standard 1% mixture in nitrogen obtained from Matheson gas products. Ethylene oxide and acetadehyde calibrations were done following a procedure identical in all respects to that used in the photolysis experiments but without laser irradiation. This calibration procedure was used for all quantitative analysis.

Hydrogen and carbon monoxide were analyzed on two different units operating at room temperature, each one fitted with a olecular sieve column (91 cm, i.d. 0.4 cm) using thermal conductivity detector with argon and helium as the carrier gas respectively. H_2 and CO calibrations were done using 2% and 3% mixtures in argon respectively.

Results

On repeated CO_2 laser irradiation, an exponential decrease in the concentration of C_2H_4O was observed. The major products were CO, H_2, CH_4, and C_2H_6. It was noticed that, the amount of C_2H_4O dissociated was equal to the amount of carbon monoxide formed (within the experimental accuracy of ±5%). The fraction of C_2H_4O decomposed per pulse, D_p, was evaluated from the slope of the plot of $\ln[(C_2H_4O)_0/(C_2H_4O)_n]$ vs. no. of pulses and was calculated to be 2.5×10^{-3} at a fluence of 0.6 J cm^{-2}.

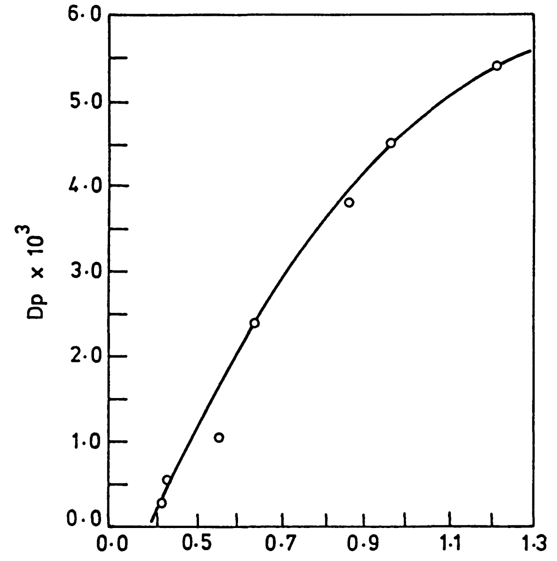

Fig. 1. Plot of dissociation yield per pulse, D_p versus fluence (for a total of 400 pulses).

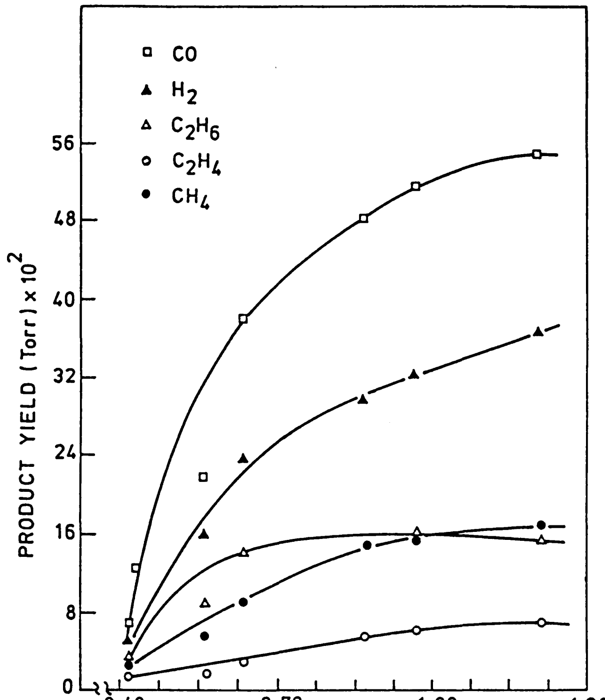

Fig. 2. Plot of product yield versus fluence (for a total of 400 pulses).

1. Effect of Fluence. SF_6 (2.3 Torr) and C_2H_4O (0.8 Torr) mixtures were irradiated at 10 P(20) CO_2 laser line at various energy fluences in the range of 0.4—1.2 J cm^{-2} for a total of 400 pulses. D_p is found to increase with increasing fluence (Fig. 1). While the yield of other products keeps on increasing, the yield of C_2H_6 decreases at higher fluence (Fig. 2).

