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TEA CO_2 laser-induced telomerization chemistry in conventional and waveguide photoreactors

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Abstract

Experimental approaches to the chemical synthesis of gas phase radicals by IR multiple photon excitation of polyatomic molecules are considered. The transversely excited atmospheric (TEA) CO_2 laser-induced telomerization reaction of C_2F_4 and CF_3I was studied in conventional and waveguide photolysis reactors. The difference in the product distribution in the two cases can be explained in terms of the various competing rate constants and the concentration of the perfluoroalkyl radicals generated in the irradiated volume.

Keywords: Telomerization; Waveguide photoreactors; Radical synthesis

1. Introduction

Infrared multiphoton absorption and subsequent dissociation (IRMPD) of molecules has provided a new method for initiating gas phase chemical reactions [1]. With the currently available lasers, photon-induced chemistry has opened up various possibilities, such as UV–visible electronic photochemistry with single and multiple photon excitation and combined vibrational–electronic (IR–UV) photochemistry with multistep excitation. We can achieve the selective production of free radicals in a short time scale (microseconds to nanoseconds) via resonant IRMPD of polyatomic molecules. The pulsed production of selective free radicals in high concentrations, together with an appropriate reagent, allows the bimolecular radical reaction to be directed to produce a desired product. This has also been used effectively to determine the bimolecular reaction rates in chemical kinetics studies [2,3].

This paper deals with the application of IR laser-induced chemistry to direct the synthesis of molecular compounds in radical bimolecular reactions in the gas phase. The insertion of one or more C_2F_4 molecules into CF_3I (telomerization) is an exothermic chain reaction. Using a pulsed CO_2 laser, we studied this reaction as a model to demonstrate laser-induced synthesis. Compounds of the type $C_nF_{2n+1}I$ are strong absorbers in the region of the transversely excited atmospheric (TEA) CO_2 laser (9.3–10.6 μm) and have low C–I bond strengths (CF_3I, 52.8 kcal mol^{-1}; C_2F_5I, 51.2 kcal mol^{-1}) leading to a low threshold for the C–I bond breaking process. IRMPD processes are generally characterized by fluence (the time-integrated intensity) rather than the power of the laser and these properties result in sizeable amounts of decomposition at a relatively low fluence of 0.5–1 J cm^{-2}.

The product $CF_3(C_2F_4)_nI$, as well as those of similar reactions, has practical interest as a synthetic intermediate. The conventional technique for this kind of reaction employs the liquid phase, high pressure (approximately 100 bar) and moderate temperature and requires an inhibitor [4]. For C_2F_4 telomerization, the following equilibrium limits the reaction temperature and the equilibrium temperature T_C (under standard conditions, C_2F_4 gas phase, radical in condensed phase) is 750 °C [4]

$$C_2F_4 + CF_3(C_2F_4)_n \rightleftharpoons CF_3(C_2F_4)_{n+1} \quad (n=0, 1, 2,\ldots)$$

Thus a higher temperature achieved during the limited reaction time of the CO_2 laser pulse may permit more conversion.

Such telomerization reactions have been studied previously by pyrolysis, conventional UV photolysis of appropriate molecules [5] and, more recently, by

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IRMPD [1]. However, for the synthesis of larger quantities, it is desirable to work at fairly moderate pressures. At such pressures, we must carefully consider the possible contribution of thermal reactions due to increased collisional vibrational–translational (V–T) relaxation, together with the laser-specific reaction.

However, certain molecules require a high fluence for efficient IRMPD which can only be achieved by focusing the laser beam in the photoreactor. Normally, a focused beam geometry leads to a small dissociation volume. In such a case, the laser photon utilization can be optimized by maximizing the volume of the zone where the dissociation occurs. This can be achieved either by using a combination of optical elements, such as a convex/concave lens system, or by condensing the beam in a waveguide (WG) reactor [6]. A WG reactor has been used in the recent past in the laser isotope separation of S, C and H. The dissociation yield of the desired isotopic molecule was improved without degrading the process selectivity. These studies demonstrate the exclusion of any laser heating process occurring in the WG reactor which would be inherently non-selective towards isotopic photochemistry. In this study, we have shown that, by carrying out the same telomerization reaction in a WG reactor, the absolute yield of synthetic chemistry can be increased and the relative product distribution can also be changed compared with a conventional cylindrical photoreactor. The difference in the product distribution in the two cases has been explained in terms of the various competing rate constants and the concentration of the perfluoroalkyl radicals generated in the irradiated volume.

