

# Frequency Dependent Kinetics of the CW CO<sub>2</sub> Laser Induced Reaction of CF<sub>3</sub>CF<sub>2</sub>Cl

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Kinetics of the decomposition of CF<sub>3</sub>CF<sub>2</sub>Cl at 50 torr by a cw CO<sub>2</sub> laser have been studied over a range of laser frequencies extending 36 cm<sup>-1</sup> below an absorption band center at 980 cm<sup>-1</sup>. At constant translational temperature, the change in the rate constant with laser frequency is a factor of 100, comparable to the effect previously observed in CF<sub>2</sub>ClCF<sub>2</sub>Cl. Arrhenius plots show an activation energy of 86.2 kcal/mole, independent of frequency.

KEY WORDS: Kinetics, CF<sub>3</sub>CF<sub>2</sub>Cl, laser induced reaction.

## INTRODUCTION

Gas phase chemical reactions induced by continuous (cw) infrared laser usually occur under conditions where the molecular collision rate exceeds the photon absorption rate per molecule by several orders of magnitude. Accordingly, there is a good opportunity for collisions to distribute the absorbed energy to other molecular vibrational states during the interval between successive photon absorptions. This is particularly true for the levels of the absorbing vibrational mode, since the collisional exchange of quanta between these levels is nearly resonant in energy, with only a small anharmonic deficit, and so a high transfer probability  $\geq 0.1$  per collision is expected<sup>1</sup>. In fact, time-resolved fluorescence measurements show that such transfers do occur in less than 30 collisions<sup>2,3</sup>. Therefore, a large ratio of the collision to

photon absorption rate should be sufficient to establish a statistical population among the levels of the absorbing mode.

Here we consider experiments in which the cw laser frequency is lowered below that of the mode's absorption band center. Due to anharmonicity, photons of the lower frequency are absorbed by an excited state rather than the ground state of the mode. However, the rapid collisional transfer processes described above should erase any memory of this initial excitation by establishing a statistical mode population among the levels of the mode, and so only the power absorbed per molecule, and not the laser frequency, should determine the steady-state mode temperature and, eventually, the molecular dissociation rate.

In agreement with this expectation, it has been shown that the cw laser induced decompositions of ethyl acetate and of  $\text{CH}_3\text{CF}_2\text{Cl}$  are indeed relatively insensitive to laser frequency<sup>4,5</sup>. For  $\text{CF}_2\text{ClCF}_2\text{Cl}$ , however, the reaction rate constant is observed to increase by more than a factor of 100 when, at constant power absorbed per unit volume, the laser frequency is lowered  $25\text{ cm}^{-1}$  below an absorption band center<sup>5,6</sup>. The absorbed power per unit volume determines the translational temperature in the beam region, and interferometric measurements using a He-Ne laser beam probe confirmed that the hundred-fold change in rate constant with laser frequency occurred at constant translational temperature<sup>5</sup>. Moreover, an increase in  $\text{CF}_2\text{ClCF}_2\text{Cl}$  pressure, and thus the collision rate, actually produces a slight enhancement of the effect of laser frequency. In these experiments, the pressures ranged from 50 to 200 torr, with the collision rate exceeding the photon absorption rate per molecule by factors of  $10^3$  to  $10^4$ .

The discrepancy between these results and the expectations described earlier is remarkable. Accordingly, it is important to see if there are other compounds with the same property. Here we report an effect of comparable magnitude in  $\text{CF}_3\text{CF}_2\text{Cl}$ , where the reaction rate constant changes by a factor of 100 at constant absorbed power and translational temperature over the laser frequency range of  $944\text{--}980\text{ cm}^{-1}$ . Arrhenius plots show an activation energy of  $86.2\text{ kcal/mole}$  at all frequencies, a value consistent with either C—C or C—Cl bond breaking in the decomposition of  $\text{CF}_3\text{CF}_2\text{Cl}$ . We also report that the addition of an inert gas or a "radical scavenger" has little influence on the magnitude of the laser frequency effect. The latter indicates that

the effect is probably not due to laser absorption by the radical intermediates involved in the overall reaction.

