

A BOTTLENECK EFFECT IN PERFLUOROPROPENE

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(Received 28 January, 1993)

By investigating the infrared dissociation yield of perfluoropropene under a convenient range of experimental conditions on pressure, laser fluence and number of irradiation shots, we have seen that i) besides the already known final products, C_2F_4 and C_2F_6 , the dissociation of this molecule also produces polytetrafluoroethylene, and ii) contrary to what one should expect from its rather large molecular size, perfluoropropene opposes a strong bottleneck effect against absorption of resonant infrared radiation, at least for irradiation fluences smaller than $\approx 1.8 \text{ Jcm}^{-2}$.

KEY WORDS: Infrared Multiphoton Dissociation; Perfluoropropene; Polytetrafluoroethylene; Bottleneck effect.

1 INTRODUCTION

Infrared multiphoton dissociation of perfluoropropene has been studied by Nip and col.¹ and by Santos and col.². These works have established that the most probable mechanism for the dissociation reaction is



It was also pointed out that some amount of C_2F_6 is also produced in the reaction in such a way that the more initial pressure of C_3F_6 , the larger proportion of C_2F_6 is formed. Also was suggested¹ that CF_3 is produced when two “hot” CF_2 radicals react



However, it is not quite clear how the resulting CF radicals could finally appear.

In the present note we reexplore the multiphoton dissociation process of perfluoropropene when it is irradiated with one single resonant wavelength. Results for the pressure and number of shots dependence of the dissociation yield and final reaction products suggest that, depending on the fluence of the irradiation, it is possible to distinguish two different behaviours in the dissociation of perfluoropropene.

Evidence is also presented for the presence of a new product formed under all studied experimental conditions.

2 EXPERIMENTAL

All experiments were performed with a TEA-CO₂ laser (lumonics K-103), equipped with a frontal multimode optics and a diffraction grating blazed at 10.6 μm, operating with a typical CO₂-N₂-He (8-8-84) mixture to give pulses of approximately 65 ns peak followed by a tail of about 1.5 μs. In all experiments the laser line R(34) at 9.603 μm was used. This line nearly coincides with the linear absorption maximum at 1036 cm⁻¹ corresponding to the C-F stretching vibration of the central carbon atom in the C₃F₆ molecule³.

The experiments were carried out in a pyrex cell 9.5 cm long with a total volume of 71 cm³ equipped with NaCl end windows. A nearly parallel geometry was employed by inserting a 2 m focal lens between the laser and the cell and different values of the incident fluence were obtained by varying their relative position. The energy was changed by placing CaF₂ plates and/or polyethylene films in the optical path controlling on the high voltage settings of the laser for a finer adjust. The fluence values were determined by the measured pulse energy divided by the laser beam pattern area produced on thermal printer paper. The estimated uncertainty in the absolute fluence is around ±15%. A pyroelectric detector Lumonics 20D was used to measure the incident pulse energy, and a photon drag detector (Rofin, model 7415) to check the time profile of the pulses.

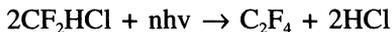
Dissociation yield measurements in the parent molecule and in the resulting products were carried out by infrared spectroscopy by using a Perkin-Elmer FTIR spectrophotometer 1725X. The study of the influence of the different experimental parameters in the reaction was made possible by introducing the two dimensionless parameters:

$$\alpha_1 = \frac{\text{Absorbance of the C}_2\text{F}_6 \text{ band at } 1251 \text{ cm}^{-1}}{\text{Change of the absorbance of the C}_3\text{F}_6 \text{ band at } 1036 \text{ cm}^{-1}}$$

and

$$\alpha_2 = \frac{[\text{C}_2\text{F}_4]}{1.5\Delta[\text{C}_3\text{F}_6]},$$

where $\Delta[\text{C}_3\text{F}_6]$ is the change in the concentration of this molecule due to dissociation, α_1 is proportional to the relation between the concentration of formed C₂F₆ and the consumed C₃F₆ and α_2 gives the proportion of dissociated C₃F₆ transformed in C₂F₄; $\alpha_2 = 1$ means that all formed CF₂ radicals are transformed in C₂F₄. The actual concentration of C₂F₄, was determined by calibrating its absorption band at 1187 cm⁻¹ using the stoichiometry of the single channel multiphoton dissociation reaction⁴



Perfluoropropene gas sample was kindly supplied by Prof. H. van den Bergh, and was used without further purification.

