Infrared Multiphoton-Induced Isomerization of Tetrafluorocyclopropene

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Infrared multiphoton excitation of tetrafluorocyclopropene (TFCP) leads to the unexpected formation of tetrafluoroallene (TFA) and tetrafluoropropyne (TFP). The ratio of TFP to TFA formed in the reaction is independent of fluence and pressure, and no other products are formed. The conversion per pulse increases as the pressure of TFCP increases but decreases as the pressure of a buffer gas or the products increases. The apparent intramolecular 1,2-fluorine migration required to form the products is discussed in terms of both unimolecular and bimolecular processes.

Introduction

Thermal or infrared multiple-photon excitation of cyclic fluoroalkanes or alkenes typically results in ring opening and elimination of difluorocarbene. For example, the thermal decomposition of a variety of fluorinated cyclopropanes results in the elimination of $: CF_2$,¹ contrasted to cyclopropane which isomerizes via a 1,2hydrogen migration to propene.² The infrared multiple-photon decomposition (IRMPD) of decafluorocyclohexene results in the formation of tetrafluoroethene (TFE) and hexafluorobutadiene (HFBD),³ and IRMPD of octafluorocyclopentene yields : CF_2 and hexafluorobutadiene as the primary products.⁴ IRMPD of octafluorocyclobutane results in the formation of TFE,⁵ but the endothermic ring opening of hexafluorocyclobutene to form HFBD is not accompanied by : CF_2 elimination.⁶ We have studied the IRMPD of TFCP and find the products to be exclusively tetrafluoroallene (TFA) and tetrafluoropropyne (TFP) instead of TFE and difluoroethyne. The conversion per pulse increases with TFCP pressure but decreases as the pressure of the products of a buffer gas increases.

Experimental Section

Tetrafluorocyclopropene was prepared by the method of Sargeant and Krespan.⁷ Briefly, 1,2-dichlorotetrafluorocyclopropane (DCTFCP) was prepared from the reaction of 1,2-dichlorodifluoroethene with hexafluoropropylene oxide, and the DCTFCP was dechlorinated to yield TFCP (¹⁹F NMR (CDCl₃, CFCl₃): δ -91.7 (t) and -138.7 (t), J_{ab} = 43 Hz). Two different preparations of TFCP were used in this work; sample 1 had been stored for 5 years at room temperature, and sample 2 was prepared during the course of this work.

A Tachisto 215G CO_2 laser tuned to the P(34) line of the $00^{0}1-10^{0}1$ band (931 cm⁻¹) was used as the excitation source. The specific laser line was identified by an Optical Engineering Model 16A CO_2 laser spectrum analyzer while the pulse energy was monitored with a Gen-Tec Model ED-500 joulemeter. Most experiments were conducted with the unfocused laser beam (1.5-cm² cross-sectional area); for other experiments a 1.5-in.diameter AR-coated germanium lens with a 6-in. focal length was placed 2.5 and 3.5 in. from the center of the reaction cell. This

amplified the fluence by factors of approximately 1.9 and 2.6, respectively.

Infrared spectra were obtained with an IBM Model 98 FTIR instrument (1-cm⁻¹ resolution, 64 scans/spectrum). The gas cells (10 cm long, 2.1-cm i.d. or 2.54 cm long, 2.54-cm i.d.) had NaCl windows; the pressure of TFCP in the cells was measured by means of a MKS Baratron (222BHS) 100-Torr capacitance manometer and/or infrared absorption intensities. The spectrum of the products was obtained by subtraction of the spectrum of TFCP from that of the mixture of products and TFCP; integrated band intensities were obtained with a straight base line drawn between the limits indicated below. The subtraction coefficients necessary to remove the spectrum of TFE from the spectra of the mixtures of products were used to determine TFE pressures; the reference TFE spectrum was determined by calibration with pure TFE samples.

