Kasai et al.[20] give evidence for monoligand π-type complexes generated with M = Cu or Au, but a "bona fide" complex cannot be identified with M = Ag; the diligand complexes are observed with the three metals. In addition, McIntosh et al.[8] have observed the optical spectra of the three monoligand complexes CuC_2H_4, AgC_2H_4, and AuC_2H_4 while they found that only copper forms di- and triligand complexes. In summary, (i) the case of AgC_2H_4 is of particular interest because it does not appear in ESR observations, but its optical spectrum has been identified and presents great differences with respect to optical spectra of CuC_2H_4 and AuC_2H_4 and (ii) the three diligand complexes are identified by ESR experiments but not by UV–visible investigations. Further theoretical investigations would give useful arguments for the interpretation of all these observations.

In addition, our calculations have shown that electrons of the 3d closed shell of copper are not directly involved in the metal–olefin bonding or in the optical spectrum. This will make it possible

to treat the metal atom as a one-electron system including the nd^{10} electrons in the atomic core. Test calculations taking into account the polarization of the d^{10} manifold through a perturbative method have been carried out on copper-containing molecules such as Cu_2[39–41] and CuOH[42] and have led to satisfactory results.

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LASER CHEMISTRY, MOLECULAR DYNAMICS, AND ENERGY TRANSFER

Infrared Multiphoton-Induced Concerted :CF₂ Elimination in Octafluorocyclopentene by a Pulsed CO₂ Laser

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On infrared multiphoton excitation, octafluorocyclopentene (OFCP) undergoes a ring-opening reaction to give difluorocarbene and hexafluorobutadiene as unstable primary products which undergo further reactions; the former dimerizes to tetrafluoroethylene, and the latter isomerizes to its thermodynamically stable cyclic isomer. The multiphoton dissociation (MPD) yield of OFCP shows a strong fluence dependence, with a threshold of 0.3 J/cm² for the 10R(32) line of the CO_2 laser for inducing the reaction. Two characteristic peaks in the MPD spectra have been observed, both red-shifted from the ν_{20} ring deformation mode absorption peak of OFCP. Increase in pressure of OFCP or foreign gas addition has shown to deteriorate the MPD yield.
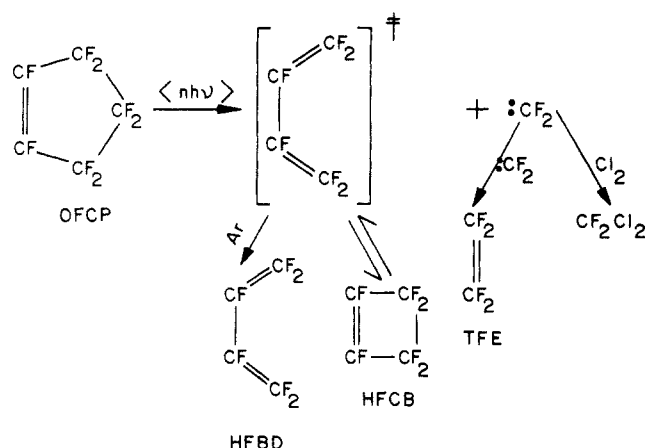
Introduction

Infrared multiphoton excitation (IRMPE) is a unique technique available for inducing unimolecular reaction[1] from the ground electronic state under collision-free conditions. In this process the parent molecule absorbs many photons in rapid succession, until the energy-dependent reaction rate becomes comparable to the optical pumping rate. A lifetime limited excitation level which has a fairly large amount of excess energy over and above the molecular threshold energy for decomposition is reached by this means. If the threshold energy of the reaction E_{th} and the reaction enthalpy ΔH are comparable in size, then the amount of energy available for partitioning between product translation and internal degrees of freedom will be fairly small. Otherwise, for a molecule

dissociating from the highly energized level E^*, as in the case of IR laser irradiation, $(E^* - \Delta H)$ amount of excess energy will be available for partitioning between the products. Further, if the reaction mechanism involves concerted processes in which bonds are broken and formed simultaneously, the partitioning of energy will depend on the substantial potential energy barrier in the exit channel and the structure of the transition state. If the bonds which are to be broken are greatly extended in the transition state, significant vibrational excitation in the products may be expected. In the six-center C_2F_4 elimination from perfluorocyclohexene,[2] reported earlier by us, the nascent hexafluorobutadiene (HFBD) formed was in such a highly vibrational excited state, due to the large exit barrier in the retro-Diels–Alder dissociation process, that it undergoes a prompt isomerization reaction to hexafluorocyclobutene (HFCB), the cyclic isomer. The exit barrier results from the C—C=C—C· in the reactant converting to a conjugated C=C—C=C system in the primary product.

