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DIFFERENCE BETWEEN INFRARED MULTIPHOTON AND THERMAL REACTIONS OF $HClC{=}CClH$ AND $HClC{=}CCl_2$

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The differences of mechanisms between the reaction induced by infrared multiphoton dissociation and pyrolysis are elucidated in the cases of 1,2-dichloroethylene and trichloroethylene. The interpretation presented here may be applied in the reactions of many molecules.

There have been a number of experiments on infrared laser induced reactions which demonstrated that their products were different from those of pyrolysis in many cases even when a CW laser was used. Although the process of infrared multiphoton reaction should be distinguished from simple heating of molecules, the unlikeness between these reactions has not been analysed on the basis of their mechanism.

In the present article we want to elucidate the circumstances which bring about the difference between the thermal and infrared multiphoton reactions, based on the recent theoretical investigations of infrared multiphoton dissociation. Previously we reported that the major product of infrared photoreaction of trans=1,2-dichloroethylene induced by a TEA CO_2 laser with power output of 1 J and pulse width of 100 nsec was the cis form, minor products being C_2H_2 and C_2HCl with concentration ratio of 1 : 3[1)]. Ambartzumian et al. have detected C_2H_2 molecule and C_2 and CH radicals as minor products when they investigated the infrared photoisomerization of trans-1,2-dichloroethylene using the TEA CO_2 laser with power output of 2 J, while the production of C_2HCl has not been observed[2)]. These experimental results indicate that C_2H_2 is mainly produced in the infrared multiphoton dissociation of this molecule. On the other hand, the production of C_2H_2 was unobserved in the pyrolysis of 1,2-dichloroethylene,although the main reaction was isomerization and a trace of C_2HCl was detected[3)].

The activation energy of isomerization reaction of this molecule is 1.8 ev and the dissociation energy of the weakest bond C-Cl is about 3 ev. Therefore, multiphoton excitation by infrared laser with photon energy $h\nu = 0.1$ ev or thermal heating gives rise most easily to the isomerization reaction, where it is difficult to distinguish both reactions. The remarkable difference between the infrared multiphoton dissociation and the pyrolysis is the production of C_2H_2 in the former and C_2HCl in the latter.

To understand their difference of the reactions, it is appropriate to analyse the process of infrared multiphoton dissociation of molecules. The relevant energy levels are divided into three groups ; region I is characterized by discrete levels, region II being quasicontinuum state where the integrated energy of laser pulse plays a dominant role in their excitation, and the infrared laser of wide range of frequencies can be absorbed[4,7)]. Region III is the true continuum state above the dissociation limit E_{dis}. When the molecules are excited to the region III, overcoming anharmonicity bottleneck in the region I, it results in the dissociation of the weakest bond.

Phenomenological model calculations on quantitative behavior of infrared multiphoton excitations and dissociation of polyatomic molecules have demonstrated that the multiphoton excitation is not equivalent to the thermal heating. In the analysis of infrared multiphoton dissociation of SF_6, Grant et al. have shown that the molecules dissociate mainly from those levels $(6 \sim 11)h\nu$ above the dissociation limit E_{dis}, i.e. the dissociation energy of S-F bond, when the 100 nsec rectangular laser pulse with 200 mJ was used[5)]. In the primary dissociation of SF_6 into SF_5 and F, their beam experiment has shown that less than $h\nu$ of the total excess energy appears as recoil energy of the fragments, and therefore the rest is retained by SF_5 in its vibrational degrees of freedom[6)]. In a previous paper we reported that the initial reaction of C_2F_3Cl induced by the TEA CO_2 laser irradiation was $C_2F_3Cl \rightarrow C_2F_3 + Cl$[7)]. Our calculation of infrared multiphoton dissociation has shown that the excess energy of fragments are in the range of $(5 \sim 13)h\nu$ with distribution maximum at 8 $h\nu$ when the rectangular pulse of 100 mJ with 100 nsec duration is applied[8)]. As the translationql energy is less than $h\nu$, the rest of the energy is distributed among the internal degrees of freedom of the C_2F_3 radical. In general, the excitation of vibrational quantum number $v = 3 \sim 4$ gives rise to the quasicontinuum state in a polyatomic molecule or radical.

