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Efficient $:CF_2$ Generation by IR Multiphoton Dissociation; Time Resolved Observation of Infrared Chemiluminescence from the $:CF_2+O_2\rightarrow COF_2+O$ Reaction

Pradyot Kumar CHOWDHURY
Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India

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IR multiphoton dissociation of Octafluorocyclopentene is used as an efficient means for the generation of $:CF_2$. Time resolved infrared chemiluminescence has been observed from the reaction of ground state $:CF_2$ ($\tilde{X}\ ^1A_1$) radicals with molecular oxygen, generating COF_2 as a product. IR emission observed around 5 μm region has been assigned to ν_1 and $2\nu_2$ modes of COF_2. The kinetic measurements of the reaction as a function of oxygen pressure suggest a rate constant to be 5×10^{11} $cm^3\ mol^{-1}\ s^{-1}$, which corresponds to a $:CF_2$ temperature of $\leq$3650 K.

Infrared multiphoton dissociation (IRMPD) has been established as an useful technique for the generation of reactive radicals in the gas phase. In recent papers,[1,2] a few novel routes of dissociation from the ground electronic state have been observed in the infrared multiphoton excitation (IRMPE) of polyatomic molecules. In the process of infrared multiphoton excitation the parent molecule absorbs many photons in rapid succession, until the energy dependent dissociation rate becomes comparable to the optical pumping rate.[3,4] The competitive dissociation rate determines the average lifetime of the excited molecules which dissociate before absorbing a further IR photon. This lifetime limited excitation level which has a fairly large amount of excess energy, over and above the molecular threshold energy for dissociation, is reached by this means. A molecule dissociating from such highly energized level E^*, $(E^*-\Delta H)$ amount of excess energy will be available for partitioning between the products degrees of freedom, where ΔH is the reaction enthalpy.

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 five center $:CF_2$ elimination from octafluorocyclopentene, the nascent hexafluorobutadiene (HFBD) has been formed in such highly vibrational excited state, due to the large exit barrier in the dissociation process, that it undergoes a prompt isomerization reaction to hexafluorocyclobutene (HFCB), the cyclic isomer.[5] That the initial energy of the nascent primary HFBD is high has been probed by direct observation of about 50 nm red shift in the time resolved UV-spectra.[6] The exit barrier results from the $\cdot CF_2-CF=CF-CF_2\cdot$ biradical in the reactant converting to a conjugated $CF_2=CF-CF=CF_2$ system in the primary product. Nevertheless, some of the product energy will be distributed in favor of $:CF_2$ ($\tilde{X}\ ^1A_1$), the primary photoproduct, which may undergo addition reaction with a suitable reactive quencher. The quencher can be so chosen that the nascent product chemiluminescence be detected easily.

With a view to extend this work to find whether the energy partitioned in the $:CF_2$ ($\tilde{X}\ ^1A_1$) primary product is sufficient undergoing reaction with oxygen by surmounting a significant activation barrier, multiphoton dissociation of Octafluorocyclopentene (OFCP) was studied in presence of oxygen and the results are reported in this paper. The real time detection of infrared emission from the nascent excited COF_2 in the 5.5 μm wavelength range are made to probe the rate of its formation in the $:CF_2+O_2$ reaction. The same $:CF_2$ ($\tilde{X}\ ^1A_1$) is also produced in the stratosphere by the photodissociation of chlorofluoromethane by sunlight and therefore is an interesting species with respect to atmospheric photochemistry.

Experimental

The experiments were performed with a static system at room temperature. The conventional set-up which includes a photolyzing laser, a stainless steel cell and an infrared detector with appropriate signal processing system is shown in Fig. 1.