2. Experimental details

Trifluoroiodomethane (CF_3I) and tetrafluoroethylene (C_2F_4) (PCR Chemicals) were used after several freeze–pump–thaw cycles. Gas chromatography and IR spectrophotometry did not reveal any impurities.

A 0.5 Hz repetition rate commercial CO_2 laser (Lumonics model TEA 103-2) was used for the generation of radicals in the IRMPD route. The cavity (length, 2.2 m) of the laser (discharge cross-section, 9 cm^2) was formed with a Littrow mounted blazed grating and a ZnSe output mirror ($R = 10$ m). As the laser mode quality is crucial for satisfactory coupling and transmission through the WG, an aperture of 10 mm diameter was inserted in the laser cavity. The temporal profile, as monitored by a photon drag detector, consisted of an initial spike (full width at half-maximum (FWHM), 100 ns) followed by a 1 μs tail with 80% of the energy contained in the initial spike. All irradiations were carried out using the 9R (24) (1081.08 cm^{-1}) laser line. The pulse energy was measured by a calibrated pyroelectric detector.

In a typical MPD experiment, a laser beam propagates centrally and axially through the reactor and is focused in the centre of the cell, while keeping the fluence at the cell windows lower than the damage threshold of the window material. The schematic diagram of the focused beam geometry is shown in Fig. 1. All irradiations were carried out at room temperature using a cylindrical Pyrex cell (length, 40 cm; internal diameter, 2.9 cm) and a WG cell (length, 50 cm; internal diameter, 2.6 mm) with an appropriate window section. This WG reactor was used in a previous study of the IRMPD of the CTF_3/CDF_3 system [6,7] where its characteristics have been discussed in detail. The laser beam was focused either at the WG entrance or at the centre of the conventional cell by a BaF_2 lens of 50 cm focal length.

In order to avoid any bending of the WG cell which would be detrimental to the transmission, the WG was mounted on a rigid support. Using an optical bench, the WG was first aligned with an He–Ne laser and the final alignment was done by maximizing the transmitted CO_2 laser energy. Typically, about 80% of the incident energy was transmitted. This procedure was very delicate and much care had to be taken to keep the beam geometry the same throughout, so as to avoid any involvement of possible thermal reactions at the wall.

Products were analysed by a commercial gas chromatograph (GC) (Shimadzu model GC R1A), IR spec-

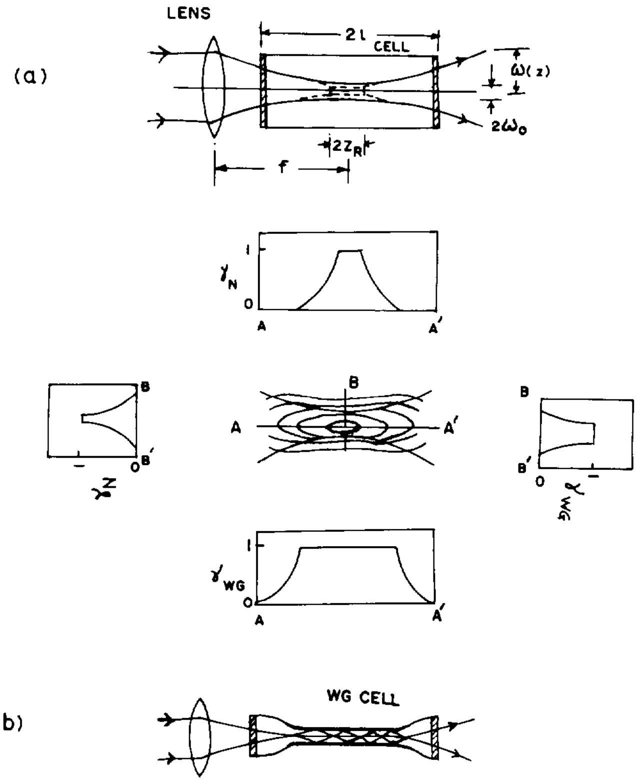

Fig. 1. Schematic diagram of focused beam irradiation with normal (a) and WG (b) cell. Also shown are the transverse and axial distribution of $\gamma(\phi)$ for a gaussian profiled laser beam.

trometry (Perkin–Elmer model 180) and mass spectrometry (VG Micromass 7070F). The GC was equipped with a thermal conductivity detector and Porapak Q column (80/100 mesh; length, 1.5 m; internal diameter, 3 mm; Pyrex) and, for separation, the column temperature was raised from 100 to 150 °C at a rate of 4 °C min^{-1} with a carrier gas of He at a flow rate of 55 ml min^{-1}.

