TEA CO_2 Laser Induced Photoreactions of Ethylene, Chloroethylenes and Chloroethanes

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TEA CO_2 laser induced chemical reactions of ethylene, chloroethylenes and chloroethanes have been investigated. Since these compounds have absorptions at wavelengths of 10.6 or 9.6 μm band of the CO_2 laser, strong excitation of the molecular vibration gives rise to an infrared photochemical reaction. In chlorine derivatives, the cleavage of the C–Cl bond by the laser irradiation appears to initiate decompositions of these materials. The final products were mainly brought about by molecular elimination of HCl, H_2, or Cl_2. The present results demonstrate that the CO_2 laser induced reactions differ form their thermal reactions.

Since the development of infrared lasers, a considerable number of investigations on infrared photochemical reactions induced by continuous wave (CW) or transverse excited atomospheric (TEA) CO_2 laser irradiation have been reported.[1–4] Braun and Tsang[5] have observed TEA CO_2 laser induced chemical reactions for isobutyl and ethyl chlorides, bromides and iodides. For all except the iodides the reaction took place *via* the molecular elimination of hydrogen halides. With respect to the iodides, cleavage of the C–I bond competed with the elimination of hydrogen halide. The infrared photochemical reactions of ethylene, chloroethylenes, chloroethanes and mixtures of these compounds with SF_6 or H_2 induced by TEA CO_2 laser irradiation have been observed. In those cases, the vibrationally excited molecules took direct part in chemical reactions. Irradiation by infrared laser pulse gives rise to an elevation of the specific vibrational temperature of molecule, keeping the translational temperature almost unchanged. Therefore, in this respect the infrared laser induced reactions differ from the thermally induced ones, although the reaction products are similar.

Experimental

The TEA CO_2 laser constructed and used was a double discharge type with three pairs of Rogowski electrodes of 60 cm length each.[6] The cavity length was about 200 cm, being formed by a 20 m radius aluminum-coated concave mirror and a flat uncoated germanium output ethalon. Under ordinary conditions, the simultaneous oscillation of multiple lines of multi-modes was observed, and the strongest line was P(20) of the 10.6 μm band. The oscillations of P(14)—P(22) and R(16) of this band with less than 1/10 of the intensity of the P(20) line were also observed. The power output was about 1 J with a pulse duration of 100 ns; its repetition rate was about 1 Hz. The absorption cell of about 3 cm length was inserted into the laser cavity for a selective oscillation of appropriate lines of the laser. When SF_6 gas of 150 Torr was introduced into the cell, the oscillation of the 9.6 μm band was accomplished, and its power output was slightly less than that of the 10.6 μm band. The oscillation of R branch of the 9.6 μm band was obtained by using C_2H_3Cl gas of about 150 Torr.

Reaction cells made of duralmine were used. One had the dimensions of 100 mm length and inner diameter of 30 mm, and the other was 50 mm length and 20 mm diameter. The reaction cell was closed by two KCl windows permitting passage of the laser beam. The sample gas in the reaction cell was irradiated by the laser pulse focused with germanium lens of f=5 cm; the diameter of the focal spot was ≈0.5 mm. The peak power of the laser at the focus was more than 1 GW/cm^2, but its irradiation did not show any appreciable temperature elevation of the sample gas. The products of the infrared photoreaction were examined by infrared absorption. No appreciable differences of products were found with changing cell dimensions.

Results and Discussion

For a pressure of sample gas higher than 50 Torr, the irradiation by high power laser gives rise to a dielectric breakdown. This produces an avalanche of electrons, and the reactions caused by the breakdown have been shown to be the same as those initiated by an electric discharge.[8] Therefore, the infrared laser induced reactions have been observed in the pressure range of 10—50 Torr, where the reaction was mainly infrared-photochemical. Although the dielectric breakdown was unobserved at these pressures, the emission of visible luminescence was observed around the focus of the lens.

Typical results, including the experimental conditions, are presented in Table 1. The products listed in this table were obtained after an irradiation of 30—60 min. A more detailed examination of the results is now given.