2. Effect of No. of Pulses. A mixture of SF_6 (2.3 Torr) and C_2H_4O (0.8 Torr) was irradiated at a constant fluence of 0.6 J cm^{-2}. Different no. of pulses were given to the sample. The products H_2, CH_4, C_2H_6, and CO start building even after 10 pulses. Upto 50 pulses C_2H_4 was not detected, there after its amount keeps on increasing (Fig. 3). No C_2H_2 or HCHO was detected among products even under the conditions of maximum dissociation.

3. Effect of Argon Addition. Various amounts of argon (3.1 to 15.3 Torr) were added to the mixture of C_2H_4O (1.5 Torr) and SF_6 (4.5 Torr). On laser irradiation, it is found that with increasing pressure of argon, the amount of CH_3CHO stabilized increases. Table 1 shows the effect of argon pressure on CH_3CHO stabilization for 1000 pulses at a constant fluence of 0.6 J cm^{-2}.

4. SF_6+CH_3CHO Irradiation. When a mixture of SF_6 (2.3 Torr) and CH_3CHO (0.8 Torr) is irradiated under identical conditions, the nature of end products is found to be similar. The dissociation yield is only 5% (in contrast to 90% for C_2H_4O) after irradiating for 1000 pulses.

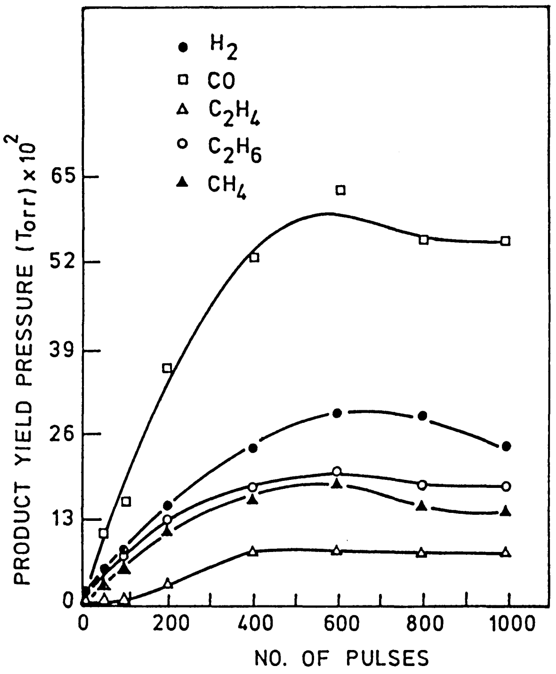

Fig. 3. Plot of product yield versus no. of pulses (at 0.6 J cm^{-2} fluence, at 0.8 Torr ethylene oxide).

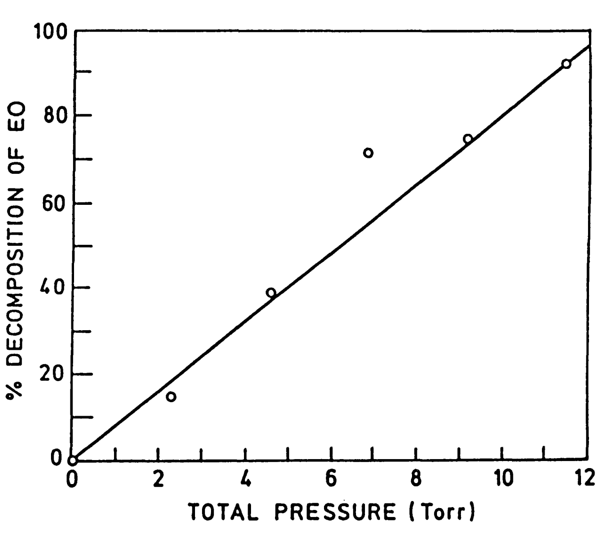

Fig. 4. Plot of % decomposition of ethylene oxide (EO) versus total pressure (200 pulses at a fluence of 0.6 J cm^{-2}).

5. Effect of Total Pressure. Figure 4 shows that % dissociation increased with increasing total pressure at constant SF_6 to C_2H_4O ratio of 3:1 at a fluence of 0.6 J cm^{-2}. The mixture was irradiated for 200 pulses. The pressure was varied from 2.3 to 11.5 Torr. The observed dissociation of C_2H_4O ranged from 14 to 92%.