The stainless steel cell used in this IR chemiluminescence

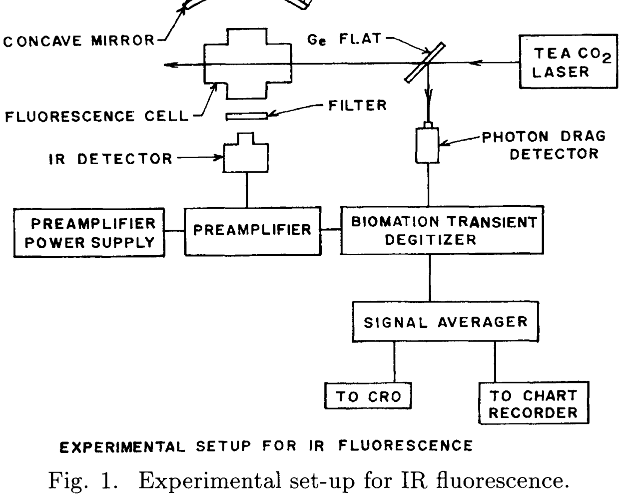

Fig. 1. Experimental set-up for IR fluorescence.

experiment has two orthogonal pairs of optical windows made of KCl. Radiation from a pulsed CO_2 laser (Lumonics model no. TEA 103-2) entered and exited through one pair of KCl windows. The IR emission was collected at right angles to the laser beam by another pair of KCl windows. A two inch diameter f/2 gold coated concave mirror was placed behind one of the KCl window for enhancing better collection to the detector placed in front of the other window. The radiation after appropriate filtering with band pass filters and cold gas cell was detected by an In–Sb detector (Judson Infrared Inc., J-10 D, Photovoltaic type) cooled at 77 K. The signals from the detector were amplified with a wide band amplifier (PAR Model-115) and digitized by a Biomation 8100 transient digitizer. The stored signal was transferred to a signal averager (Nicolet 1170) for averaging the measurements. The output of the averager was either displayed on an oscilloscope and photographed or plotted using a Y–T chart recorder. The laser pulse picked up with the photon drag detector (Rofin model 7415) was used as a trigger for the transient digitizer. The overall time response of the system was about 1 μs but it was found to be susceptible to electrical interference from the laser. Therefore, the whole apparatus, apart from the laser was contained in a Faraday cage to minimize electrical interference.

An unfocussed and collimated laser beam was used for irradiating the sample mixture and band pass filters including a cold gas cell were used to isolate the proper wavelength region. The IR emission spectrum was obtained by using a circular variable IR filter (CVF, OCLI 902) which was directly mounted on the detector for the maximum signal collection efficiency. The band-pass of the CVF filter, in the experimental configuration, was about 100 cm^{-1}.

The infrared absorption spectra was recorded with a Perkin–Elmer Model 577 infrared grating spectrophotometer. A conventional greaseless glass vacuum system was used for sample preparation. The octafluorocyclopentene (OFCP) was supplied by PCR Research Chemicals Inc. (Gainesville, FL, USA).

Results and Discussion

Laser Induced Chemistry. Our earlier investigation,[5)] employing IR laser frequency corresponding to the ring deformation mode of octafluorocyclopentene, has shown a new channel in the decomposition of OFCP to generate $:CF_2$ and C_4F_6 as primary products. Both the primary products are unstable and undergo further reactions. The $:CF_2$ dimerizes to give C_2F_4. The nescent hexafluorobutadiene (HFBD), $C_4F_6{}^{\dagger}$, is formed with an energy above its isomerization threshold (about 36 kcal mol^{-1}) and thereby isomerize to hexafluorocyclobutene (HFCB), the thermodynamically stable isomer. A five-center ring-opening mechanism is responsible for the primary yields. Such a process is likely to follow Woodward-Hoffmann rules for pericyclic reaction.[7)] In concerted processes the simultaneous bond breaking and formation results an exit channel barrier.[8)] 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.[8)] Further, it has been observed in the IR multiphoton induced reaction that most of the excess energy above the unimolecular dissociation threshold remains as internal energy of the products.[9)] However, a significant fraction of the total energy released will be partitioned in favor of $:CF_2$ fragments translational and internal degrees of freedom.