Results

The infrared spectrum of a 4-Torr sample of TFCP is shown in the lower trace of Figure 1 and is in agreement with that reported by Craig⁸ except for weak bands due to DCTFCP as discussed below. The spectrum of the products obtained after irradiation by 16 pulses (unfocused) is shown in the upper trace of Figure 1; the spectrum of the remaining TFCP has been subtracted. The spectrum is almost entirely due to TFA and TFP.9.10

The ratio of the area of a TFP band (integration limits $2395-2295 \text{ cm}^{-1}$) to that of a TFA band (2100-1975 cm⁻¹) was used to monitor the product distribution. For initial TFCP pressures ranging from 0.4 to 8.5 Torr, pulse energies from 0.8 to 2 J, and percent conversions from 1% to 50%, the ratio of areas for the 22 experiments remained constant at 0.206 ± 0.009 as shown in Figure 2.

The amounts of TFA and TFP formed were directly proportional to the loss of TFCP; typical results are shown in Figure 3 for two experiments with an initial TFCP pressure of 4 Torr. The total pressure of sample 1 was also determined as a function of percent conversion and varied from an initial pressure of 7.60 Torr to 7.54 Torr after 80 pulses (0.8 J/pulse) which resulted in a 26% conversion. The pressure of sample 2 increased from an initial value of 7.95 Torr to 8.33 Torr after 80 pulses (5 J/pulse, 50% conversion).

The conversion per pulse increased markedly with an increase in initial TFCP pressure but decreased as the pressure of the products increased as illustrated in Figure 4. With unfocused radiation and an initial TFCP pressure of 0.2 Torr, there was no change in the spectrum after 1100 pulses, whereas with an initial pressure of 8 Torr, 29% of the TFCP was converted to TFA and TFP after a single 2-J pulse. For a unimolecular decomposition unaffected by collisions and with no back-reactions, the dissociation

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Figure 1. Absorbance spectra of TFCP (lower trace) and of the products which resulted from multiphoton excitation (upper trace); the spectrum of the remaining TFCP has been subtracted from the latter.



Figure 2. Integrated intensity of a TFP band (C=C str) divided by the intensity of a TFA band (C=C str) as a function of percent conversion of TFCP: O, collimated beam; Δ , convergent beam used for excitation.



Figure 3. Integrated intensity of an allene band $(2100-1975 \text{ cm}^{-1})$ as a function of TFCP pressure loss. The data shown are from two different experiments with an initial TFCP pressure of 4 Torr.

yield β would be given by $\ln (p/p_0) = n \ln (1 - \beta V_r)$, where p is the pressure of the reactant after n pulses and V_r is the ratio of the irradiated volume to the total volume of the cell.¹¹ However,



Figure 4. Percent conversion of TFCP as a function of the number of pulses (P34 line, 1.7 J/pulse). Initial TFCP pressure: □, 8 Torr; 0, 4 Torr.

the calculated value of βV_r for the isomerization of TFCP decreased rapidly as products were formed; with an initial pressure of 8 Torr, for example, βV_r was 0.29, 0.18, 0.14, 0.12, and 0.029 after 1, 2, 3, 4, and 24 pulses, respectively. Based on the area of the burn pattern on thermal paper, the first pulse caused nearly 100% conversion of the TFCP in the irradiated volume in the 2.54-cm-diameter cell. The initial extent of isomerization increased markedly with pressure; the directly observed or extrapolated values of βV_r after one pulse ranged from 0.0024 with $p_0 = 0.4$ Torr to 0.29 with $p_0 = 8$ Torr. No extensive studies of the reaction at higher pressures were performed, but the value of βV_r at 8.5 Torr (0.19) was lower than that at 8.0 Torr.

With an initial pressure of 2 Torr, 128 pulses of unfocused radiation resulted in 13% conversion, but the same irradiation of a sample containing 1.5 Torr of TFCP and 6.6 Torr of argon produced no change in the TFCP spectrum. In every case, the isomerization reaction did not consume more than about 50% of the initial TFCP. For example, 100 pulses of unfocused irradiation of a sample with an initial pressure of 8.1 Torr resulted in 40% of the TFCP isomerized to TFA and TFP; 1000 additional pulses resulted in a total of 50% loss of TFCP, but there was also a 4% loss of TFA and a 10% loss of TFP relative to the amounts present after 100 pulses. After isomerization of 42% of the TFCP in a sample with an initial pressure of 8.5 Torr, the CO_2 laser frequency was changed to 1039 cm⁻¹ (P28 line of the $00^{\circ}1-20^{\circ}0$ band) where TFA has a strong absorption band but TFCP does not. After 66 pulses (1.3 J each), no changes were observed in the infrared spectrum of the sample.