6. Effect of Cl_2 Addition. When a mixture of C_2H_4O (1.1 Torr) and SF_6 (3.5 Torr) was irradiated in presence of Cl_2 (2.5 Torr) for a total of 500 pulses at a fluence of 0.6 J cm^{-2}, CH_3Cl was observed as a major product along with small amount of CH_4 and C_2H_6. At 5 Torr Cl_2, no CH_4 or C_2H_6 was observed whereas the yield of CO remained nearly unaffected.

7. Mass Balance. Under the experimental conditions of 0.4—1.2 J cm^{-2} laser fluence, dissociation of SF_6 or C_2H_4O did not occur in a single component system. In a mixed system, appreciable dissociation of C_2H_4O was observed with stable products CH_4, C_2H_6, C_2H_4, CO, and H_2. Intermediate CH_3CHO is stabilized only when argon is added. In the absence of argon, amount of CO formed accounted for the total oxygenated products (within the experimental accuracy of ±5%), suggesting the latter to be the major oxygen bearing decomposition product. The stoichiometric need requires that

$$\text{Moles of } CH_3 = \text{Moles of CHO}$$

methyl radicals are consumed as methane or ethane, and all the formyl radicals form CO thus

$$\text{Moles of } CH_3 = \text{Moles of } CH_4 + 2\,(\text{Moles of } C_2H_6)$$
$$\text{Moles of CHO} = \text{Moles of CO}$$

$$X = \frac{(\text{amount of } CH_4) + 2\,(\text{amount of } C_2H_6)}{(\text{amount of CO})}$$

X should ideally be 1, if no other oxygen containing products are present. In the present studies X is found to vary from 1.1 to 0.9 as a function of no. of pulses in the range of 10 to 1000 at 0.6 J cm^{-2} fluence. Whereas X varies between 1.1 to 1.2 for the fluence range 0.4 to 1.2 J cm^{-2} for 200 pulses. The results are indicative of either no or negligible oxygen containing products other than CO. The overall mass balance between the yields of these products and the C_2H_4O dissociated was within experimental accuracy.

Discussion

1. Primary Products. In the present work, ethylene oxide dissociation is induced by vibrational energy transfer from IR multiphoton excited SF_6. As a result of collisions with energised SF_6, C_2H_4O is produced in the excited state. The excited C_2H_4O can isomerize to either CH_3CHO or CH_2=CH-OH (vinyl alcohol).

Vinyl alcohol is known to be highly unstable and tautomerizes to CH_3CHO very fast. Thus in either case the final product is CH_3CHO which then dissociates to give products as shown below.

$$SF_6 \xrightarrow[10P(20),\ 10.6\ \mu,\ CO_2\ \text{laser}]{[nh\nu]} SF_6^*$$

$$SF_6^* + C_2H_4O \longrightarrow SF_6 + C_2H_4O^*$$

$$C_2H_4O^* \longrightarrow [CH_2{=}CH\text{-}OH]^* \longrightarrow [CH_3CHO]^*$$

$$C_2H_4O^* \longrightarrow [CH_3CHO]^* \longrightarrow \text{Products}$$

In case of C_2H_4O the activation energy for isomerization and exothermicity of the reaction goes into the product acetaldehyde. The acetaldehyde so produced contains a minimum of 84 kcal mol^{-1}. Further, in laser induced MPD reactions it has been observed that most of the excess energy above the unimolecular dicsociation threshold remains as internal energy of the products.[11] The total energy content of nascent CH_3CHO^* due to all these contributions is sufficiently high to dissociate it into CH_3 and CHO radicals. The formation of CH_3 and CHO radicals from acetaldehyde requires an activation energy of 81 kcal mol^{-1}.[12] Therefore CH_3 and CHO radicals are the most likely primary products of C_2H_4O decomposition. The formyl radical may further dissociate to give CO+H since the dissociation energy for this process is only 16 kcal mol^{-1}.[9] That CH_3 is formed as a primary radical is further supported by experiments in presence of Cl_2 where CH_3Cl is a major product along with small amount of hydrocarbons. Formation of CH_3Cl is a clear evidence of presence of a radical mechanism. The CH_3 radical in the absence of Cl_2 reacts with parent/H or another CH_3 to give rise to stable products CH_4 or C_2H_6. As CH_3Cl was also observed as a product in SF_6+CH_3CHO irradiation in presence of Cl_2, it is apparent that CH_3 radical is produced via CH_3CHO^* intermediate.

