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Multiphoton geometrical isomerization of ClFC=CFCl. Selective purification of the *trans* isomer

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Abstract. A selective purification of the *trans* isomer of CFCl=CFCl was accomplished by multiphoton induced isomerization. The effect of pressure and fluence on the isomerization yield was also investigated.

Keywords. Geometrical isomerization; selective purification; ClFC=CFCl; IRMPI.

1. Introduction

There are several studies on multiphoton induced isomerization (MPII) of alkenes (Glatt and Yogev 1976; Buechele *et al* 1979; Teng *et al* 1982). The synthesis of ClFC=CFCl results in a mixture of the *cis* and *trans* isomers, very difficult to separate by standard methods (Craig and Evans 1965). Since the infrared spectrum of the *cis* ClFC=CFCl presents a strong absorption at 949 cm^{-1} while that the *trans* isomer is negligible, selected IR laser excitation was feasible.

2. Experimental

The experiments were performed by irradiating mixtures of the *cis* and *trans* isomers in an initial *cis/trans* ratio of 0·90 with the $P(14)$ line of a pulsed TEA CO_2 laser. After irradiation with a selected number of pulses the composition of the sample was analysed by FTIR spectroscopy or by gas chromatography using 5% DMSO on alumina column. The experiments were carried out at a total reactant pressure in the range 0·1–3 Torr and initial incident energy of 0·8–5·1 J/cm^2. The incident fluence was varied by slightly focusing the laser beam with BaF_2 lenses.

3. Results

A typical FTIR spectrum before and after the irradiation of the sample is shown in figure 1. The absorption bands of the *cis* and *trans* isomers are also indicated. Figure 2 illustrates how the fractional yield of isomerization increases with fluence. The low values of the fractional yield indicate that, even at the highest fluence investigated, a

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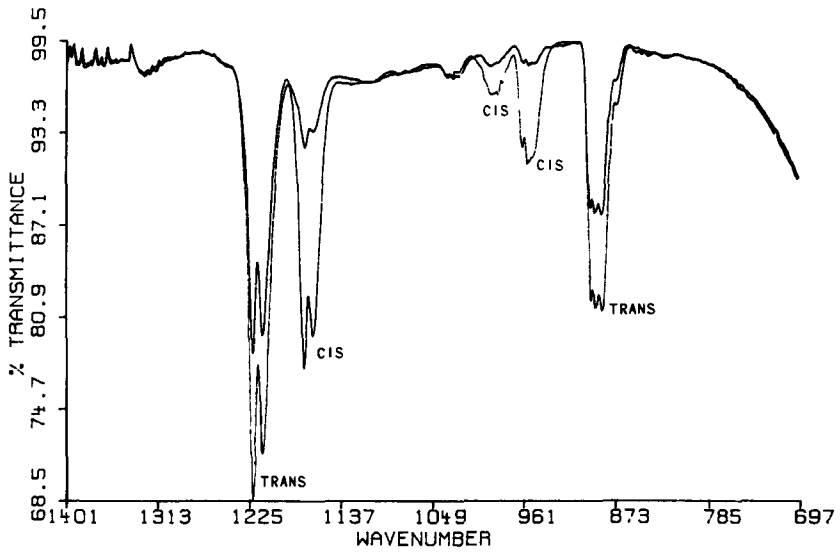

Figure 1. FTIR spectrum of *cis* and *trans* ClFC=CFCl before and after laser irradiation. Fluence: 5.1 J/cm^2, 1200 pulses. Pressure: 1·2 Torr.