3. Results and discussion

The IRMPD of CF_3I has been studied very extensively, and it undergoes C–I bond rupture with a critical fluence ϕ_c of 0.5 J cm^{-2} giving rise to CF_3 radicals. In the presence of C_2F_4, the CF_3 radical can undergo an addition reaction (Eq. (3)) or dimerization (Eq. (2)) in addition to the recombination reaction (Eq. (4)). The overall reaction sequence can be presented as

$$CF_3I \xrightarrow{nh\nu} CF_3^{\cdot} + I^{\cdot} \tag{1}$$

$$CF_3^{\cdot} + CF_3^{\cdot} \longrightarrow C_2F_6 \tag{2}$$

$$CF_3^{\cdot} + C_2F_4 \longrightarrow C_3F_7^{\cdot} \tag{3}$$

$$CF_3^{\cdot} + I^{\cdot} + M \longrightarrow CF_3I + M \tag{4}$$

$$C_3F_7^{\cdot} + I^{\cdot} + M \longrightarrow C_3F_7I \tag{5a}$$

$$C_3F_7^{\cdot} + CF_3I \longrightarrow C_3F_7I + CF_3^{\cdot} \tag{5b}$$

CF_3I (6 Torr) with different pressures of C_2F_4, was irradiated at its ν_1 band (centre at 1075.1 cm^{-1}) using the 9R(24) (1081.08 cm^{-1}) CO_2 laser line of pulse energy 0.7 J. Fig. 2 shows the yield ratio $Y[C_3F_7I]/Y[C_2F_6]$ as a function of C_2F_4 pressure. As expected, the ratio increases due to the competitive telomerization reaction (reaction (3) vs. reaction (2)) with increasing C_2F_4.

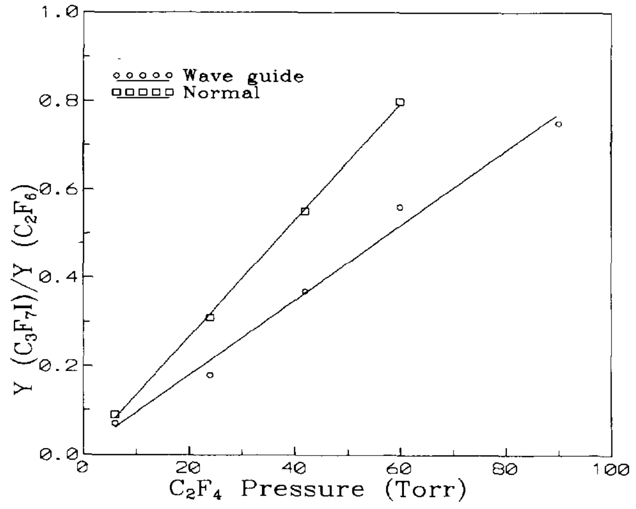

Fig. 2. $Y[C_3F_7I]/Y[C_2F_6]$ ratio as a function of C_2F_4 pressure for the telomerization reaction of 6 Torr CF_3I (irradiation with 9R(24) CO_2 laser line of 700 mJ pulse energy in normal and WG reactor).

A quantitative estimate of the rate constant ratio k_3/k_2 can be obtained by solving the above reaction scheme [8]

$$\frac{Y[C_3F_7I]}{Y[C_2F_6]} \propto \frac{k_3}{k_2}\frac{[C_2F_4]}{[CF_3]_0} \tag{6}$$

where $[CF_3]_0$ is the initial concentration of CF_3 radicals. This implies that the slope of the $Y[C_3F_7I]/Y[C_2F_6]$ vs. $[C_2F_4]$ line will give an estimation of $k_3/k_2[CF_3]_0$.

The usefulness of IRMPD for the generation of a high concentration of radicals can be assessed from the following consideration. The experimental value of $[CF_3]_0$, obtained from post-photolysis IR spectrometric analysis, is the cell-averaged concentration in the photolysis cell. Assuming that these radicals are produced in the laser beam volume, the concentration is actually higher. The concentration of CF_3 radicals (in Torr) in the beam can be determined from the relation [9]

$$(P)^{CF_3}_{\text{beam}} = (V_{\text{beam}})^{-1} V_R P_i \tag{7}$$

where V_R is the dissociation yield and P_i is the initial pressure of CF_3I. The beam volume in the case of an unfocused beam is estimated simply from the incident beam radius (r), i.e. $V_{\text{beam}} = 2\pi r^2 l$, while in the case of a focused beam of radius ω_o, as used in the experiment, $V_{\text{beam}} = 2al + 2/3bl^3$, computed from the laser beam envelope integrated over the cell length $2l$, where $a = \pi\omega_o^2$ and $b = \lambda^2/\pi\omega_o^2$. At the pressure level employed in this study, it is quite likely that a collisional exchange of energy occurs among CF_3I^* molecules in the irradiated zone in the time scale of $CF_3^{\cdot}$ production. Therefore we can assume a uniform distribution of radicals in the beam volume. In the case of the WG reactor, this volume is greater (by the volume of the WG section) than that of the normal cell. In the present case, V_{beam} in WG is calculated to be about 1.5 times that of the normal cell.