Ethylene. The reaction product of C_2H_4 was C_2H_2 and the yield was proportional to the pressure of ethylene in the range of 10—50 Torr. The reaction is one of elimination of the H_2 molecule. When the mixture of C_2H_4 and H_2 (20 Torr: 20 Torr) was irradiated, the partial pressure of the product C_2H_2 was found to be 1.5 Torr, which is almost the same order of magnitude as that of the pure C_2H_4. The addition of H_2 did not produce any detectable change in the rate of decomposition of ethylene.

Chloroethylene. The main reaction of the chloroethylenes was the elimination of hydrogen chloride from the initial reagent. Under the irradiation conditions, C_2H_3Cl at 22 Torr produced C_2H_2 at 2.2 Torr. The presence of C_2HCl was not detected in the products, indicating the difficulty of eliminating H_2 compared with that of HCl. It is reasonable to predict this since the energy required for the elimination of H_2 is estimated to be 75 kcal/mol from the energies of C–H and H–H bonds, while the energy required for the elimina-

TABLE 1. PRODUCTS OF CO_2 LASER INDUCED PHOTOCHEMICAL REACTIONS

Reagents, pressures	Reaction products, partial pressures	Irradiation conditions
C_2H_4 (20 Torr)	C_2H_2 (1.8 Torr)	10.6 μm P, 3000 shots
C_2H_3Cl (22 Torr)	C_2H_2 (2.2 Torr)	10.6 μm P, 3000 shots
CCl_2=CH_2 (10 Torr)	C_2HCl (1.5 Torr) C_2H_2 (0.5 Torr)	9.6 μm P+R, 1500 shots[a]
C_2HCl_3 (18 Torr)	C_2Cl_2 (5 Torr) C_2HCl (0.5 Torr)	10.6 μm P, 3000 shots
C_2HCl_3 (20 Torr) +H_2 (20 Torr)	C_2H_2 (2.7 Torr) CCl_2=CH_2 (0.7 Torr) C_2HCl (0.1 Torr)	10.6 μm P, 3000 shots
C_2H_5Cl (20 Torr)	C_2H_4 (5 Torr) C_2H_2 (1 Torr)	10.6 μm P, 3000 shots
$CHCl_2$-CH_3 (10 Torr)	C_2H_2Cl (1.7 Torr) C_2H_2 (1 Torr)	10.6 μm P, 1500 shots[a]
$CHCl_2$-CH_3 (10 Torr)	C_2H_3Cl (4.4 Torr) C_2H_2 (1.4 Torr)	9.6 μm P, 1500 shots[a]
$CHCl_2$-CH_3 (10 Torr) +SF_6 (1 Torr)	C_2H_3Cl (1.5 Torr)	10.6 μm P, 1500 shots[a]
CH_2Cl-CH_2Cl (20 Torr)	C_2H_3Cl (<0.1 Torr)	10.6 μm P, 3000 shots
CH_3-CCl_3 (20 Torr)	Cl_2C=CH_2 (<0.1 Torr)	10.6 μm P, 3000 shots
$CHCl_2$-CH_2Cl (11 Torr)	Cl_2C=CH_2 (1.1 Torr) CHCl=CHCl (*trans*) (0.3 Torr) CHCl=CHCl (*cis*) (0.5 Torr)	10.6 μm P, 3000 shots

[a] A smaller reaction cell was used.

tion of HCl is about 50 kcal/mol.[5,7] Since this molecule absorbs at a wavelength of 9.6 μm, the 9.6 μm laser photochemical reaction was also observed. However, the production of C_2H_2 was slightly less than that by the 10.6 μm irradiation.

The ν_8 vibrational mode of Cl_2C=CH_2 is infrared active and the absorption can be observed at the 9.6 μm R branch of the CO_2 laser. Hence, the reaction was induced by the irradiation of the TEA CO_2 laser with the R branch of 9.6 μm radiation. The reaction products were C_2HCl and C_2H_2 at a ratio 5:1. The following processes may be suggested for the production of the C_2H_2 molecule.