Observation of Infrared Chemiluminescence. The infrared multiphoton dissociation of OFCP in presence of oxygen gave COF_2 as a product. Infrared absorption spectrum of the post-irradiated sample was taken which is shown in Fig. 2A. Absorption features appeared around 5.5 μm are characteristic of COF_2, due to its ν_1 and $2\nu_2$ absorption modes.[10)] It is well-known that the thermal reaction of $:CF_2$ with O_2 leads to the formation of COF_2.[11)] On excitation, a mixture of 4 Torr OFCP and 10 Torr oxygen by the CO_2 laser operating at 10R(32), very strong infrared fluorescence was observed. The fluorescence spectra was taken (Fig. 3) by using the circular variable filter, which shows one broad band near 5.5 μm. The emitting state at 5.5 μm has been assigned to the vibrationally excited product COF_2. Since COF_2 is completely composed of heavy atoms, most of the fundamental vibrational frequencies are low. The C–F symmetric stretch overtone $2\nu_2$ is strongly coupled to C=O stretch mode ν_1 by Fermi resonance.[12)] Due to energy level closeness of the ν_1 and $2\nu_2$ states, their Boltzmann factors are expected to be similar, results in the equipartition of their state populations. The time resolved IR chemiluminescence detected at 5.5 μm has been assigned to the ν_1 and $2\nu_2$

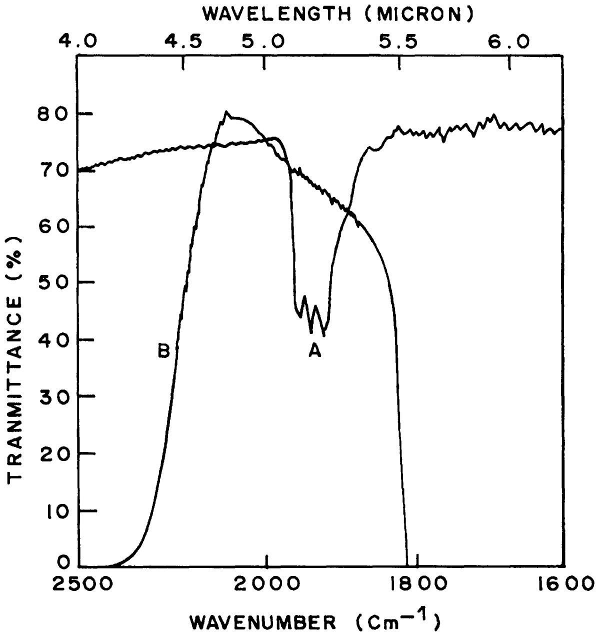

Fig. 2. (A) IR absorption spectra of COF_2 generated in the IR multiphoton dissociation of 2 Torr OFCP in presence of 6 Torr oxygen. (B) Transmittance curve of the band-pass filter and the cold gas cell.

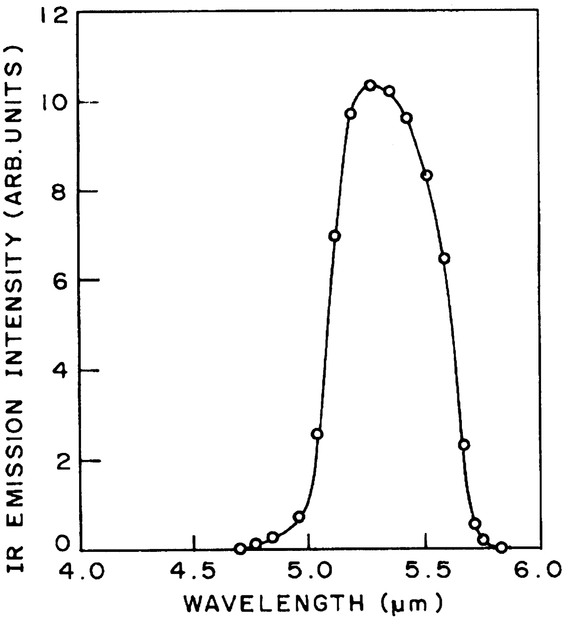

Fig. 3. IR emission spectrum at 10 μs after the CO_2 laser pulse, for 4 Torr OFCP and 10 Torr O_2 at a laser energy fluence of 2 $J\,cm^{-2}$.

modes of nascent COF_2.