2. Energy Absorption and V-V Energy Transfer. In the present system SF_6 is the only species that absorbs photons from pulsed CO_2 laser. Energy transfer from these excited SF_6 molecules will be governed by the kinetics of the V (SF_6)→V,R,T (SF_6, C_2H_4O) processes. Intermolecular V-V energy transfer is two orders of magnitude faster than V-T transfer.[13—15] Under our experimental conditions of 3-6 Torr (SF_6+C_2H_4O) pressures the V-T equilibration time is few tens of microseconds. Therefore it may be assumed that intermolecular equilibration of vibrational energy is nearly achieved during the laser pulse. At this stage, when V→R,T equilibration is yet to achieve we may assume an initial vibrational temperature for the SF_6-C_2H_4O ensemble. Under the experimental conditions of 0.6 J cm^{-2} fluence, 100 ns laser pulse width, direct determination of absorbed laser energy gave 35 kcal mol^{-1} of SF_6 as input energy into the system, which gives average number of photons absorbed per SF_6 molecule to be $<n>=13$. This energy corresponds to a vibrational temperature of 1400 K for the ensemble, as calculated from the considerations of vibrational partition functions of SF_6 and C_2H_4O. Temperatures of this magnitude are frequently encountered in SF_6 sensitized reactions even at moderate fluences.[16] In the absence of any other additive, this vibrational temperature deteriorates to about 1000 K in the irradiation volume if V-T relaxation is confined to such a volume. The V-T relaxation rate for SF_6 has been reported to be 150 μs Torr.[17] Further experiments indicated that the extent of laser energy absorption remained nearly same either in the neat 2.3 Torr SF_6 or in a mixture containing 2.3 Torr SF_6, 0.8 Torr C_2H_4O, and 15.3 Torr argon. Thus collisional processes during the laser pulse due to C_2H_4O and Ar addition are not influencing the extent of laser power absorbed by SF_6.

3. Product Distribution. Table 1 gives the product distribution in the present studies which has been compared with high-temperature pyrolysis and UV photolysis studies also. In high-pressure pyrolysis experiments, the high yields of CH_4 (Table 1) as compared to C_2H_6 and H_2 have been explained on the basis of a chain mechanism involving CH_3 radicals.[5] From the lower yields of CH_4 obtained in the present studies under low fluence conditions, it appears that very little or no chains are involved in the reaction mechanism. In shock tube studies,[9] it was suggested that 10 percent of methane is formed directly from the excited acetaldehyde, by dissociative isomerization reaction generating methane and carbon monoxide. Under our experimental conditions, this channel does not seem to be operative. Evidence for this comes from quenching experiments in the presence of Cl_2. At 2—3 Torr Cl_2 pressures a drastic decrease in the yield of CH_4 was observed and 5 Torr of Cl_2, no CH_4 was obtained. However, the CO yield remained same as found in the experiments without Cl_2. This shows that methane is formed mainly by methyl radical reaction.

Under high fluence conditions (>0.6 J cm^{-2}) the yield of C_2H_6 obtained is less than or comparable to that of CH_4 (Table 1). However, at low fluences (<0.6 J cm^{-2}), the yield of C_2H_6 is appreciably higher than CH_4. This sudden increase in the yield of C_2H_6 is also accompanied by a sharp decrease in the C_2H_4 yield. The other products were observed even after 10 pulses. However,

Table 1. Relative Yields of Products[a)]

	CO	H_2	CH_4	C_2H_6	C_2H_4
Pyrolysis[b)]	1.0	0.15	0.77	0.14	—
UV Photolysis[c)]	1.0	0.64	0.21	0.40	0.07
Hg sensitized[d)]	1.0	0.92	0.18	0.20	—
IR Photolysis[e)]					
1.2 J cm^{-2}	1.0	0.66	0.31	0.27	0.12
0.9 J cm^{-2}	1.0	0.62	0.29	0.32	0.12
0.6 J cm^{-2}	1.0	0.62	0.25	0.37	0.07
0.4 J cm^{-2}	1.0	0.42	0.23	0.41	0.07

a) Taking CO yield to be unity. b) Ref. 4. c) Ref. 7. d) Ref. 6. e) This work.

no C_2H_4 is detected even upto first 50 pulses. It was futher observed that C_2H_4 slowly keeps building at the expense of C_2H_6 with increasing number of pulses. These results are indicative of C_2H_6 undergoing secondary dissociation to C_2H_4 at high fluence irradiation. This is responsible for the lower yields of C_2H_6 as compared to CH_4.