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SCHEME I

Figure 1. (a) Infrared spectra of OFCP (—). (b) IR spectra of the mixture of OFCP and products (---) formed after irradiation at the 10R(32) CO_2 laser line.

With a view to extend this work to other homologues, octafluorocyclopentene (OFCP) was studied, and the results are reported in this paper. Previous to our studies, both pyrolysis[3] and IR laser photolysis[4] of cyclopentene were studied, the latter employing laser frequencies corresponding to the CH_2 rocking mode. Molecular hydrogen elimination was found to be the principal reaction channel. However, thermolysis of OFCP gave, among other products, perfluorinated 1-methylcyclopentene, 1,2-dimethylcyclopentene, and mesitylene.[5] In contrast to the above results, our present investigation, employing IR laser frequencies corresponding to ring deformation mode of OFCP, gave tetrafluoroethylene (TFE) and hexafluorocyclobutene (HFCB) as end products which could be attributed to a new channel for the primary decomposition of OFCP.

The primary decomposition could be a five-center ring-opening process leading to difluorocarbene ($:CF_2$) and hexafluorobutadiene (HFBD) which is followed by isomerization of the vibrationally excited HFBD to the thermodynamically more stable HFCB. Addition of argon as buffer gas arrested the isomerization reaction and facilitated the identification of the initial product HFBD. The $:CF_2$ radicals, generated as the primary product, recombine to give tetrafluoroethylene (TFE). However, in the presence of a sizable amount of scavenger such as chlorine during IRMPD of OFCP, CF_2Cl_2 was obtained as a product with no $CF_2{=}CF_2$ formed, as detected by gas chromatography. It appears that the primary product $:CF_2$ is transformed into CF_2Cl_2 by reactive collisions with Cl_2. The observed reactions are given in Scheme I.

Experimental Section

A grating-tuned multimode Lumonics-103 TEA CO_2 laser was used. A typical pulse consisted of a 100-ns spike followed by a 2-μs tail. About two-thirds of the laser pulse energy was contained in the spike, as measured by a photon drag detector (Rofin Model 7415). A spectrum analyzer supplied by Optical Engineering Co. was used for identifying the tuned laser frequency. A factory-calibrated Lumonics-20D pyroelectric detector was used for energy measurements. The energy of the incident beam was attenuated by introducing polyethylene films of various thicknesses. Two types of irradiation geometry were employed. In the first type the CO_2 laser beam was condensed by a long focal length ($f =$ 100 cm) BaF_2 lens coated with an antireflection material, and a 5 cm optical path length stainless steel cell containing the sample was positioned intermediate between the lens and focal spot. Under these conditions a nearly parallel beam passes through the experimental sample, the variation of the laser fluence within the cell being about 5% when the cell is positioned midway. Depending on the position of the cell, the average fluence can be varied over a wide range. The stainless steel cell employed for the nearly
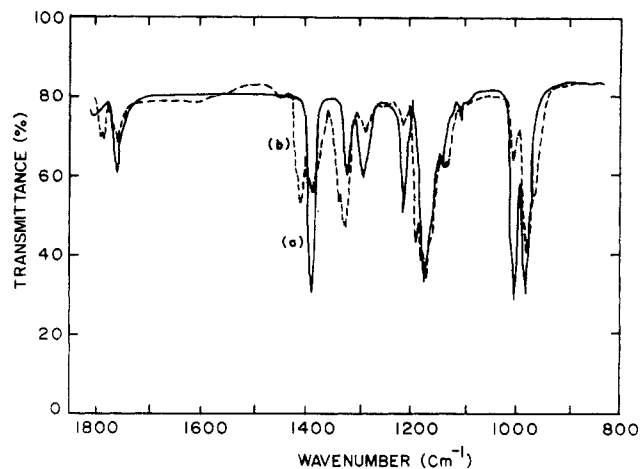
uniform fluence experiments has a volume of about 35 cm^3 and was provided with end KCl windows. The cross section of the laser beam was determined from the burn patterns on a heat-sensitive paper held at a position corresponding to the center of the cell. In the second arrangement, the laser beam was focused with a short focal length ($f =$ 10 cm) antireflection coated BaF_2 lens, the focal spot falling at midpoint within a stainless steel cell of 45.5-cm^3 volume. Very high fluences corresponding to focal fluence are accessible for sample irradiation by this dog bone type of geometry. Pulse energy measurements with and without either type of empty stainless steel cell enabled corrections for window losses and accurate evaluation of laser fluences seen by the sample. A conventional greaseless glass vacuum system was used for sample preparation. Prior to each run the vessel was filled with the reactant gas, evacuated, and then refilled to the desired pressure. All the fluoro compounds used in this work were supplied by PCR Research Chemicals Inc. (Gainesville, FL). An indigenously built gas chromatograph[2] with a flame ionization detector was employed for gas analysis. The reactant and product gases were analyzed by using two 5-ft-long columns connected in series and filled with 10% dodecyl phthalate and 20% diethyl glycol succinate, respectively. With nitrogen as carrier gas, this combination of columns gave sharp and well-separated peaks for C_2F_4, C_4F_6, and c-C_5F_8. Gas chromatographic analysis of these gases, OFCP, C_2F_4, C_4F_6, and CF_2Cl_2 verified their purity to be better than 99%. Research grade chlorine and analytical reagent grade bromine were obtained respectively from Matheson and Mallinckrodt. The progress of the laser-induced reaction was monitored with a Perkin-Elmer Model 577 infrared grating spectrophotometer, at the OFCP absorption at 1008 cm^{-1} ($\epsilon =$ 4.46 $\times$ 10^{-2} cm^{-1} $Torr^{-1}$).