3 RESULTS AND DISCUSSION

For quantifying the dissociation yield we have used the fraction of C_3F_6 molecules dissociated per laser pulse, in the irradiated volume, f ,⁵ defined by

$$f = \frac{V_c}{V_l} \left\{ 1 - \left(\frac{[\text{C}_3\text{F}_6]_n}{[\text{C}_3\text{F}_6]_0} \right)^{\frac{1}{n}} \right\}$$

where V_c is the cell volume, V_l is the irradiated volume, n is the number of laser pulses and $[\text{C}_3\text{F}_6]_0$ and $[\text{C}_3\text{F}_6]_n$ are, respectively, the C_3F_6 concentration before and after the irradiation with n laser pulses.

For $[\text{C}_3\text{F}_6]_0 = 6.10 \cdot 10^{-6}$ mol/l, using 10 laser shots per experiment, the obtained f shows a typical strongly fluence-dependent pattern, with a dissociation threshold at around 1.2 Jcm^{-2} which saturates at $f \approx 0.45$ for $\phi \geq 4.4 \text{ Jcm}^{-2}$. It has been also shown, for the above conditions, that both parameters α_1 and α_2 vary in a nearly but opposite linear way with fluence, with a positive slope for α_1 , meaning a favouring of C_2F_6 formation against C_2F_4 as fluence increases.

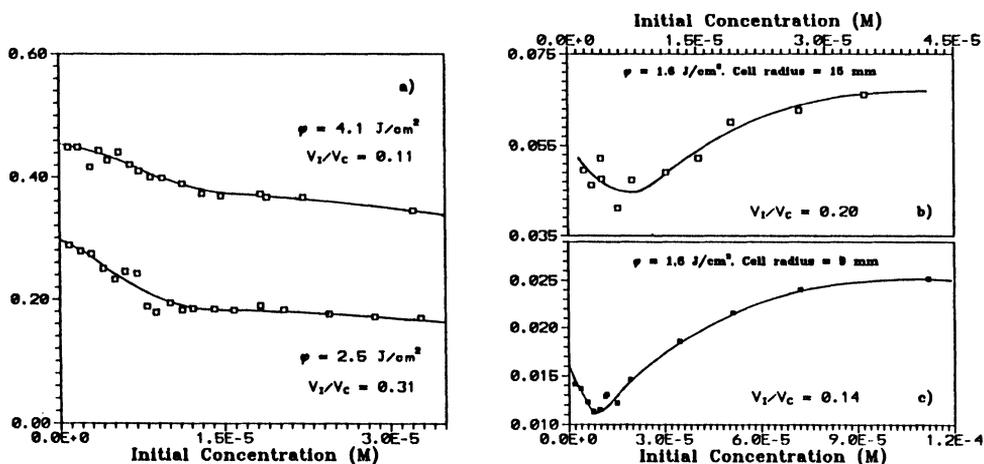


Figure 1 Fraction, f , of C_3F_6 molecules dissociated per laser pulse vs. $[\text{C}_3\text{F}_6]_0$. Curves a) and b) were obtained with 10 laser pulses and curve c) with 50 laser pulses.

Figure 1 shows how the fraction f behaves with $[\text{C}_3\text{F}_6]_0$. Depending on the fluence being used, two different behaviours appear. For the larger fluences (Figure 1a), f first continuously decreases until an initial concentration of around 10^{-5} mol/l, keeping a rather constant value thereafter. The behaviour for smaller fluences (Figure 1b), is in

fact quite different after initial concentration an 10^{-5} mol/l, for f then clearly increases along the explored concentration interval. This behaviour becomes more apparent when a larger proportion of the molecules in the cell are irradiated (Figure 1c); in this case the plot also tends to saturate from below at the largest concentration. These results complete, in the low concentration region and at low fluences, our previous ones².

