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The Mechanism of the TEA CO_2 Laser-induced Reaction of 1,1-Dichloroethane

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Synopsis. In a TEA CO_2 laser-induced reaction of 1,1-dichloroethane, the relative quantities of the products, C_2H_2 and $ClHC{=}CH_2$, were found to vary with the laser wavelength, indicating that the C_2H_2 molecules are produced by two processes, directly and indirectly from $Cl_2HC–CH_3$ within the duration of a single laser pulse.

There have been a number of investigations demonstrating that infrared laser-induced reactions differ from thermal reactions. However, their reaction processes and mechanisms have not been elucidated. In a previous paper, we reported on TEA CO_2 laser-induced photoreactions of chloroethylene and chlorinated ethanes.[1] The experimental results for chlorinated ethanes have shown that rather larger amounts of acetylene than their thermal reaction products were obtained in addition to the major product of ethylene or chloroethylene. The acetylene may be produced by the following two processes, the direct process and the indirect 2-step process:

(a) The C_2H_2 molecules are directly produced from the ethane derivative by the irradiation of a single laser pulse.

(b) In the first process of the reaction, C_2H_4 or its chlorine derivative is produced; a subsequent infrared laser reaction of those molecules gives rise to the production of the C_2H_2 molecule.

In the previous study, no quantitative discussions of these reaction processes were made. Since the $Cl_2HC–CH_3$ molecule has infrared absorptions at the wavengths of four regions of the CO_2 laser, *i.e.*, at P and R branches of both the 9.4 μm and 10.4 μm bands, their wavelengths are 9.6 μm, 9.3 μm, 10.6 μm, and 10.2 μm respectively. The irradiation of one of these lasers gives rise to the production of C_2H_3Cl and C_2H_2 in various concentrations. The TEA CO_2 laser-induced reaction of chlorine derivatives of hydrocarbons gives rise to the elimination of HCl from those molecules, and C_2H_3Cl molecules may be produced in the first stage of the present experiment. As the reaction product, C_2H_3Cl, has no absorption at the wavelength of 9.3 μm, the C_2H_2 molecule must be produced by the direct process in the 9.3 μm laser-induced reaction.

Recently we have made an analysis of the infrared laser-induced multiphoton dissociation of C_2F_3Cl by the phenomenological model calculation based on the Rice-Ramsberger-Kassel-Marcus statistical theory for unimolecular dissociation.[2] We thus confirmed that the observed results were in good agreement with the calculation. Together with the theoretical analysis of the infrared multiphoton dissociation of the SF_6 molecule by Grant *et al.*,[3] our analysis of the reaction of C_2F_3Cl can help to understand the reaction mechanism of the infrared photochemistry of $Cl_2HC–CH_3$.

For a detailed analysis of the reaction mechanism, we have observed the relative yields of the reaction products of C_2H_3Cl and C_2H_2 by the irradiation of various CO_2 laser lines; the analysis of the results enable us to understand the process of the production of C_2H_2.

The TEA CO_2 laser used in the present experiment was described in a previous paper.[1] The power output was about 1 J, with a pulse duration of 100 ns, its repetition rate being almost 1 Hz. For a selective oscillation of the appropriate line among the P and R branches of the 9.4 μm or 10.4 μm band, SF_6 or C_2H_3Cl gas of various pressures was introduced into a small cell in the laser cavity. A reaction cell was 50 mm in length and 20 mm in diameter. The sample gas in the reaction cell was irradiated by the laser pulse focused with a germanium lens of $f=5$ cm. The peak power of the laser at the focus was 1 GW/cm^2 when the laser of 1 J was used. The pressure of the sample gas was 10 Torr.

The relative amounts of the products obtained by the infrared photoreaction induced by the various branches of the CO_2 laser with the same power output of 500 mJ are listed in Table 1. The experimental results for the P branch of 10.4 μm band is not shown here, because the absorption at the wavelength of this region is weak for this molecule, and hence the yield of the reaction is relatively small.

The total amounts of the products, C_2H_3Cl and C_2H_2, depend upon the laser line used in the reaction, the yield being greatest for the 9.6 μm laser and least for the 9.3 μm laser; the ratio of the yields is 48: 100: 22 for the 10.2 μm, 9.6 μm, and 9.3 μm lasers respectively.

The ratio of the C_2H_3Cl to the C_2H_2 were determined to be 55: 45, 72: 28, and 80: 20 respectively in the products of 10.2 μm, 9.6 μm, and 9.3 μm laser reactions. As was described above, the productions of the C_2H_2

TABLE 1. RELATIVE QUANTITIES OF MOLECULES PRODUCED BY THE INFRARED PHOTOREACTIONS OF $Cl_2HC–CH_3$ INDUCED BY VARIOUS BRANCHES OF THE CO_2 LASER