Results

The infrared absorption spectrum of OFCP between 900 and 1800 cm^{-1}, shown in Figure 1a, shows two absorption bands[6] at 1008 cm^{-1} (ν_5 mode: skeletal deformation) and 985 cm^{-1} (ν_{20} mode: skeletal deformation), corresponding to the output of the CO_2 laser. Initial studies using 0.1 Torr of sample showed that unfocused irradiation at 983 cm^{-1} R(32), corresponding to $00^01{-}10^00$ CO_2 laser transition, results in efficient decomposition of OFCP. For this preliminary study, a 50-cm-long Pyrex irradiation cell of 630-cm^3 volume was employed. After about 100 pulses of laser irradiation, the contents of this large cell were transferred to a small 5 cm path length cell having 35-cm^3 volume, and the infrared spectrum of the gas mixture was taken and is shown in Figure 1b. The absorption peaks at 980 and 985 cm^{-1} together with the peak at 1418 cm^{-1} identify the HFCB product. The absorption at 1186, 1332, and 1342 cm^{-1} was due to TFE. However, the IR absorption due to hexafluorobutadiene (HFBD)

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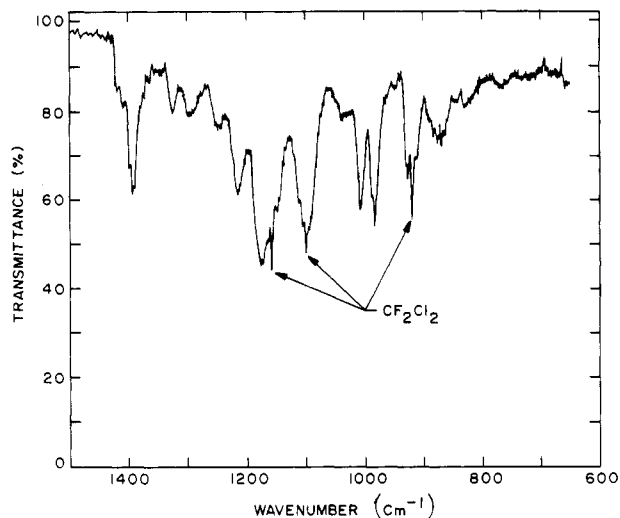(6) Harris, W. C.; Longshore, C. T. *J. Mol. Struct.* **1973**, *16*, 187.

Figure 2. Infrared spectra after irradiation of a mixture of OFCP and Cl$_2$ at the same 10R(32) CO$_2$ laser line.

at 972, 1330, and 1766 cm^{-1} was not as well developed as the absorption due to its cyclic analogue. A little absorption at 1766 cm^{-1} indicated that less than 5% butadiene was present in the end products. However, when the irradiation was carried out in the presence of added argon, all the absorption peaks typical of butadiene grew at the expense of those typical of cyclobutene. The formation of perfluorinated ethylene and cyclobutene as products, in the irradiation of neat OFCP, was further confirmed by gas chromatographic analysis of the contents of the cell after irradiation. No visible light emission accompanied the irradiation. While laser frequencies nearly resonant with the OFCP ν_{20} absorption were effective, no photodecomposition was observed at laser frequencies far away from the absorption band which lead us to conclude that the multiphoton decomposition process rather than dielectric breakdown was responsible for the product formation.

Effect of Additives. Infrared multiphoton dissociation of OFCP in the presence of chlorine gave CF$_2$Cl$_2$ as product. No CF$_2$=CF$_2$ was observed. Figure 2 shows absorption peaks at 1167, 1098, and 923 cm^{-1} due to CF$_2$Cl$_2$ and no absorption corresponding to TFE. As yet, another radical trap, C$_2$F$_4$, was deliberately added to OFCP, and the mixture was irradiated with the CO$_2$ laser at 982 cm^{-1}. The C$_2$F$_4$ infrared peaks had become more intense, and peaks due to perfluorocyclobutene appeared in the irradiated sample. No additional products which could be attributed to C$_3$ or C$_6$ fluorocarbons could be detected.