The formation of final products can be followed by giving the variation of the parameters α_1 and α_2 . In Figure 2 we represent the variation of these parameters vs. $[C_3F_6]_0$ for the three values of fluence used in Figure 1. It can be observed that whereas α_2 remains nearly unchanged, α_1 increases with $[C_3F_6]_0$ at rates which tend to be larger for lower fluences. These results could not be satisfied by invoking just the proposed mechanisms (1) and (2) for dissociation and/or recombination of the fragments.

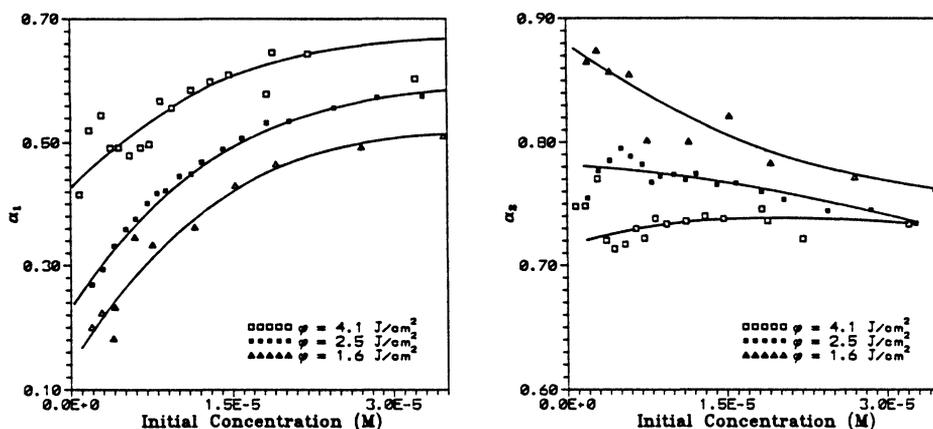


Figure 2 Parameters α_1 and α_2 vs. $[C_3F_6]_0$ for the three curves shown in Figure 1. 10 pulses were used in all the experiments.

The dependence of the dissociation yield of C_3F_6 on the number of irradiation pulses for two different conditions of fluence and initial concentration of C_3F_6 have also been studied. In all the cases f decreases with the number of pulses, the lower the fluence the quicker the decrease. Both α_1 and α_2 decrease when increasing the number of pulses, with the largest relative decrease being obtained for the highest fluence and smallest initial concentration (Figure 3). Again this result do not fit the proposed dissociation and/or recombination mechanisms.

As we have pointed out above, from the parameters α_1 and α_2 we can quantify the exact amounts of C_2F_4 but not the C_2F_6 quantity formed in the dissociation process; however, we can still measure the relation between the variations in α_1 and α_2 for different points of a given plot. This has been carried out for the different experimental curves comparing the results with that would be predicted for the variations of α_1 and α_2 if just reactions (1) and (2) were operating. Once again, and quantitatively this time, we have obtained that (1) and (2) fail to describe

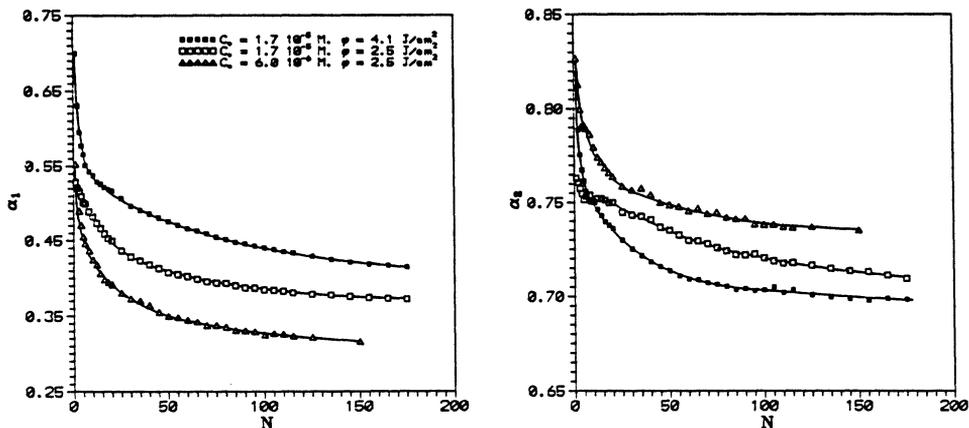


Figure 3 Parameters α_1 and α_2 vs. the accumulated number of pulses for two different conditions of fluence and $[C_3F_6]_0$.