1) The infrared laser irradiation brings about a cleavage of the C–Cl bond and creates a ClC=CH_2 radical.

2) The transfer of an H atom produces a HClC=CH radical.

3) The cleavage of the C–Cl bond of the radical HClC=CH by the laser irradiation yields the C_2H_2 molecule.

The process assumed above is equivalent to the elimination of a Cl_2 molecule, following the scrambling of the H atom.

Since Cl_2C=CH_2 has no absorption at the wavelength of 10.6 μm TEA CO_2 laser, its irradiation produced no reaction in the pure sample. However, the SF_6 sensitized reaction of Cl_2C=CH_2 was induced by the 10.6 μm laser irradiation, but the quantity of products was too small for complete identification. The results of the direct and sensitized reactions are listed in Table 2. The absorption coefficients of the mixture of Cl_2C=CH_2 and SF_6 (14 Torr: 1 Torr) were measured by using the laser with 4 mJ output. The observed value at 10.6 μm was 5 times as large as the absorption coefficient at 9.6 μm. Although the irradiated laser power of 10.6 μm was about 1.5 times as large as the power of 9.6 μm band, the reaction rate of the direct process was larger by an order of magnitude. In the mixture of SF_6 and Cl_2C=CH_2, the ν_3 mode of SF_6 was excited successively to its higher vibrational levels by the incident 10.6 μm laser. The vibrational energies of SF_6 transfered to the vibrationally excited levels of Cl_2C=CH_2, giving rise to the dissociation of this molecule. It should be noted that any decomposition of SF_6 molecule in the present mixture was not detected. The observed results in Table 2 indicate that the direct laser excitation of the ν_6 vibration of Cl_2C=CH_2 (CH rocking mode) accelerates the reaction rate significantly.

TABLE 2. TEA CO_2 LASER INDUCED CHEMICAL REACTION OF Cl_2C=CH_2

	Direct excitation	SF_6 sensitized reaction
Sample	Cl_2C=CH_2 (14 Torr)	+ SF_6 (1 Torr)
Laser line	9.6 μm R	10.6 μm P
Relative laser power	1	≈1.5
Relative absorption coefficient (4 mJ)	1	≈5
Reaction rate	>6	1

In a previous paper the TEA CO_2 laser induced isomerization and decomposition of ClHC=CHCl has been reported.[8] The observed reactions promoted by the direct excitation or SF_6 sensitization using TEA CO_2 laser are listed in Table 3. The absorption coefficient of the mixture of ClHC=CHCl (*trans*) and SF_6 (10 Torr: 1 Torr) at 10.6 μm is 50 times as large as that of the pure substance, but the reaction rate of the sensitized excitation is only 6 times as fast as the rate of the direct excitation. Although the main reaction was the *trans-cis* isomerization in both cases, the production of C_2H_2 and C_2HCl were also observed in the

TABLE 3. TEA CO_2 LASER INDUCED CHEMICAL REACTION OF ClHC=CHCl (*trans*)

	Direct excitation	SF_6 sensitized reaction
Sample	ClHC=CHCl (10 Torr)	ClHC=CHCl (10 Torr) + SF_6 (1 Torr)
Laser line	10.6 μm P	10.6 μm P
Relative absorption coefficient (4 mJ)	1	≈50
Relative reaction rate	1	6
Ratio of products C_2H_2/C_2HCl	0.6	0

case of direct excitation. In the SF_6 sensitized reaction, only the C_2HCl molecule was obtained, indicating that the reaction resembles the pyrolysis of ClHC=CHCl.[9] The infrared photoreaction induced by the direct excitation of ClHC=CHCl differs then from the thermal one.