Dissociation Yield as a Function of Laser Frequency. The decomposition of OFCP as a function of the number of laser pulses, n, was studied, and the results followed the relation [OFCP] = [OFCP]$_0$ exp($-\alpha n$) from which α, the dissociation yield per pulse, was evaluated. A series of experiments were carried out at different laser frequencies close to the ν_{20} mode of OFCP. By using f = 10 cm BaF$_2$ lens for focusing and suitably attenuating the laser beam, we maintained a uniform input energy of 240 mJ/pulse within the sample cell. The IR multiphoton dissociation spectrum so obtained is shown in Figure 3a where α, the dissociation yield per pulse, was plotted as a function of laser frequency. Comparison of IRMPD spectra with the IR absorption spectra of OFCP (Figure 3a, b) shows that the most efficient laser frequencies for inducing IRMPD are red-shifted with respect to the two absorption maxima by as much as 10–20 cm^{-1}. It is of interest to note that the higher frequency MPD peak at 982 cm^{-1} is only 3 cm^{-1} red-shifted from the lower frequency ν_{20} absorption peak at 985 cm^{-1}. The other MPD peak is as much as 13 cm^{-1} red-shifted and appears at 972 cm^{-1}. At this frequency the OFCP molecule has a relatively low absorption, which suggests that the probability for multiphoton absorption is not derived primarily from the oscillator strength for the one-photon transition. It appears that the structure in the quasi-continuum might be responsible for such a characteristic off-resonant IRMPD spectrum.
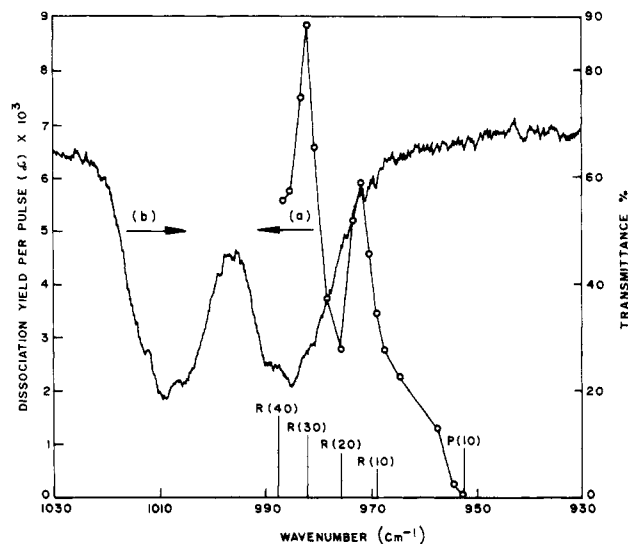

Figure 3. (a) Multiphoton dissociation spectra of OFCP, i.e., plot of dissociation yield per pulse (α) vs. laser frequency used for the irradiation of OFCP in the focused condition. The input energy for all the laser lines was 240 mJ/pulse. (b) IR spectra of 1 Torr of OFCP near the CO$_2$ laser output region at a resolution of 0.4 cm^{-1}.
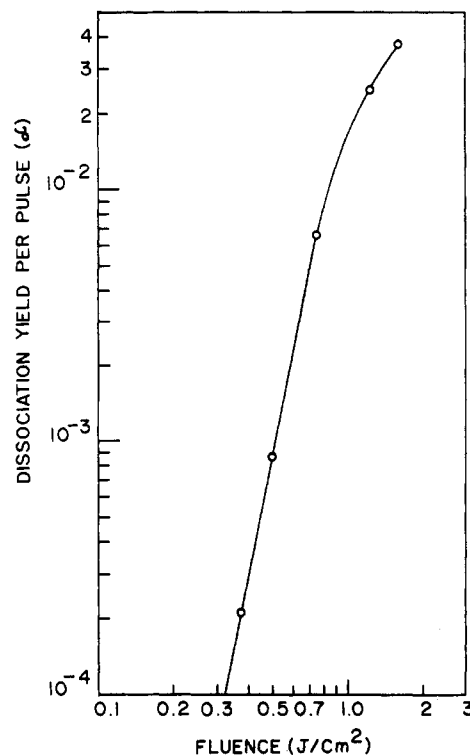

Figure 4. Dissociation yield per pulse (α) in the MPD of 0.4 Torr of OFCP vs. energy fluence (J/cm^2) at the 10R(32) CO$_2$ laser unfocused condition.