The IR emission signal level, when detected through the circular variable filter, was very low. To improve the signal quality, bandpass filters were used to isolate the 5 μm fluorescence signal, the spectral region of which is shown in Fig. 2B. The observation of 5 μm fluorescence is experimentally convenient because of the availability of good IR detectors in this region and the feasibility of eliminating 10.6 μm laser scatter. A typical fluorescence signal consisted of a fast rising peak followed by a slower decay is shown in Fig. 4.

Time Resolved Infrared Chemiluminescence. The $:CF_2+O_2 \rightarrow COF_2+O$ reaction investigated in this study is moderately exoergic, releasing 51 $kcal\,mol^{-1}$ with the COF_2 product.[13] A significant exoergicity is a necessary requirement for the infrared chemiluminescence technique since the reaction must deposit sufficient energy into vibration of the polyatomic product that a measurable fraction remains in the ν_1 and $2\nu_2$ mode of COF_2 after intramolecular randomization. Shortly after the photolysing CO_2 laser pulse, infrared emission was observed to rise in 5 μm region from COF_2 product. No infrared emission is observed unless both the reagents are present in the cell. The time dependence of the infrared chemiluminescence from COF_2 is used to follow the kinetics of the reaction.

The kinetic scheme appropriate for these fluorescence measurement is given in Eqs. 1, 2, 3, and 4.

$$\mathrm{OFCP} \xrightarrow[\text{Laser}]{CO_2} \mathrm{HFBD} + :CF_2 \tag{1}$$

$$:CF_2 + O_2 \xrightarrow{k_r} COF_2{}^{\dagger} + O \tag{2}$$

$$COF_2{}^{\dagger} \xrightarrow{k_f} h\nu + COF_2 \tag{3}$$

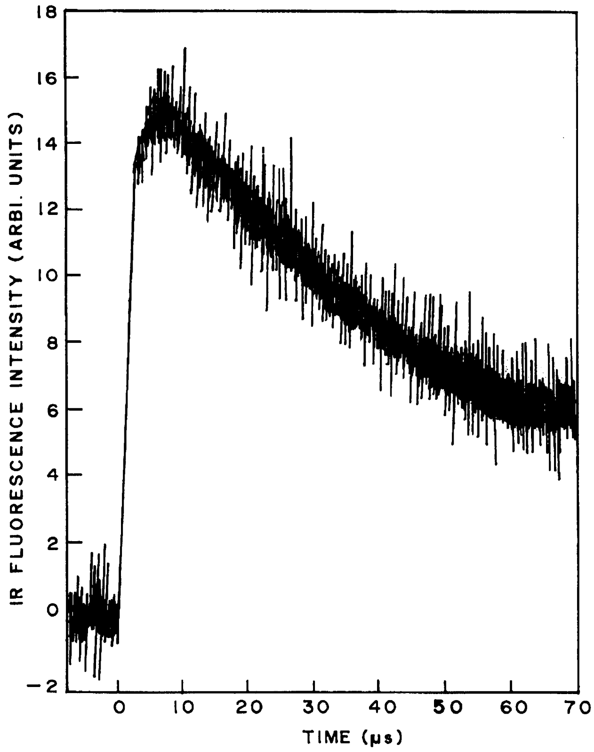

Fig. 4. A typical time resolved IR fluorescence profile consisted of a fast rising peak followed by a decay. The filter and cold gas assembly was used for collecting 5 μm photons. 2 Torr OFCF and 9 Torr oxygen was used at a laser energy fluence of 2 $J\,cm^{-2}$.