The frequency of the ν_{12} vibrational mode of ClHC=CCl_2 coincides with the 10.6 μm TEA laser, and the irradiation of 3000 shots produced 5 Torr of C_2Cl_2 and 0.5 Torr of C_2HCl from 18 Torr of this molecule. The ratio of the products, C_2Cl_2 and C_2HCl, may be given by the activation energies of the elimination of HCl and Cl_2 molecules. Goodall and Howlett reported that the thermal reaction products of ClHC=CCl_2 were C_6Cl_6 and HCl.[10] Although the presence of C_2Cl_2 molecules has not been detected in the pyrolysis of ClHC=CCl_2, the C_6Cl_6 molecule may be formed at higher translational temperatures from activated C_2Cl_2 molecules, which are presumably produced by the elimination of hydrogen chloride from the parent molecules. Appreciable amounts of C_6Cl_6 were not detected in the laser induced reaction products, suggesting that elevation of the translational temperature is insufficient to allow the reaction $3\ C_2Cl_2 \rightarrow C_6Cl_6$. It is evident from our observation that the infrared laser induced reaction of ClHC=CCl_2 is significantly different from that of the pyrolysis. Furthermore, in the 10.6 μm laser induced reaction of the mixture of ClHC=CCl_2 and H_2 (20 Torr : 20 Torr) the products were C_2H_2 of 2.7 Torr, Cl_2C=CH_2 of 0.7 Torr and C_2HCl less than 0.1 Torr, but C_2Cl_2 was not detected in contrast to the case of pure ClHC=CCl_2. The major products obtained from the 10.6 μm laser irradiated mixture of ClHC=CCl_2 and D_2 were CHD=CCl_2, CD_2=CCl_2, and H_2C=CCl_2. The productions of C_2D_2, C_2HD, and a trace of C_2H_2 were also observed. These results seem to indicate that the CO_2 laser irradiation gives rise to a cleavage of C–Cl bond of ClHC=CCl_2 molecule.

Chloroethanes. The reaction products of C_2H_5Cl at 25 Torr were C_2H_4 and C_2H_2 with partial pressure of 5 and 1.5 Torr respectively. At less than 25 Torr, the quantities of the products were proportional to the initial pressures of the samples. When increased to 40 Torr, the partial pressures of the products, C_2H_4 and C_2H_2, reached 6 and 3 Torr respectively. Assuming that the infrared laser irradiated C_2H_5Cl gives rise to the production of C_2H_4 alone and the reaction product C_2H_2 of the present experiment is brought about by the irradiation of C_2H_4 by the same laser, then the partial pressure of C_2H_2 must be less than 1/5 of the really observed value. Therefore, we may conclude that the major part of C_2H_2 must be directly, and almost simultaneously, produced from C_2H_5Cl by the CO_2 laser irradiation. Barton and Howlett have reported that the pyrolysis of this material gives rise to the production of C_2H_4 but not to noticeable amounts of C_2H_2.[11] These experimental results demonstrate that the mechanism in both reactions is different.

Infrared absorption of Cl_2HC–CH_3 was observed at wavelengths of the 9.6 μm P, R and 10.6 μm R bands of the CO_2 laser, but not at the 10.6 μm P band. Hence, the irradiation of the R branch of 10.6 μm laser pulse produced C_2H_3Cl of 1.7 Torr and C_2H_2 of 1 Torr from 10 Torr of Cl_2HC–CH_3. The irradiated products with the P branch of the 9.6 μm band were C_2H_3Cl of 4.4 Torr and C_2H_2 of 1.4 Torr. Since the production of C_2H_2 is almost of the same order as that of C_2H_3Cl, only a small part of C_2H_2 may be assumed to be produced by the laser induced reaction of C_2H_3Cl which is given from Cl_2HC–CH_3 by the 9.6 or 10.6 μm R infrared photodissociation. This is because the yield of C_2H_2 from the laser induced reaction of C_2H_3Cl is less than 10% of the parent molecule. The 9.6 μm R laser irradiation produced 1.2 Torr of C_2H_3Cl and 0.3 Torr of C_2H_2 from 10 Torr of Cl_2HC–CH_3. Since the C_2H_3Cl molecule does not absorb in the 9.6 μm R line, C_2H_2 in the present observation must be directly produced from Cl_2HC–CH_3 by the 9.6 μm R laser irradiation. The experimental results obtained by Barton and Howlett indicate that C_2H_2, the thermal decomposition product of Cl_2HC–CH_3, is only 3% of the major pyrolysis product C_2H_3Cl,[11] suggesting the different mechanisms between the pyrolysis and the infrared laser induced reaction.