experiment. Consistent with this conclusion is the presence of a new dissociation product, so far unnoticed, which we have uncovered by performing a closer inspection of the infrared spectra. In fact, the infrared spectrum recorded on a carefully evacuated reaction cell, (Figure 4), presents two absorption features centered at around 1150 and 1210 cm^{-1} . We have identified these absorptions to the presence of polytetrafluoroethylene, $(CF_2-CF_2)_n$, a solid polymer whose occurrence has been only reported, to the extent we know, in dissociation experiments of CF_2HCl by a continuous discharge CO_2 laser⁷, and constituted an interesting finding in glass etching initiated by excimer laser photolysis of CF_2Br_2 ⁸.

It is difficult to exactly measure the proportion of polymer formed in the dissociation of a definite amount of C_3F_6 , due to the fact that we do not know how the polymer layer is distributed on the walls of the reaction cell. However, an estimate of the proportion of C_3F_6 transformed in polymer can be done from the absorption coefficient given in the literature⁶, assuming an uniform distribution of the newly formed polymer on the cell walls. Thus, a proportion of around 20% of the dissociated C_3F_6 transformed into $(CF_2)_n$ has been obtained for experiments of Figure 1a. Of course, one should take into account the formation of the polymer for such a high proportion.

One interesting point is to elucidate of how this compound is produced. One can imagine two extreme situations for which a) it might be formed through a secondary process from the CF_2 radicals (or mixture of CF_2 and C_2F_4) produced in the dissociation process or, b) it might be directly created from the excited C_3F_6 . Using the α_1 and α_2 values obtained from the different experiments, we have found conversions of C_3F_6 into $(CF_2)_n$ in both extreme situations, that are in agreement with the quantity estimated above from the infrared spectra. These results suggest that these two mechanisms would probably contribute the real C_3F_6 dissociation and recombination processes. On the other hand, the fate of CF radicals could well be interwoven with the formation of the long polymer chains and, if the polymer chains would actually incorporate most of the formed CF radicals, then one could explain the lack of gaseous compounds

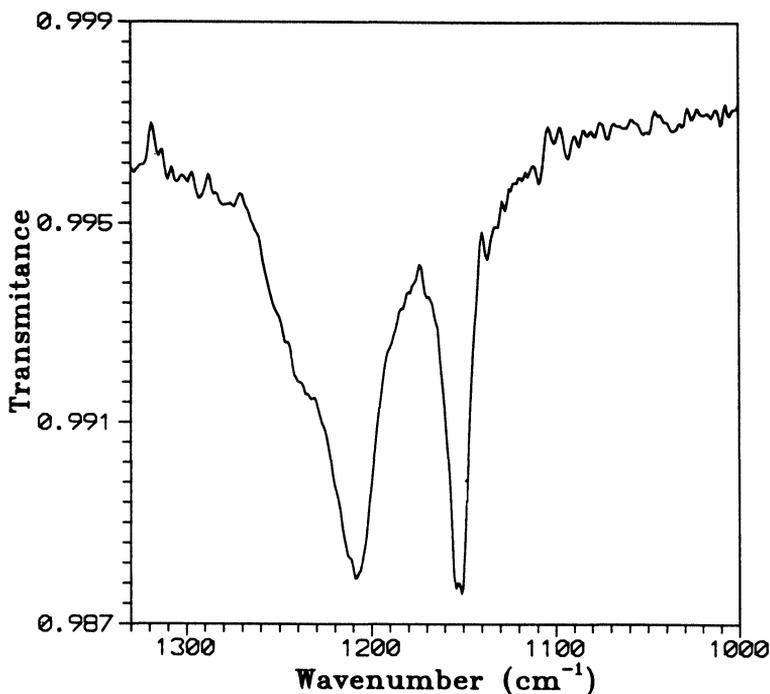


Figure 4 Infrared spectrum of the solid material deposited on the cell windows after several experiments.

containing CF, at the cost of very slight changes in the infrared absorption features of the polymer.