All the observed products can be understood on the basis of the following mechanism:

1 $C_2H_4O^* \longrightarrow CH_3CHO^*$
2 $CH_3CHO^* + Ar \longrightarrow CH_3CHO + Ar$
3 $CH_3CHO^* \longrightarrow CH_3 + CHO$
4 $CHO \longrightarrow CO + H$
5 $CH_3 + CHO \longrightarrow CH_4 + CO$
6 $H + CHO \longrightarrow CO + H_2$
7 $H + H \longrightarrow H_2$
8 $CH_3 + H \longrightarrow CH_4$
9 $CH_3 + CH_3 \longrightarrow C_2H_6$
10 $CH_3 + C_2H_4O \longrightarrow CH_4 + CH_3CO$
11 $H + C_2H_4O \longrightarrow H_2 + CH_3CO$

The concentrations of primary radical species like CH_3, CHO are calculated by means of C_2H_4O dissociation yield per pulse, D_p. Taking these values and considering the reported rate constants[9] for various steps in the mechanism an attempt is made to understand the product distribution. The hydrogen atom is weakly bound in CHO with the dissociation energy of 16 kcal mol^{-1} and it is lost easily. Therefore major route for CO formation is the reaction 4 i.e $CHO \rightarrow CO + H$, which follows the initiation reaction (step 3). The H atoms so produced can either recombine or abstract another H from the parent to generate H_2. The rates of reaction 5, 8, 9, and 10 which are involved in CH_4 and C_2H_6 formation are compared. It is found that reaction 5, 8, and 10 can not compete with reaction 9 which is an efficient bimolecular process. It may be considered as the major process responsible for C_2H_6 formation. This conclusion is supported by the product distribution at low fluences where the yield of C_2H_6 is more than that of CH_4.

4. Acetaldehyde Stabilization. Experiments in presence of argon resulted in the partial stabilization of CH_3CHO. This indicates that acetaldehyde is an intermediate in C_2H_4O decomposition. With the increasing partial pressure of argon in the system, it is observed that the percent stabilization of CH_3CHO increases (Table 2). However, the dissociation yield of C_2H_4O decreased with increasing argon pressure. This is due to the fact that argon not only removes excess energy from CH_3CHO^* but in the process deactivates SF_6^* and $C_2H_4O^*$ also. In the absence of argon, the products obtained were same except for acetaldehyde. To assess the role of CH_3CHO, a mixture of SF_6 and CH_3CHO was irradiated (section 4 of results). The results indicate that, though the vibrational temperature (ca. 1400 K) reached is comparable but the dissociation yield of acetaldehyde is much less as compared to C_2H_4O. This can be attributed to the high activation energy for CH_3CHO dissociation as compared to C_2H_4O isomerization. Irrespective of the low yield, the nature of the end products was found to be the same. This suggests involvement of CH_3CHO in the product formation.

5. Energetics of Isomerization and Dissociation. At 3—6 Torr total pressure employed the average unimolecular rate constant for C_2H_4O isomerization should be higher than 4×10^4 s^{-1} for the reaction to be competitive with the V–T relaxation. From RRK considerations, the unimolecular rate constant of dissociation, k is given by the expression

$$k = A[(E - E_\circ)/(E)]^{s-1} > 4\times10^4 > 1/t_{\mathrm{V-T}},$$

where s is the no. of vibrational degrees of freedom and A is frequency factor. It is observed that in the activation of a molecule only a part of the total no. of vibrational degrees of freedom is used. It varies from 50 to 80% (for $N=4$ to 22) of the total degrees of freedom for different molecules depending on the molecular complexity.[18] Ethylene oxide and acetaldehyde ($N=7$) are neither very small nor very large molecules so we take about 66% of total vibrational degrees of freedom i.e. $s=10$. Activation energy and frequency factor for C_2H_4O isomerization are reported to be $E_\circ=57.2$ kcal mol^{-1} and $A=1.21\times10^{14}$ s^{-1}.[9] According to RRK expresion E comes out to be >62.5 kcal mol^{-1} for the given rate.