The infrared photochemical decomposition of $CHCl_2$–CH_2Cl was also investigated. The decomposition products were *cis*- and *trans*-CHCl=CHCl and CCl_2=CH_2 in a concentration ratio of 0.5:0.3:1.1. The pyrolysis of $CHCl_2$–CH_2Cl has been investigated by Williams[12] and by Teramoto *et al.*,[13] and they have proposed both processes—radical chain and unimolecular reactions—for the decomposition. The ratio of the decomposition products H_2C=CCl_2 and ClHC=CHCl was found to be 0.7. Teramoto *et al.* have also confirmed that the product H_2C=CCl_2 decreased when the radical chain reaction was inhibited. In the infrared laser induced reaction, we obtained a value 1.4 for the ratio of the products, H_2C=CCl_2 and ClHC=CHCl. From our experimental results it may be concluded that the infrared laser induced reaction of $CHCl_2$–CH_2Cl is mainly promoted by the radical reaction.

Translational and Vibrational Temperatures. Recently the impulsive opto-acoustic effect has been reported. This gives rise to a temperature change in a certain gas by the absorption of the CO_2 laser pulse.[14] When the infrared laser pulse is absorbed by the gas, the population of relevant vibrational levels deviates from the thermal equilibrium for the short duration of the laser pulse. The energy supplied by the laser pulse as an increment of the vibrational energy is finaly transformed into translational energy of the molecule by the vibrational-translational relaxation, giving rise to elevation of the translational temperature. When the pressure of gas is 20 Torr, about 10 ms after irradiation the translational temperature of the molecules decreases to the initial value. This is caused by the dissipation of the translational energy to the cell wall or other surroundings.

In the present study of the laser induced reaction, the translational temperature increase of sample gas may be observed only in a short duration of about 10 ms. Ambartzumian *et al.*[15] have estimated that the temperature increase of ClHC=CHCl by the TEA CO_2 laser irradiation was less than 350 °C which gave the maximum temperature of the gas at about 650 °C. Furthermore, they observed that the gas was kept at around 650 °C only for a short duration of 10^{-4} s. Under these conditions thermal reaction was assumed to be negligible. The same discussion may be applied in our case. In the present study, the temperature increase of sample gas by the irradiation of 3000 laser pulses was assumed to be negligible. Therefore, the energy supplied by the laser provided the elevation of vibrational temperature which gave rise to the infrared photochemical reaction. The experimental results support the present assumption that the thermal and infrared laser reactions are not the same.

The infrared laser dissociation of SF_6 molecules was understood on the assumption that the molecules are excited to the true continuum of the levels above the dissociation limit through the exciattion of quasicontinuum of the vibrational levels. From the measurement of dissociation thresholds of SF_6, almost 20 photons/molecule were deposited by the ultrashort laser pulse, implying a vibrational temperature of $T=1800$ K.[16)]

The numbers of photons needed for dissociation of molecules in the present investigation are in the order of 20—40, which depends upon the molecules. Since the threshold power for molecular dissociation was unobserved in the present case, the vibrational temperature at the threshold could not be determined, even if it could be defined. However, the number of normal modes and the process of the laser dissociation may be almost the same as those of SF_6. The vibrational temperature at around the dissociation threshold may be an order of 2000 K.

Conclusion

The TEA CO_2 laser induced chemical reactions of ethylene, chloroethylenes and chloroethanes have been observed. The results demonstrate that the reactions are caused by multiple steps or multiple absorptions of the infrared photons, following the elimination of hydrogen or hydrogen chloride molecules, or by the cleavage of the C–Cl bond. Furthermore, the experimental results indicate that the products and the reaction mechanisms are somewhat different from those of thermal reactions. It is rather difficult to elucidate the complete mechanism of the infrared laser induced photoreaction from the present observations, since its mechanism seems to vary with molecules. However, the detailed studies on the reaction of the individual substances will give information on the reactions of molecules whose vibrations of a certain mode are highly excited.

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