Laser wavelength	10.2 μm	9.6 μm	9.3 μm
Relative quantities of products	48	100	22
% of products			
C_2H_3Cl	55	72	80
C_2H_2	45	28	20
% of C_2H_2 produced by			
(1) direct process	20	20	20
(2) 2-step process	25	8	0

molecules in the present experiment can be brought about by the two processes, the direct and indirect ones. It is appropriate to define the present classification of the reaction more rigidly. The infrared laser action gives rise to the cleavage of the C–Cl bond, producing the ClHC–CH_3 radical in an quasicontinuum state when the vibrational quantum number, v, is larger than 3. The interaction between Cl and the ClHC–CH_3 radicals eliminates the H atom from the latter, resulting in the production of the ClHC=CH_2 molecule in various vibrational states. The ClHC=CH_2 molecules in the quasicontinuum state can absorb infrared lasers of any frequency. Though the ClHC=CH_2 molecules in the ground state have no absorption at the 9.3 μm line of the CO_2 laser, the molecule in the quasicontinuum state absorb its infrared laser. Hence, if the laser field is still present for a sufficiently long time after the formation of the ClHC=CH_2 molecule in the quasicontinuum state, these molecules can readily absorb additional photons and the subsequent reaction may occur, producing the C_2H_2 molecule. The reaction process presented here is the direct production of the C_2H_2.

On the other hand, the indirect process is defined as the 2-step reaction in which the C_2H_3Cl molecules in the vibrational ground state or the discrete vibrational level (generally its vibrational quantum number $v<3$) are produced at the first stage of the reaction, and the successive absorption of the laser by C_2H_3Cl molecules gives rise to the reaction of these molecules. However, in the 9.3 μm laser-induced reaction of Cl_2HC–CH_3, the indirect process is prohibited, because the C_2H_3Cl molecule in the ground state or in the discrete levels (lower vibrational state) cannot absorb the 9.3 μm laser radiation. It is suggested, therefore, that all of the C_2H_2 molecules, 20% of the products, were produced directly from Cl_2HC–CH_3 when the 9.3 μm laser was used.

For the laser reaction of the 10.2 μm or 9.6 μm line, the rates of the C_2H_2 in the total amount of the products were 45% and 28% respectively. If we assume that the direct process in the 10.2 μm or 9.6 μm laser-induced reaction produces the same rate of the C_2H_2 as in the reaction of the 9.3 μm laser, the differences in the proportions of C_2H_2 between the reactions induced by the former lasers and the latter, (45—20)% and (28—20)%, are the proportions of the indirectly produced C_2H_2 by the 10.2 μm and 9.6 μm lasers respectively. The ratio of the amounts of C_2H_2 produced by the 2-step process with the 10.2 μm laser and that of the 9.6 μm laser is $0.25/0.08=3.1$, while the ratio of the amounts of C_2H_2 produced from C_2H_3Cl by the 10.2 μm laser and the one produced by the 9.6 μm laser irradiation was 2.8. These values are almost equal, supporting our assumption presented here.

The relative concentrations of the C_2H_3Cl and C_2H_2 products were unaffected even when the repetition rates of the laser pulse were varied from 1 Hz to 0.1 Hz. In the latest repetition of the laser, the time interval of the two pulses is 10 s; therefore, the molecules, which have been dissociated by the first pulse at around the focus of the lens, may diffuse from this region before the second pulse is irradiated. This indicates that the 2-step reaction, Cl_2HC–CH_3→ClHC=CH_2→C_2H_2, may occur within a very short duration of 100 ns of the single laser pulse.

The conclusion derived above is supported by the theoretical analysis of the multiphoton dissociation, which has recently been applied to the 9.4 μm laser-induced chemical reaction of C_2F_3Cl. Our model calculation of the infrared photochemistry of C_2F_3Cl showed that if the rectangular pulse of 500 mJ with a 100 ns duration was employed, the following results were obtained:

1) Almost 80% of the molecules dissociate within 50 ns.

2) The decomposed molecules or radicals have excess energy in the range of $v=8$—16, the maximum distribution being in $v=12$. The average energy distribution in these molecules or radicals depends on the power output of the exciting laser.

These results have been obtained from the model calculation of the reaction yield for the 9.4 μm laser-induced photodissociation of C_2F_3Cl. It should be mentioned that the qualitative aspect of the infrared multiphoton reaction of any molecule can be deduced from the consideration presented here. The experimental results of the TEA CO_2 laser-induced reaction of Cl_2HC–CH_3 suggest that its reaction process is similar to that of C_2F_3Cl.

It may be concluded that the C_2H_2 molecules, 20% of the total products of the CO_2 laser-induced photochemistry of Cl_2HC–CH_3, are directly produced from the parent molecule, another part of the C_2H_2 being produced by the 2-step process within the time duration of the single laser pulse.

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References

1) K. Nagai and M. Katayama, *Bull. Chem. Soc. Jpn.*, **51**, 1269 (1978).

2) M. Katayama, *Oyo Buturi*, **48**, 502 (1979).

3) E. R. Grant, P. A. Schulz, Aa. S. Sudbo, Y. R. Shen, and Y. T. Lee, *Phys. Rev. Lett.*, **40**, 115 (1978).

4) M. Katayama and Y. Mizugai, *Chem. Lett.*, **1979**, 965.