The MPD bands are rather narrow (fwhm = 7 cm^{-1}) as compared to the ν_{20} absorption (fwhm = 18 cm^{-1}) at 985 cm^{-1}. Further experiments to obtain a correlation between the MPD and IR spectrum are in progress using optoacoustic and laser-induced fluorescence techniques. It is possible that unresolved P, Q, and R components in the ν_{20} mode may be responsible for the observed narrow MPD bands, any structure in the quasi-continuum accentuating the MPD process at those frequencies. It is pertinent to recall that, in the MPD of cyclopentene, the laser lines corresponding to the dissociation yield maxima fall on both sides of the Q branch of the IR absorption band; the dissociation yield is minimum at the Q maximum absorption frequency.

Dependence on Fluence. The fluence dependence of α for R(32) laser frequency irradiation of 0.4 Torr of neat OFCP is shown in Figure 4. There is an apparent threshold for the dissociation
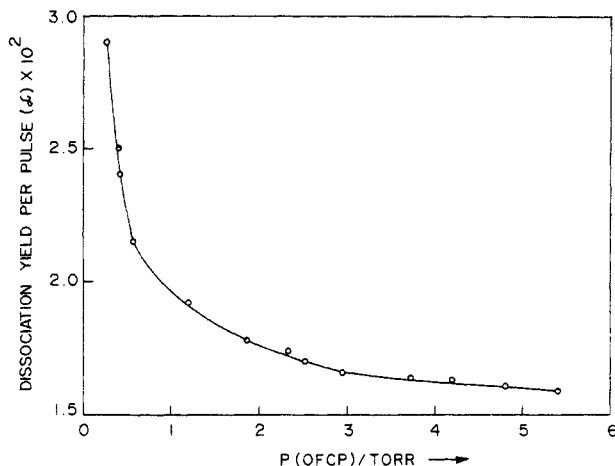
Figure 5. Plot of α vs. pressure of OFCP with the 10R(32) laser line for irradiation at an energy fluence of 1.25 J/cm².

of OFCP at $\phi \sim 0.3$ J/cm². The steep rise of α with fluence at low dissociation yields follows a power law for a higher order multiphoton process $\alpha \sim \phi^n$, the order of the multiphoton process n being 4.8 for these experiments. The dependence of α on fluence tends to be less pronounced at higher fluence level.

Dependence on Substrate Pressure. Figure 5 shows that an increase in the substrate OFCP pressure for the same laser fluence of 1.25 J/cm² decreases the dissociation yield per pulse. The product distribution, ho\weer, remains the same, i.e., C_2F_4 and c-C_4F_6 being the final products throughout the range of OFCP pressures studied.

Dependence on Added Foreign Gas. Addition of different buffer gases to a fixed 0.4-Torr partial pressure of OFCP adversely affected the compound's decomposition. Plots of ln (α) vs. quencher pressures yielded straight lines as shown in Figure 6. It is apparent that SF_6 is a more efficient quencher than argon. From the relative slopes of the two plots in Figure 6, the collisional deactivation efficiency of argon is about 0.1 times that of SF_6. It is of interest to note that while argon stabilizes HFBD as the end product, SF_6 still gives c-C_4F_6 and C_2F_4 as final products. It appears therefore that collisions with large polyatomic molecules, SF_6/OFCP, quench only the overall decomposition yield, α, but do not suppress the isomerization reaction HFBD† → c-C_4F_6.

Discussion

The above results clearly show that, following IR laser irradiation, perfluorocyclopentene undergoes primary decomposition into :CF_2 and C_4F_6† species. Both the primary products are unstable and undergo further reactions. The :CF_2 dimerizes to give C_2F_4. When the nascent C_4F_6† is formed with an internal energy above the isomerization threshold of hexafluorobutadiene and hexafluorocyclobutene, the structure of the nascent C_4F_6† would not be characteristic of either of the isomers. By radiative loss and collisional energy transfer, the excited C_4F_6† acquires the structure of one of the isomers in its ground state. It has been demonstrated[7] by the time-resolved infrared fluorescence technique that the fluorescence spectra of HFBD and HFCB do overlap for the first microsecond after it is formed in the excited state but after several hundred microseconds they start to separate, each of them moving toward the respective isomer. It is possible that a five-center ring-opening mechanism is responsible for the primary yields which were obtained in stoichiometric proportion. Such a process is likely to follow Woodward–Hoffmann rules for pericyclic reactions.[8] A similar five-center concerted ring-opening reaction has been reported in the literature,[9] IR laser irradiation essentially providing a fast vibrational excitation in the ground
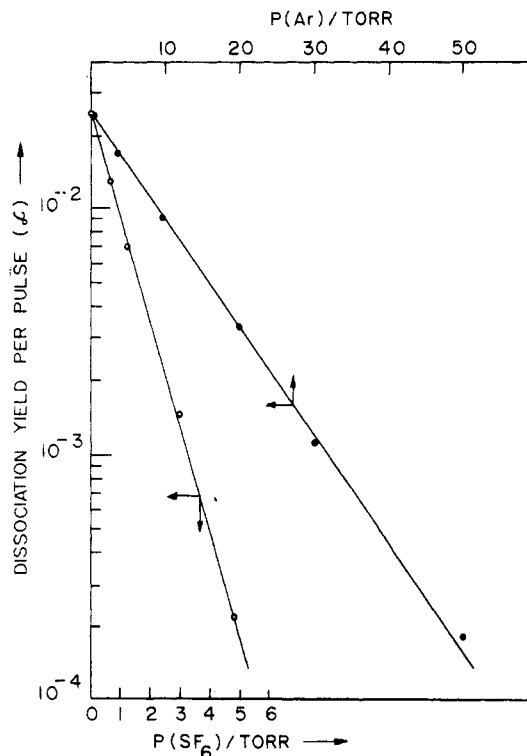