Using this methodology, $[CF_3]_0$ can be estimated for each composition in the two types of reactor. These values were used with the experimental slopes of Fig. 2 to estimate the temperature of the irradiated zone. The dimerization rate constant k_2 is reported to be 1.32×10^{12} cm^3 mol^{-1} s^{-1} [10] and the telomerization reaction rate constant k_3 is reported to be 3.47×10^{10} $\exp(-1.4/RT)$ cm^3 mol^{-1} s^{-1} [11]. Using these two values, it was estimated that, under most of the operating conditions, the irradiated zone had a temperature of 550 K or more. Such an estimation serves only as a guideline in the absence of any actual temperature measurement which is quite difficult. In this kinetic treatment, we would like to point out the possible influence of wall effects on these rate constants, and a change in the heat transfer properties of the reactor could modify significantly such a temperature estimation.

The yield of CF_3I dissociation in the WG cell was found to be about twofold greater than that in the normal cell (Fig. 3). A similar observation was made in the dissociation of CF_3Br, while molecules such as SF_6 and CTF_3, whose critical fluences are higher than

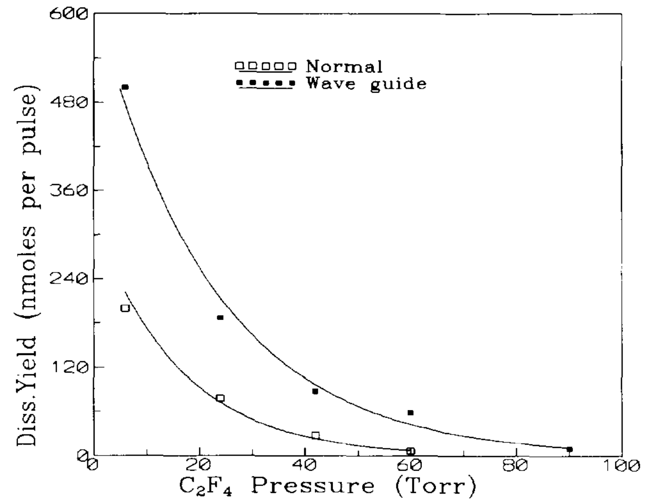

Fig. 3. The dissociation yield of 6 Torr CF_3I with various pressures of C_2F_4 under the conditions given in Fig. 2.

that of CF_3I, showed a 5–7 times enhancement in the dissociation yield [6]. The difference can be understood in the following way: firstly, because of the higher ϕ_c requirement in the second case, the dissociation volume in the normal cell is much smaller than in the WG reactor; secondly, the post-pulse recombination process associated with the CF_3I system is rapid. The radicals CF_3 and I from the primary MPD process can regenerate the starting compound CF_3I. This recombination reaction has been studied quite extensively over a large pressure and temperature range and can proceed at a rate [2] similar to the dimerization of $CF_3^{\cdot}$ radicals ($(1.3\text{–}6.5) \times 10^{12}$ cm^3 mol^{-1} s^{-1}). The impact of the focused, high-energy laser pulse may also lead to heating of the WG cell, and the temperature rise is proportional to the transmission loss in the WG [12]. Such a recombination reaction can therefore be enhanced on the hot WG surface. Hence the intrinsic fast recombination process in the CF_3X ($X \equiv I$, Br) system may be modified further in the WG so as to give a net low enhancement of the guiding effect.

In both the normal and WG cell, the dissociation yield of CF_3I has been found to decrease with C_2F_4 pressure (Fig. 3). This may be due to the collisional relaxation of excited CF_3I by C_2F_4. This behaviour is characteristic of IRMPD. When a compound is excited in the presence of a buffer gas, the yield initially increases due to the removal of the rotational bottleneck and then decreases when the collisional relaxation of the excited species dominates at higher buffer gas pressures. In our experimental conditions, it is probable that we are in the descending region of the yield vs. buffer gas pressure plot.