## REACTION

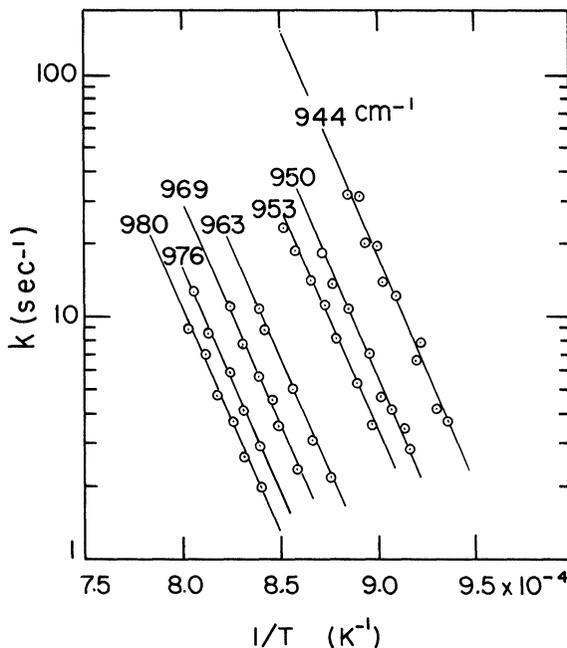
No reports of the kinetics of the pyrolysis of  $\text{CF}_3\text{CF}_2\text{Cl}$  were found in the literature. The infrared multiphoton dissociation of  $\text{CF}_3\text{CF}_2\text{Cl}$  by a pulsed TEA- $\text{CO}_2$  laser has been investigated with a crossed molecular beam apparatus<sup>7</sup>. The results suggested that initial decomposition is predominantly by way of Cl elimination in the limit of low beam fluence (a condition most similar to that of the present work) with an estimated activation energy of 83 kcal/mole. The major carbon-containing products observed ( $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_2\text{F}_6$ ) are those obtained in the present experiments. The reaction pathways leading to the products are complex, and the details of the set of reactions involved are unclear.

## EXPERIMENTAL

$\text{CF}_3\text{CF}_2\text{Cl}$  was purchased from Linde, Inc. with a stated minimum purity of 98% and was used as purchased. The experimental techniques employed throughout are the same as those used in earlier studies<sup>4,5,8</sup>. Reaction rates were measured in real time by observing the growth of the  $921\text{ cm}^{-1}$  absorption peak of the reaction product  $\text{CF}_2\text{Cl}_2$  during laser irradiation, and only initial rates corresponding to small product conversions were used for data. The absorption bands of other products such as  $\text{CF}_3\text{Cl}$  were not used for rate measurements because of their overlap with parent  $\text{CF}_3\text{CF}_2\text{Cl}$  bands. Translational temperatures were determined from measurements of absorbed laser beam power in short path length cells.

## RESULTS

Figure 1 shows Arrhenius plots of the laser-induced rate constant  $k$  versus the reciprocal of the translational temperature  $T$  at various laser frequencies. Here,  $k$  actually represents the rate constant for the



**Figure 1** Rate constant *versus* reciprocal translational temperature at various laser frequencies for the decomposition of  $\text{CF}_3\text{CF}_2\text{Cl}$  at 50 torr.

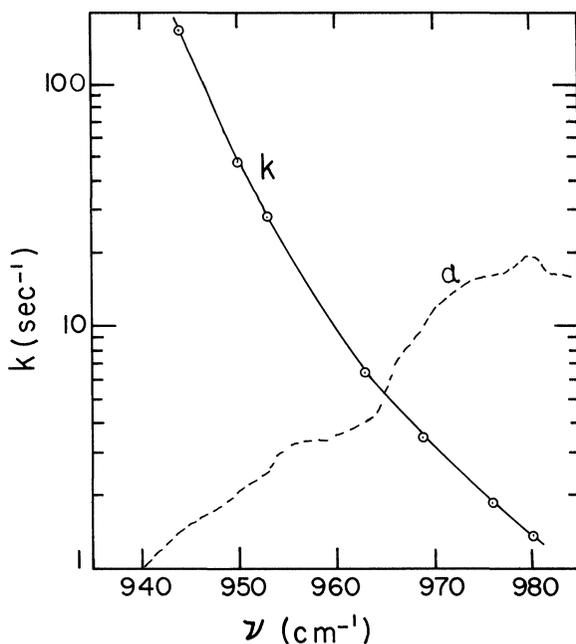
formation of the product  $\text{CF}_2\text{Cl}_2$ , and for simplicity the reaction has been assumed to be first order. The  $\text{CF}_3\text{CF}_2\text{Cl}$  pressure is 50 torr. Reaction kinetics could not be studied with reliable precision at laser frequencies below  $944\text{ cm}^{-1}$  because in that range the change in reaction rate with laser power was so large that small fluctuations in laser power produced unacceptable fluctuations in the rate data.