Figure 6. Dissociation yield per pulse (α) in the MPD of OFCP as a function of added buffer gas pressure (SF_6 and Ar) at a laser energy fluence of 1.25 J/cm².

electronic state of the molecule, and unimolecular decomposition occurs before thermalization of the internal energy content of the molecule. In concerted processes the simultaneous bond breaking and formation results in an exit channel barrier. In the case of c-C_5F_8, the exit energy barrier may be considered as due to rearrangement of bonds as the reaction proceeds from transition state to the products. A fraction of the exit channel energy is likely to be converted into the internal energy of the products.[10] In the MPD reaction it has been observed that most of the excess energy above the unimolecular dissociation threshold remains as internal energy of the products.[11] This total internal energy will be distributed between the :CF_2 and C_4F_6 fragments. The vibrational degrees of freedom are mostly responsible for acquiring this energy. C_4F_6 species will have ≥90% of the internal energy released in products, if statistical partitioning of the energy is assumed.[12] As a result, the nascent HFBD has a large amount of internal energy associated with it. This enables the molecule to undergo prompt isomerization

$$CF_2{=}CF{-}CF{=}CF_2 \rightarrow \text{c-}C_4F_6$$
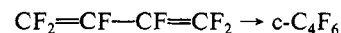
to the thermodynamically more stable cyclic end product. The nature of the initial MPD product HFBD could therefore be obtained only in the presence of an appreciable pressure of added buffer gas argon which removes the excess energy and stabilizes the primary product.[13] Thus, two consecutive Woodward–Hoffmann type pericyclic reactions occur on pulsed laser irradiation of OFCP:

$$\text{OFCP} \rightarrow \text{:}CF_2 + \text{HFBD}^\dagger$$

$$\text{HFBD}^\dagger \rightarrow \text{HFCB}$$
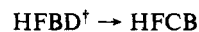
the isomerization taking place after the laser-induced primary

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reaction. Similar consecutive pericyclic reactions were noticed earlier with c-C$_6$F$_{10}$.[2]

The formation of C$_2$F$_4$ observed in the neat IRMPD of OFCP can be explained by an initial difluorocarbene formation and its subsequent recombination

$$2\ddot{C}F_2 \rightarrow C_2F_4$$
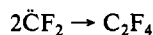
The radical recombination rate constant for :CF$_2$ was reported[14] to be 2.2 × 10^{10} cm^3/(mol s), whereas the rate constant for the reaction of :CF$_2$ with C$_2$F$_4$ has been reported[15] to be less than 3 × 10^6 cm^3/(mol s). In a recent paper by Hack and Langel[16] it has been argued that :CF$_2$ is surprisingly unreactive, probably more similar to carbon monoxide than to true free radicals. This is in conformity with our present experiments where C$_3$ products as well as the :CF$_2$ adduct with the parent molecule OFCP could not be determined even when 4 Torr of C$_2$F$_4$ was added with 1.5 Torr of OFCP before irradiation.