A vibrational temperature of 1320 K would satisfy the above kinetically competitive scheme, using Arrhenius equation for $k=4\times10^4$ s^{-1}. At a vibrational temperature of 1400 K, applicable for the system from the

Table 2. Effect of Argon Pressure on Acetaldehyde Stabilization

Serial no.	Pressure of Ar Torr	(AcH+CO)/(EO)[a] %	(AcH)/(AcH+CO) %
1.	0.0	90.3	0
2.	3.1	79.3	5.2
3.	5.3	60.4	10.0
4.	9.4	41.8	17.4
5.	12.2	31.4	32.0
6.	15.3	23.8	43.7

a) AcH and EO stand for acetaldehyde and ethylene oxide.

Table 3. Dissociation Rate Constants of Acetaldehyde (AcH) in the Presence of Argon

P(Ar)/Torr	AcH/CO (%)	k_d/s^{-1}
3.1	5.5	2.8×10^7
5.3	11.4	2.3×10^7
9.4	21.1	2.2×10^7
12.2	47.0	1.3×10^7
15.3	77.7	9.8×10^6

absorbed energy considerations, the Arrhenius rate for the C_2H_4O isomerization is 1.3×10^5 s^{-1} which corresponds to E equal to 63.5 kcal mol^{-1} according to RRK expression. The mean energy associated with CH_3CHO^* obtained from such a level of C_2H_4O would be 90.5 kcal mol^{-1} and its RRK dissociation rate constant comes out to be 1×10^7 s^{-1} considering E_o and A values to be 81 kcal mol^{-1} and $10^{15.8}$ s^{-1} respectively.[12)]

The acetaldehyde decomposition is partially quenched by addition of argon to the system. The relative yields of $(CH_3CHO)_{\text{stabilized}}/(CO)$ follow the relation,

$$(CH_3CHO)/CO = k_Q[M]/k_d$$

where k_Q is the quenching rate constant (s^{-1} Torr^{-1}) of excited AcH at M Torr quencher and k_Q is the dissociation rate constant (s^{-1}) of CH_3CHO. We note that no observable stabilization of (CH_3CHO) occurred in absence of argon. At P_{Ar}=0, CH_3CHO^* finds itself in a hot bath of (SF_6–C_2H_4O). The bath though vibrationally hot has much less energy per bath molecule than the nascent CH_3CHO^* (>85 kcal mol^{-1} as discussed in section 1). In this sense some deactivating collisions of SF_6 and C_2H_4O with CH_3CHO^* may be occurring even in the absence of argon. However, the small amount of CH_3CHO so stabilized is perhaps below the detection limit of the gas chromatograph in a mixture of C_2H_4O and CH_3CHO.

In the presence of argon, 5 to 40% stabilization of CH_3CHO was observed as a function of argon pressure (Table 2). The collision efficiency of argon for quenching the IRMPE polyatomic molecule is reported to be about 0.05.[19,20)] The hard sphere collision frequency (10^7 s^{-1} Torr^{-1}) with the above efficiency factor gives a quenching rate constant $k_Q=5\times10^5$ Torr^{-1} s^{-1}. Using this value, the range of k_d as a function of argon pressure is given in Table 3. The dissociation rate in the absence of argon is obtained by plotting k_d vs. pressure of argon and extrapolating to zero argon pressure. The intercept leads to k_d as 3.2×10^7 s^{-1}. When this value is substituted to RRK expression, the energy of CH_3CHO^* is found to be 92 kcal mol^{-1}, which implies that excited C_2H_4O should have 65 kcal mol^{-1}. With this energy the RRK rate of isomerization is 6.4×10^5 s^{-1} which is about sixteen times faster than the V–T relaxation rate. Thus V–V transfer to C_2H_4O from SF_6, isomerization of C_2H_4O to CH_3CHO and dissociation of excited acetaldehyde, proceed on a time scale which is faster than the V–T equilibration time.

Conclusion

In summary ethylene oxide (C_2H_4O) dissociation has been induced by intermolecular energy transfer from CO_2 laser multiphoton excited SF_6 when the latter is pumped in the ν_3 mode. The process appears to be driven by vibrational excitation of C_2H_4O. The excitation energy of C_2H_4O molecule is found to be 65 kcal mol^{-1} and a vibrational temperature of the ensemble has been evaluated to be 1400 K. C_2H_4O on excitation isomerizes to intermediate CH_3CHO which dissociates to CH_3 and CHO radicals. CH_3 radicals could be trapped by their reaction with chlorine, forming CH_3Cl as a stable product and the intermediate acetaldehyde could be partially stabilized in presence of argon.

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