The obtained results for the dependence of f versus the initial concentration of C_3F_6 , number of pulses and fluence, when this last parameter is kept above 2.4 J/cm^2 (Figures 1b and 3), are as one should expect for a rather big molecule⁹: a decrease and subsequent saturation of f when the initial concentration is increased and a fairly high dissociation probability obtained for moderate fluences. In principle, though these results would be taken as a proof for the lack of any bottleneck effect during energy absorption, the increase in the dissociation yield when the initial concentration of C_3F_6 raises from 10^{-5} to 10^{-4} mol/l at low fluences (Figure 1b and c) points out to the existence of some kind of bottleneck against the absorption process. This bottleneck, produced by the large anharmonicity of the active mode, would operate just above the few first transitions before the large density of vibrational and rotational levels couple to form the quasicontinuum. This effect would manifest only when the irradiation of the molecules is made at low values of fluence, becoming undetectable for fluences larger than 2.4 J/cm^2 . In this way, the fluence becomes a crucial parameter when one is trying to classify the molecules in small or large respect to the dissociation.

The trends exhibited in Figure 1 can be now easily explained. At both fluence regimes, shown in Figure 1a and b, in the low pressure region where the time between collisions

is larger than the time pulse but smaller than the time needed for the dissociation process to be completed¹⁰, the collisions prevent the dissociation of C_3F_6 to occur. The larger the proportion of irradiated molecules, the clearer is this effect shown. When the pressure is high enough for the molecules to collide within the time pulse, the bottleneck effect, present in the low fluence experiments, is overcome by the effect of these collisions¹¹, increasing the fraction of molecules with the ability to proceed absorbing laser photons. It follows that collisions have two opposite effects on the dissociation yield. Assuming that there are no V-T relaxation at the minimum of Figure 1b and c, and, hence, that molecules possess a thermal mean velocity at room temperature, we can estimate that, even for an effective pulse width of $1 \mu s$, the number of collisions at the minimum concentration is as long as $1 \mu s^{-1}$ in the hard-sphere approximation¹², that is a high efficiency of collisions in removing the bottleneck effect present in this molecule when is irradiated at low fluence.

Other mechanisms increasing the decomposition yield with pressure, such as vibrational energy pooling and rotational hole filling should also be considered¹¹. Nevertheless, experiments carried out in our laboratory for multiphoton dissociation of several initial concentrations of C_3F_6 in the presence of Ar¹³ have shown a noticeable decrease of the yield along the Ar pressure interval 0–3 millibars. Actually, the larger the initial concentration of the parent molecule the smaller the inhibitory influence of the buffer gas. These results seem to confirm that the importance of a possible rotational hole filling is very small compared to the circumvention of the anharmonic bottleneck effect through homogeneous collisions. The contribution of a VV energy pooling mechanism to the increase of the yield is rather difficult to evaluate. The results obtained for the higher fluence values (Figure 1a and b) indicates, however, that its contribution has to be fairly small.

We have shown that a rather large molecule as C_3F_6 has, in low fluence irradiation conditions, a multiphoton dissociation behaviour similar to that of smaller molecules. Further experimental work is needed to check whether the general features that the smaller molecules show in multiphoton absorption can be extended for any molecular size by suitably choosing the irradiation conditions, or it is a particular behaviour of perfluoropropene.

Acknowledgements

The authors wish to acknowledge Prof. H. van den Bergh of the Polytechnic University of Lausanne for supplying the C_3F_6 sample, and to C. L. Sigüenza and L. Díaz-Sol for useful discussions. This work has been carried out with financial support provided by the Comunidad Autónoma de Madrid under Project number C187/91.

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