The pressure dependence of the total yield is a direct indication of the relative importance of collision-assisted vis-à-vis collision-deactivated processes. Two possible collision-assisted effects, both of which could increase the yield by increasing the amount of energy absorbed, are pressure broadening of the absorption line and rotational hole filling.[1a,17] Figure 6 shows that α decreases monotonically with pressure of bath gases, whereas if the above-mentioned collisional processes were operating, α should have increased initially. Collision-assisted rotational hole-filling mechanisms are of importance for small molecules and help in increasing the number of molecules which are excited effectively by the radiation (i.e., an increase in the so-called q factor). The q factor indicates the fraction of molecules excited by the radiation. As the buffer gas pressure increases, the q factor initially increases and reaches a saturation, $q = 1$. At $P > P_{q=1}$, the vibrational deactivation processes become competitive with radiative excitation of molecules. Any increase in dissociation yield, due to rotational relaxation, ceases at some pressure $P_{q=1}$, and thus for $P > P_{q=1}$ the dissociation yield has to fall with rising pressure. In the case of OFCP, the q factor is apparently close to one even in the collisionless case; that is to say, $P_{q=1} \sim 0$. Another possible collisional effect is energy pooling of two intermediate energized molecules.[18] The result in Figure 5 shows no enhancement in α with the increase in OFCP pressure. This rules out vibrational energy pooling as a bottleneck for this laser-induced decomposition.

From the linear relationship of log (α) vs. pressure in Figure 6, we consider that initially a fraction f of the OFCP molecules exposed to laser irradiation absorb sufficient energy for dissociation. They either would dissociate with a finite energy-dependent rate constant, $k(E)$, or are deactivated by collisions with the buffer gas. We may further consider that the competitive multiphoton excitation and collision-induced intermolecular vibrational relaxation processes would lead to a broader distribution of vibrational energy and a lowered mean rate constant $\langle k \rangle$ for unimolecular decomposition of OFCP compared to narrower higher vibrational energy distribution and higher decomposition rate constant k_0 under collisionless conditions. Such a situation prevails under isofluence, i.e., nearly parallel beam irradiation geometry maintained in the present work. The mean rate constant $\langle k \rangle$ is an average value over the range of vibrational energy distribution

$$\langle k \rangle = \int_{E_0} k(E) f(E) \, dE \qquad (1)$$

the vibrational energy distribution function $f(E)$ being determined by MPE and collision frequency. The latter is given by $\omega\beta P$, where ω is the Lennard-Jones collision frequency, β is the collision deactivation efficiency of the quencher, and P is the pressure of

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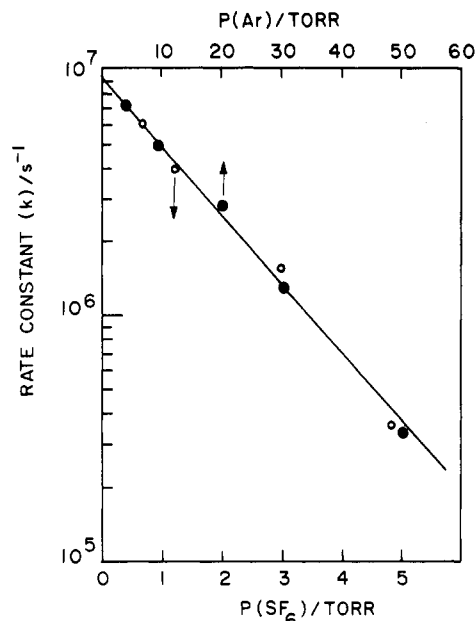

Figure 7. Multiphoton dissociation rate constant (k) as a function of buffer gas pressure of SF$_6$ (O) and Ar (●).

the added quencher. The dissociation yield, α, per pulse is then equal to f times the branching ratio $\langle k \rangle / (\langle k \rangle + \omega\beta P)$, i.e.

$$\alpha = \frac{\langle k \rangle}{\langle k \rangle + \omega\beta P} f \qquad (2)$$

where $\omega = \sigma^2 (8\pi RT/\mu)^{1/2}$; considering $\sigma(c\text{-}C_5F_8) = 6.0$ Å and $\sigma(SF_6) = 2$ Å, ω has been calculated to be 8.6×10^6 s^{-1} torr^{-1}. In the above equation, as $P \rightarrow 0$, $\alpha \rightarrow f$ giving under collisionless conditions $\alpha_0 = f$, the latter being the fraction of molecules excited to dissociation levels. At not too high pressures of added buffer gas, we may consider that the same fraction $f = \alpha_0$ undergoes excitation to vibrational energy levels above the threshold for dissociation, except that these energy levels are somewhat lower than those obtainable under collisionless conditions.

Plots of $1/\alpha$ vs. pressure gave nonlinear curves, justifying our view that $\langle k \rangle$ is not constant but a dependent function of buffer gas pressures which governs the vibrational energy distribution and interalia the OFCP dissociation. From relation 2, taking $f = \alpha_0$, we have computed the mean rate constants $\langle k \rangle$ at various quencher pressures employing our experimental results. The plot of ln (k) vs. added pressure is given in Figure 7, which shows that the mean rate constant decreases as a function of added gas pressure. Extrapolation of the plot to zero added gas pressure gives an indication of the rate constant, $k_0 \sim 9 \times 10^6$ s^{-1}, for dissociation of OFCP under collisionless conditions.