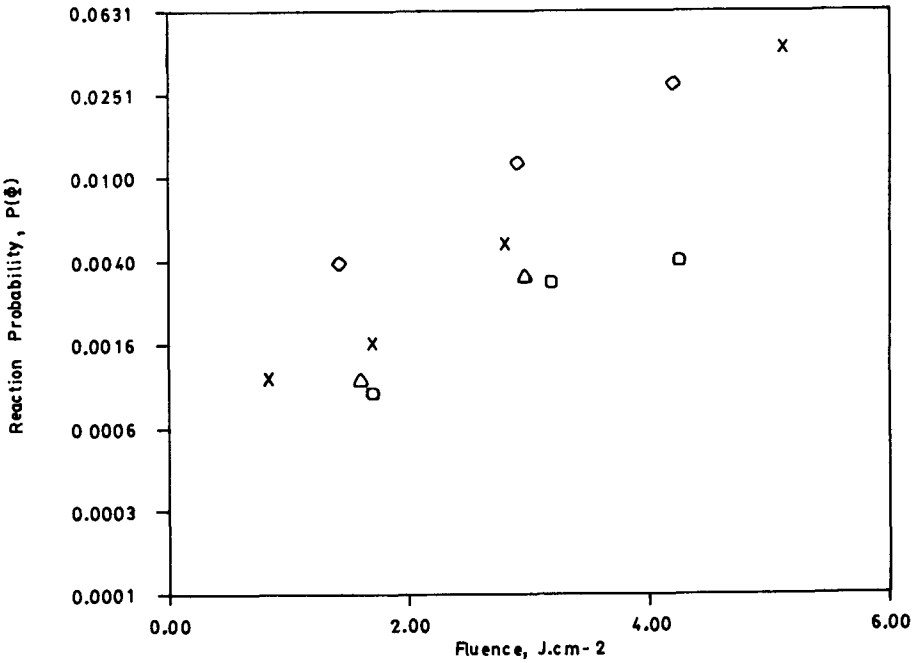

Figure 2. Reaction probability *vs* fluence at four different pressures. (□) 2; (△) 1·5; (×) 1·2; and (◇) 0·5 Torr.

100% per pulse efficiency was not achieved. Dissociation products were neither detected by FTIR spectroscopy nor by gas chromatography.

The effect of total pressure at different fluences is plotted in figure 3. It can be seen that $P(\phi)$ decreases as the total pressure increases, except at low pressures where a rotational bottleneck seems to increase the fraction of isomerization with pressure.

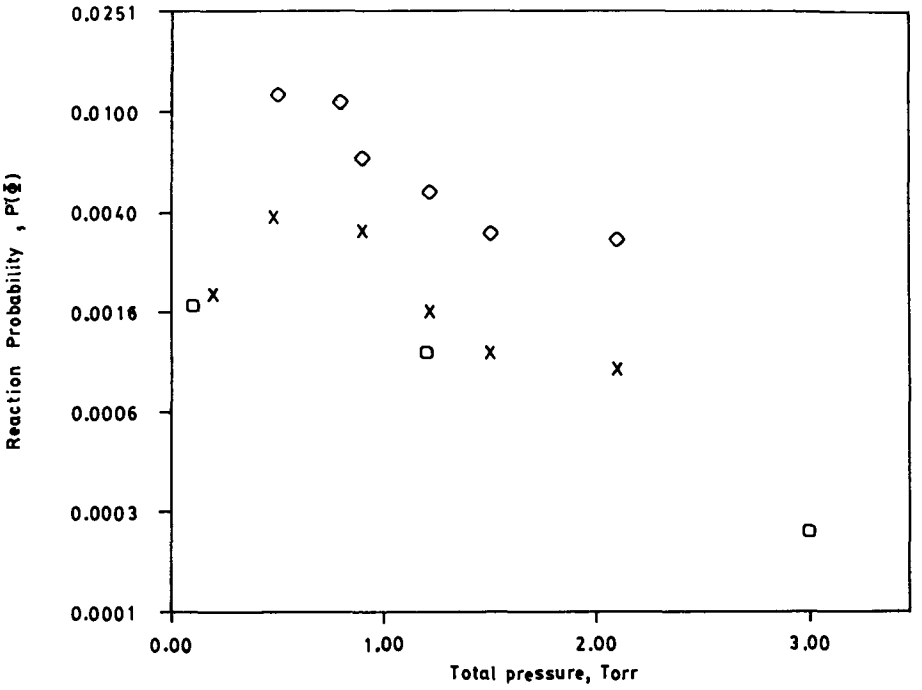

Figure 3. Reaction probability *vs* pressure at three different fluences. (□) 0·83; (×) 1·7; and (◇) 3 J/cm^2.

4. Discussion

Selective purification of the *trans* isomer can be accomplished by means of multiphoton laser induced isomerization. Thus, it is possible to obtain a 99% pure sample of the *trans* isomer after irradiating a 1·2 Torr mixture of ClFC=CFCl with 4500 pulses at a fluence of 5·1 J/cm^2 and a 99·9% pure sample with 7500 pulses. This method of purification has the advantage that it is very efficient and the loss of material is negligible.

The MPII process can be explained in terms of the following reaction mechanism:

$$cis\ \mathrm{ClFC{=}CFCl} + n\mathrm{h}\nu \rightarrow cis\ \mathrm{ClFC{=}CFCl}^*,$$

$$cis\ \mathrm{ClFC{=}CFCl}^* \rightleftarrows trans\ \mathrm{ClFC{=}CFCl}^*,$$

$$trans\ \mathrm{ClFC{=}CFCl}^* + \mathrm{M} \rightarrow trans\ \mathrm{ClFC{=}CFCl},$$

$$cis\ \mathrm{ClFC{=}CFCl}^* + \mathrm{M} \rightarrow cis\ \mathrm{ClFC{=}CFCl}.$$

In the near future, these processes will be modelled taking into account these experimental results. Further data must be obtained to reach final conclusions.

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