Therefore the fragment C_2F_3 is in the quasicontinuum state. Then if the laser field is still present for a sufficiently long time, the fragment can readily absorb additional photons and the subsequent reaction may occur.

In the infrared laser induced photochemistry of trans-1,2-dichloroethylene the same process of the reaction can be assumed. Above the quasicontinuum state, intramolecular VV relaxation is generally much faster than the rate of photon absorption, various vibrational degrees of freedom of the molecule being in the highly excited states. It results in the chemical reaction when the molecule is raised in higher energy levels than its activation energy. Since the activation energy of trans → cis isomerization is the lowest, the primary reaction of this molecule is the isomerization. A chemical reaction is considered as a statistical process, then,the subsidiary reactions may be brought about by the excitation of molecules. Since the bond energies of C-Cl and C-H of this molecule are 78.5 kcal/mole and 98.8 kcal/mol respectively$^{9)}$, the irradiation of the intense CO_2 laser gives rise to the cleavage of the weakest bond C-Cl, producing HC=CHCl radicals in the quasicontinuum state which absorb additional infrared photons to exceed the threshold for the following dissociation. Since the C-Cl bond is the weakest in the HC=CHCl radical, the dissociation in the second step produces the C_2H_2 molecule. It is the reason why the C_2H_2 molecule is detected in pure infrared multiphoton reaction of 1,2-dichloroethylene.

In the pyrolysis, however, the distribution of energy among various levels is in thermal equilibrium, the cleavage of the weakest bond C-Cl being brought about at high temperature. It produces the radical HC=CHCl at the first stage of the reaction. Since the radical is not in the highly excited state of vibration, the successive cleavage of the C-Cl bond is improbable. The interaction between the radicals HC=CHCl and Cl eliminates the H atom from HC=CHCl, producing the C_2HCl molecule as a final product.

The reaction of trichloroethylene is another example. Our recent investigation of TEA CO_2 laser induced reaction of trichloroethylene has shown that the products were C_2Cl_2 and C_2HCl with the concentration ratio of 10 : 1. According to the present interpretation of the reactions, the infrared multiphoton dissociation of C_2HCl_3 gives rise to the production of C_2HCl_2 radicals in the quasicontinuum state. Furthermore, the successive absorption of infrared photons by the C_2HCl_2 radical produces the C_2HCl molecule. Therefore, the product of the pure infrared multiphoton reaction is C_2HCl, although this substance was obtained only

1/10 of the amount of C_2Cl_2 as stated by our observation[10). The major product C_2Cl_2 may be produced by the H elimination reaction of C_2HCl_2 + Cl. Consequently, if the power output of our TEA CO_2 laser were high enough, we must have obtained the C_2HCl molecule as the majority of the products. On the contrary, in the 10 W-CW-CO_2-laser induced reaction, the successive elimination of two Cl atoms was not observed, the major products being C_2Cl_2, C_6Cl_6 and HCl. The thermal reaction products were reported to be C_6Cl_6 and HCl[11). The presence of C_2Cl_2 or C_2HCl molecules has not been detected. In the pyrolysis, the C_2Cl_2 molecules must be produced in the initial stage of the reaction by HCl elimination from the C_2HCl_3 molecule and the C_6Cl_6 molecule may be formed at high translational temperature from the activated molecules. However, the kinetic energies of the products C_2Cl_2 or C_2HCl in the infrared photoreaction are not so high to proceed the further reaction to produce the C_6Cl_6 and other products.

The reaction process described above can elucidate generally the difference between the multiphoton reaction induced by the extremely intense infrared laser and the thermal reaction of many molecules.

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