For each composition studied in the two reactors under identical conditions, it can be seen that the relative amount of C_2F_6 formation compared with C_3F_7I formation is more in the WG cell than in the normal cell (Fig. 2). This can be understood by considering the laser beam envelope in the normal and WG cell (Fig. 1). The incident fluence used in the present case offers a focal fluence which is greater than the critical fluence for IRMPD of CF_3I. Using a "power-law" model [13,14] for IRMPD, the dissociation probability $\gamma(\phi)$ can be obtained, which varies over the entire irradiation volume as

$$\gamma(\phi) = p(\phi/\phi_c)^n \quad \text{for } \phi < \phi_c$$

$$\gamma(\phi) = p \quad \text{for } \phi \geqslant \phi_c$$

where n is an integer and has a value of about 3–4 in many IRMPD cases and $0 < p \leqslant 1$. Therefore the irradiation volume is not only larger in the case of a WG reactor, but also has a large volume of uniform fluence in the WG section. Hence, in the WG section, a large concentration of CF_3 radicals is produced, which leads to substantial dimerization (reaction (2)), resulting in C_2F_6 production. Therefore in a WG reactor at any given composition, the total product yield and the amount of C_2F_6 produced are always larger than in the normal case.

The relative yield of the two channels is shown in Fig. 4 for various compositions. The selectivity S (produced product/converted reactant) of a particular channel is dependent on the composition and, at a given composition, on the reactor configuration. Although the selectivity of the two channels is apparently linear, it tends to deviate at higher C_2F_4 pressures, indicating the initiation of further addition of C_2F_4 to the product C_3F_7I to form higher telomers. In the present study, at higher pressures of C_2F_4, we obtained a mixture of higher telomers which could not be fully analysed. Indeed, Bagratashvili et al. [1] produced telomers with

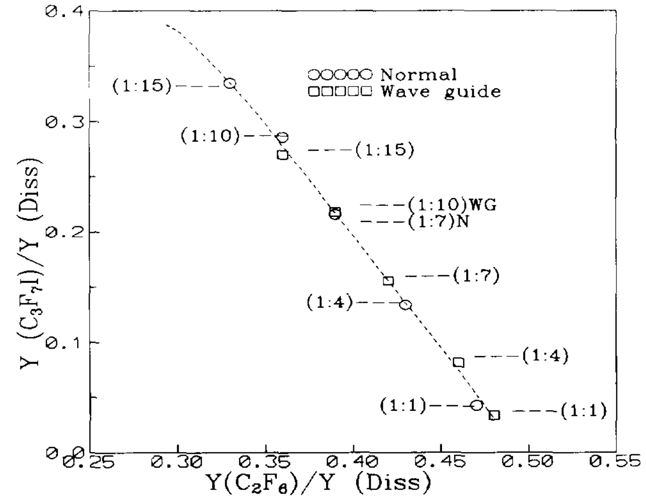

Fig. 4. The relative yield of the two channels for various compositions. The selectivity S (produced product/converted reactant) of a particular channel is dependent on the composition and, at a given composition, on the reactor configuration. The broken line shows the trend and deviation from linearity, indicating the formation of higher telomers.

a mean chain length of about 10 in a 1 : 50 CF_3Br–C_2F_4 mixture at 50 Torr using 6 J cm^{-2} CO_2 laser radiation. While estimating the temperature of the irradiated zone, we found a gradual decrease in temperature at higher C_2F_4 pressures, and it is probable that crystalline, higher telomeric products are produced at relatively lower temperature [4]. Considering the complexity of the problem, it appears that quantitative modelling requires more careful investigation. However, recently, a kinetic analysis has been made of the KrF laser-induced telomerization reaction [15], where first-order termination (self-inhibition) was reported.

4. Conclusions

We have demonstrated the telomerization reaction between CF_3I and C_2F_4 using a pulsed CO_2 laser. The laser chemistry of this system has interesting features, depending on the laser fluence, CF_3I to C_2F_4 composition and the reactor type. A higher dissociation yield for CF_3I was obtained in a WG reactor compared with a normal reactor. With an increase in C_2F_4 pressure, the dissociation yield decreased, but the relative yield of C_3F_7I increased compared with C_2F_6 in both reactors. However, the rate of increase is faster in the normal reactor than the WG reactor. The difference in product distribution can be explained in terms of the various competing rate constants and the concentration of the perfluoroalkyl radicals generated in the irradiated volume. Therefore, to synthesize a desired product with prescribed selectivity, we must optimize the substrate to additive monomer pressure and the reactor geometry.

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