In addition to the production of TFA and TFP, small amounts of TFE were formed after irradiation; the pressure of the TFE produced was about 5% of the loss of TFCP pressure for sample 1. However, the TFE production was not linearly related to TFCP loss. In the case cited above in which argon inhibited the loss of any TFCP after 128 pulses, no TFA or TFP was detected but 0.046 Torr of TFE was produced. The second TFCP sample contained 6 times as much of an impurity as the first sample, and subtraction of the TFCP spectrum of the first sample from that of the second yielded the impurity spectrum.¹² After irradiation of the second sample, the spectra of TFCP, TFA, TFP, and the impurity were subtracted from the spectrum of the mixture. The remaining features were due to TFE and trans-dichlorodifluoroethene.⁹ On the basis of the infrared spectrum of the impurity and the products of its decomposition, the impurity was identified as DCTFCP, the precursor in the synthesis of TFCP.

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In each case in which it was observable in the spectrum, the initial fraction of DCTFCP lost after irradiation was greater than that of TFCP. The thermal decomposition of DCTFCP at 3 atm also produced C₂Cl₂F₂ and products which resulted from :CF₂ elimination.1b

Discussion

The three modes of excitation most likely to occur under the conditions of our experiments are direct multiphoton excitation, V-V energy transfer, and V-T transfer followed by thermal reactions; in some cases all three modes may contribute to the decomposition reactions.¹⁴ The dependence of the isomerization vield per pulse on the pressure of TFCP, the products, and/or a buffer gas (argon) suggests that the process is collision-assisted. The very high conversion per pulse at higher pressures and the inhibition of the reaction by argon or the products of the reaction would seem to rule out rotational relaxation or pressure broadening of the absorption line as sources of the observed pressure dependence.¹⁵ Intermolecular V-V or V-T/R transfer as a result of collisions of excited TFCP with cold TFCP, TFA or TFP, or a buffer gas would be expected to cause a decrease in conversion per pulse with increasing pressure,^{11,16} but energy pooling to reach a dissociation channel as a result of the collision of two molecules at an intermediate level of excitation is a possibility.¹

As discussed above, the extent of isomerization of perfluorocyclobutene to the butadiene was increased when He was used as a buffer gas, presumably because V-T transfer from the excited butadiene prevented re-formation of the cyclobutene.⁶ The latter isomerization is 50 kJ/mol endothermic.¹⁸ The thermochemistry of the TFCP to TFA or TFP reaction is not known, but for any unimolecular isomerization reaction the product yield should increase with pressure.19,20

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One might also expect that changes in the fluence or pressure might alter the ratio of the products formed since the average energy of reacting molecules is changing, and it would be coincidental for TFA and TFP to have the same vibrational frequency patterns and heats of formation. However, we found the ratio of TFP to TFA to be the same at all fluence and pressure conditions we used, and there is no evidence for any fragmentation reactions (nor any other unexplained loss of TFCP). The observed distribution of products and the lack of fragmentation do not support a unimolecular process after the initial excitation.

An energy-pooling collision to yield one molecule with sufficient energy for ring opening might be invoked as an excitation mechanism; this would satisfy the observed pressure dependence. However, the constraints for the simple one-step unimolecular step would still be imposed.

Another possible pathway which satisfies the pressure dependence would involve the collision of two TFCP molecules (either one or both supplying sufficient energy for reaction); during the collision a fluorine atom from each molecule is transferred to the other. The vibrational energy content in either TFCP molecule would be less than the threshold required to form the biradical but sufficient to promote the transfer. The TFA/TFP ratio would be invariant with fluence and pressure; however, the rate constant would show an energy dependence. This pathway would account for the difference between collisions of TFCP with argon, TFA, TFP, and TFCP; the first three partners would remove the required vibrational energy from TFCP. Thus, as reaction proceeds the initial excitation is collisionally transferred to TFA and TFP instead of being directed to the reaction coordinate as is the case for collision with TFCP. At this time there is not sufficient evidence to establish this pathway, but the high conversion at low fluences and the pressure dependence are indicators that this may be the dominant path. We are in the process of designing future experiments that will provide information to determine the mechanism for this reaction.

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