The data show essentially the same activation energy at each laser frequency, with an average value of  $86.2\text{ kcal/mole}$ . This value is consistent with either C—C or C—Cl bond-breaking in  $\text{CF}_3\text{CF}_2\text{Cl}$  as the initial decomposition step. It is also apparent from the data that at any fixed translational temperature in the range covered, a change in laser frequency produces a marked change in the rate constant.

Figure 2 shows the change of rate constant  $k$  with laser frequency  $\nu$  at fixed translational temperature  $T$ . The points in this figure are obtained from the intercepts of the Arrhenius plots of Figure 1 with a

vertical line at  $1/T = 8.5 \times 10^{-4} \text{K}^{-1}$ . For purposes of comparison, Figure 2 also shows the corresponding spectrum of the optical absorption coefficient of  $\text{CF}_3\text{CF}_2\text{Cl}$  at room temperature. The change in  $k$  with laser frequency over the range  $980\text{--}944 \text{cm}^{-1}$  is a factor of 100, similar to the effect reported for  $\text{CF}_2\text{ClCF}_2\text{Cl}$ <sup>5,6</sup>. If the rate constant  $k$  is assumed to be determined by an effective vibrational temperature  $T_v$  according to the expression  $k = A \exp(-E/RT_v)$ , then the observed change in  $k$  with laser frequency corresponds to a change in  $T_v$  of nearly 15%.

The average photon absorption rate per molecule can be calculated from the expression  $\alpha I/n\varepsilon$ , where  $\alpha$  is the optical absorption coefficient,  $I$  is the beam intensity,  $n$  is the molecular density, and  $\varepsilon$  is the photon energy. In all of the experiments, the photon absorption rate per molecule does not exceed  $8 \times 10^4 \text{sec}^{-1}$ , which is smaller than the



**Figure 2** Rate constant  $k$  versus laser frequency  $\nu$  at the fixed reciprocal translational temperature  $1/T = 8.5 \times 10^{-4} \text{K}^{-1}$ . The dashed line is the optical absorption coefficient  $\alpha$  of the  $980 \text{cm}^{-1}$  absorption band of  $\text{CF}_3\text{CF}_2\text{Cl}$  at room temperature (arbitrary units).

calculated gas kinetic collision frequency by a factor of about  $5 \times 10^3$ . There is, therefore, ample opportunity for collisions to establish a statistical mode population between successive photon absorptions by means of rapid intramode collisional transfer, thus "erasing" the memory of the frequency of the absorbed photon.

Since radical intermediates are involved in the overall reactions of both  $\text{CF}_3\text{CF}_2\text{Cl}$  and  $\text{CF}_2\text{ClCF}_2\text{Cl}$ , there is the possibility that optical absorption by radicals is responsible for the effect being reported here. As noted earlier, the reactions of ethyl acetate and of  $\text{CH}_3\text{CF}_2\text{Cl}$  are relatively insensitive to laser frequency<sup>4,5</sup> and radical intermediates are not involved in those reactions. Accordingly, the effects of adding various radical "scavengers" such as propene and  $\text{O}_2$  were studied. While this produced new sets of reaction products, the rates of production of those products showed a dependence on laser frequency of the same magnitude as observed in the pure compounds. Thus, optical absorption by radical intermediates (e.g.,  $\text{CF}_3\text{CF}_2$  whose absorption spectrum is unknown) is probably not responsible for the laser frequency effect. Consistent with this, one can also calculate, based on estimates of radical concentrations in the beam region and their absorption coefficients, that their lifetimes before further combination are very much less than their photon absorption rate.

In further experiments, 200 torr of Ar or  $\text{N}_2$  were added in an attempt to "thermalize" the system, but the magnitude of the effect of laser frequency remained virtually unchanged.

## CONCLUSIONS

It has been established that two compounds,  $\text{CF}_3\text{CF}_2\text{Cl}$  and  $\text{CF}_2\text{ClCF}_2\text{Cl}$ , exhibit a strong dependence of reaction rate constant on laser frequency under conditions where the molecular collision rate greatly exceeds the photon absorption rate. In view of expectations based on rapid collisional intramode energy transfer as described earlier, the results are puzzling, particularly since the reactions of  $\text{CH}_3\text{CF}_2\text{Cl}$  and ethyl acetate are insensitive to laser frequency<sup>4,5</sup>. Experiments with the additions of radical scavengers indicate that optical absorption by radical intermediates is probably not responsible for the laser frequency effect in  $\text{CF}_3\text{CF}_2\text{Cl}$  and  $\text{CF}_2\text{ClCF}_2\text{Cl}$ , which also is found to be undiminished after additions of Ar or  $\text{N}_2$ .

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