That such a qualitative viewpoint is essentially correct is further borne out by the fact that the values of $\langle k \rangle$ computed for the experimental values of both SF$_6$ and Ar as additives with appropriate normalization of collision efficiencies, viz., $\beta_C(Ar)/\beta_C(SF_6) \sim 0.1$ (on the basis of Figure 6), fall on the same line in Figure 7. In other words, the monoatomic Ar requires 10 times more collisions with laser-excited OFCP to give the same vibrational energy distribution as that could be obtained with the polyatomic SF$_6$ as collision partner.

The multiphoton dissociation spectra shown in Figure 3 consist of two characteristic peaks both red-shifted from the irradiation mode ν_{20}. In the popular quasi-continuum model[19] it is assumed that in the region of high density of states no selection rule can be strict enough to suppress all the transitions to these states; therefore, the molecule will always have a transition probability for resonant photon absorption despite the anharmonicity factors at higher vibrational levels. Nevertheless, it has been argued that some resonance characteristics, with high transition probabilities,

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may still exist even at high levels of excitation when the density of states is exceedingly large. We estimate that the density of states of OFCP in the ground state at 300 K is as high as 148/cm^{-1}. At this closely spaced vibrational levels suitable infrared-active combination modes and possibly overtones of some fundamentals may come into resonance with the laser photon frequency at high excitation levels. As a result, structure in the quasi-continuum could become well-defined and observed as in Figure 3. It has recently been reported[20] that the absorption spectra of highly excited state molecular ions of energies of only 1000 cm^{-1} below dissociation are not much wider than the ground-state absorption.

Conclusions

In summary, a novel five-center ring-opening reaction in oc-

tafluorocyclopentene (OFCP) to generate difluorocarbene and hexafluorobutadiene as primary products has been demonstrated by multiphoton absorption of IR laser by OFCP in its ring deformation mode. The primary products were found to undergo further reaction in situ. The :CF$_2$ generated C$_2$F$_4$ by recombination reaction whereas C$_4$F$_6$ isomerized to c-C$_4$F$_6$ by electrocyclization reaction. The formation of :CF$_2$ as a primary product was established by the characterization of CF$_2$Cl$_2$ and no C$_2$F$_4$ as end product when irradiation took place in the presence of Cl$_2$.

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248-nm Photolysis of Tricarbonylnitrosylcobalt[1]

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Laser-based time-resolved infrared absorption spectroscopy has been applied to the study of the 248-nm photolysis of the *psuedo*-nickel carbonyl, tricarbonylnitrosylcobalt, in the gas phase. Co(CO)$_3$NO dissociates by a series of sequential ligand eliminations to give predominantly CoCO. This species reacts back with parent Co(CO)$_3$NO with a gas kinetic rate constant of $(6.4 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} to form a binuclear species, [Co$_2$(CO)$_4$NO], of unknown structure. Added CO results in the formation of Co(CO)$_3$ and finally Co(CO)$_4$. The rate constant for the reactions of CO with Co(CO) is $(6.2 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} which is also a lower limit for the rates of reaction of CO with Co(CO)$_2$ and Co(CO)$_3$. This behavior shows marked similarity with recent work on other carbonyls and begins to establish a general pattern for metal carbonyl photolysis.

Introduction

Transition-metal carbonyl photochemistry continues to be of major interest due to the photocatalytic properties of metal carbonyls. The role of photogenerated, coordinatively unsaturated transient species as active catalytic agents is well-established in solution[4-7] and has also recently been demonstrated in the gas phase.[8-10] The study of these species has been achieved through trapping in low-temperature matrices,[11] while information on their reactivity in solution[4-7] and in the gas phase[9,10,12] has come from indirect chemical trapping and product yield experiments. An important recent development is the application of time-resolved spectroscopic techniques to monitor these coordinatively unsaturated species directly, under more relevant reaction conditions.

Visible absorption studies of the photodissociation of Cr(CO)$_6$ and Mn$_2$(CO)$_{10}$ have been carried out on the nanosecond and picosecond time scales,[13-15] and time-resolved infrared absorption techniques have been applied to several systems.[16-24]

Although less developed than visible flash photolysis techniques, time-resolved infrared absorption techniques are attractive because they are capable of yielding both structural and kinetic information. Their power is evident in recent studies on the gas-phase photodissociation of Fe(CO)$_5$[16,17] and Cr(CO)$_6$[18-20] and on the solution-phase photodissociation of M(CO)$_6$ (M = Cr, Mo, W), Mn$_2$(CO)$_{10}$, FeCO$_5$,[21-23] and [(Cp)Fe(CO)$_2$]$_2$.[24] Here we present the results of such a study on the gas-phase photolysis of the

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