$$COF_2{}^{\dagger} + M \xrightarrow{k_d} COF_2 + M \tag{4}$$

The major reaction channels for the oxygen atoms are expected to be the following:[14,15]

$$O + O_2 + M \rightarrow O_3 + M$$

$$O + O_3 \rightarrow 2O_2$$

The photodissociation step is instantaneous on the time scale of the other events.[16] The nescent $:CF_2$ reacts with O_2; producing vibrationally excited $COF_2{}^{\dagger}$ as the product. The final step in the kinetic scheme is the collisional loss of vibrational energy from the $COF_2{}^{\dagger}$. Taking the intensity of infrared emission $I(t)$ as proportional to the product concentration, one obtains for the time dependence:

$$\begin{aligned} I(t) &= \frac{k_f k_r [O_2][CF_2]_0}{k_r[O_2] - k_d[M] - k_f} \\ &\quad \times \{\exp(-k_d[M] - k_f)t - \exp(-k_r[O_2])t\} \end{aligned} \tag{5}$$

where $[:CF_2]_0$ is the initial concentration of $:CF_2$ produced. The above expression is of the form:

$$I(t) = A[\exp(-t/T_d) - \exp(-t/T_r)] \tag{6}$$

This function is used to fit the observed time dependence of the data, where T_d and T_r both can be evaluated from the single trace. The double exponential trace yields two time constants in the limit where they are separated by more than a factor of 3—5 in time.[17)]

The reciprocals of the rise time constants obtained under these conditions are plotted against O_2 pressure and the same is shown in Fig. 5. The slope gives a reaction rate for $:CF_2+O_2 \rightarrow COF_2+O$ reaction. The rate constant for this reaction is found to be $k=3.1\pm0.3\times10^4$ $s^{-1}\,Torr^{-1}$ (1 Torr=133.322 Pa), which is equivalent to 5×10^{11} $cm^3\,mol^{-1}\,s^{-1}$ in absolute units. Similarly, by using the reciprocal of the decay constant against the total pressure employed in the experiment, the average decay constant was evaluated to be $1.7\pm0.1\times10^3$ $s^{-1}\,Torr^{-1}$.

The thermal reaction of $:CF_2$ ($\tilde{X}\,^1A_1$) with O_2 is very slow at room temperature.[11)] However, the absolute reaction rate has been reported to be,

$$k=(2.01\pm0.3)10^{13}\exp\left\{\frac{-26500\pm600}{RT}\right\}\ cm^3\,mol^{-1}\,s^{-1} \tag{7}$$

By comparing this shock tube temperature dependent rate constants, the absolute rate constant obtained in this study 5×10^{11} $cm^3\,mol^{-1}\,s^{-1}$ corresponds to a temperature of 3650±100 K. A translational temperature of 2300 K with the nascent $:CF_2$ has been reported by Stephenson and King,[18)] in their concerted HCl elimination from IR multiphoton excited CF_2HCl. As the multiphoton dissociation level increases with the increasing molecular size, so that the excitation rate becomes competitive with the RRKM rates of dissociation. Such a highly excited $:CF_2$ species may be expected in the photodissociation of OFCP. Further, considering that both the reactant translational and vibrational energy can contribute in overcoming the activation barrier of a bimolecular reaction, the $:CF_2$ temperature of 3650 K is assumed as an upper limit.

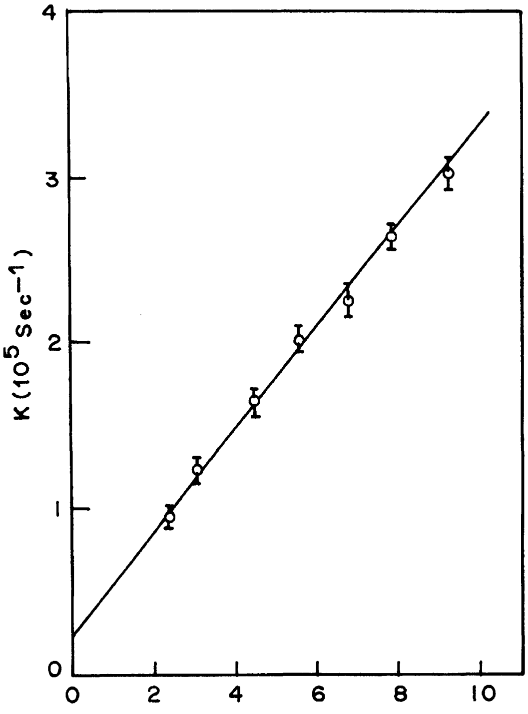

Fig. 5. Plot of k (s^{-1}), the reciprocal of the rise time constant, as a function of oxygen pressure.

In a different view, considering that the translational and rotational energy relaxation is completed within 10—30 gas kinetic collisions,[19)] the CF_2 translational and rotational motion may be thermalized before the reaction. The thermalized temperature of the irradiated ensemble, measured in millisecond time scale,[6)] has been found to be 625 K. On vibrational excitation of one of the reactant, the rate constant of a bimolecular reaction having a significant activation energy barrier has been reportedly enhanced by even 11 orders of magnitude.[20)] The vibrational energy (E_v) of the reagent, if utilized efficiently, appears to reduce the activation energy barrier (E_a) of the reaction. The rate enhancement may be expressed[21)] as:

$$k_v/k_t=\exp\left[-(E_a-E_v)/RT_t\right] \tag{8}$$

where k_v is the enhanced rate constant with E_v amount of vibrational energy in the reactant and k_t is the thermalized rate constant at a temperature of T_t. Using $T_t=625$ K, our measured $k_v=5\times10^{11}$ $cm^3\,mol^{-1}\,s^{-1}$, gives a vibrational energy in the CF_2 to be 21890 $cal\,mol^{-1}$. With such a high internal energy, the vibrational energy is expected to be randomized among the low frequency vibrational degrees of freedom of CF_2 showing a common vibrational temperature, i.e.,

$$E_v=sRT_v \tag{9}$$

where s is the number of vibrational degrees of freedom and T_v is the vibrational temperature. With an $E_v=21890$ $cal\,mol^{-1}$ in CF_2, which has only 3 vibrational degrees of freedom ($s=3$), gives a vibrational temperature of $T_v=3650$ K.

It is interesting to note that the vibrational temperature evaluated and the overall temperature found in this study, i.e. CF_2+O_2 reaction, are coincidentally the same viz. 3650 K. When all the translational and internal degrees of freedom of all the species are equilibrated in the shock tube condition, in this experiment O_2 molecules are cold. The nascent CF_2, generated in the IR multiphoton dissociation, appears to have a common vibrational and translational temperature of 3650 K. The translational motion relaxed, however, the vibrational excitation utilized effectively to enhance the reaction rate with oxygen.

Conclusions

On multiphoton absorption of IR laser, octafluorocyclopentene (OFCP) undergoes five center ring-opening reaction to generate difluorocarbene ($:CF_2$) and hexafluorobutadiene as primary products. When the above reaction is carried out in presence of oxygen, IR emission around 5 μm has been observed. The exoergic reaction of the primary product $:CF_2$ ($\tilde{X}\ ^1A_1$) with O_2 may lead to the formation of vibrationally excited COF_2 followed by emission via its ν_1 and $2\nu_2$ modes. The absolute rate constant for the reaction has been evaluated by monitoring the time resolved IR chemiluminescence from COF_2 to be 5×10^{11} $cm^3\,mol^{-1}\,s^{-1}$, which corresponds to a temperature of $\leq$3650 K for the $:CF_2$ primary product.

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