

Carbon-13 Enrichment by IR Laser Chemistry of $\text{CHF}_3\text{-Cl}_2$

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Abstract. IR laser chemistry of CHF_3 is investigated in both neat form and in the presence of Cl_2 for carbon-13 enrichment. Infrared multiple-photon dissociation of CHF_3 is an order of magnitude more efficient in the scavenged system compared to the neat case. The photolysis of CHF_3/Cl_2 mixture results in two products, viz., CF_2Cl_2 and $\text{C}_2\text{F}_4\text{Cl}_2$ but with different enrichment factors. The parametric studies show that $\text{C}_2\text{F}_4\text{Cl}_2$ arises due to MPD of CF_2Cl_2 in secondary photolysis.

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Laser isotope separation (LIS) of carbon-13 at laboratory scale level by IR laser chemistry has been well established [1]. It is essential to opt for a “two-stage, closed chemical cycle” involving a fluorohalocarbon and a scavenger for practical scales of ^{13}C enrichment at $\geq 90\%$. There is intense activity to identify useful systems among $(\text{CF}_3\text{Br}, \text{CF}_2\text{Br}_2)/\text{Cl}_2$, $(\text{CF}_3\text{Cl}, \text{CF}_2\text{Cl}_2, \text{CF}_2\text{HCl})/\text{Br}_2$, $(\text{CF}_2\text{HCl}, \text{CF}_2\text{Cl}_2, \text{CF}_2\text{Br}_2, \text{CF}_2\text{ClBr})/\text{HI}$, $\text{CF}_2\text{Br}_2/\text{O}_2$ (cf. references in [1]). Ma et al. have shown that in cases like $\text{CF}_2\text{Br}_2/\text{HI}$ [2], $\text{CF}_2\text{HCl}/\text{HI}$ [3], and $\text{CF}_2\text{Br}_2/\text{Cl}_2$ [4], the stage-1 product need not be isolated as it undergoes ^{13}C selective MPD at the same wavenumber like its precursor. ^{13}C selective IR MPD has been reported in neat CF_3X molecules ($\text{X} = \text{H}, \text{D}$) [5–7] and in CHF_3/O_2 [6]. Burning of $^{13}\text{CF}_3\text{H}$ is expected to give better selectivity in the fluoroform system for T/H separation [8]. Neat CF_3X MPD, in general, gives a very low yield and requires high fluences ($20\text{--}30\text{ J cm}^{-2}$). It would be of interest to study MPD of these species in the presence of a highly reactive but chemically compatible scavenger like Cl_2 . This work shows that Cl_2 addition modifies the laser chemistry of CHF_3 and enhances the ^{13}C decomposition in natural fluoroform significantly.

1 Experimental

All studies were done in a 50 cm long pyrex cell (volume = 440 cm^3) fitted with BaF_2 windows. A line tunable, com-

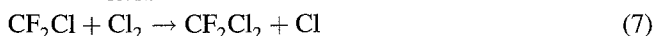
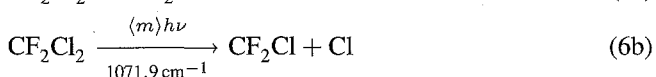
mmercial TEA CO_2 laser (Lumonics 103-2) was used without N_2 in the laser gas mixture. The pulse duration was 100 ns FWHM as seen by a photon-drag detector (Rofin 7415). A calibrated pyroelectric detector (Lumonics 50D) measured the pulse energy. The laser beam was focussed by a BaF_2 lens (focal length, $f = 25/50\text{ cm}$) and fluence at the beam waist was estimated from the burn pattern on thermal paper. Commercial samples of CHF_3 (Matheson), CF_2Cl_2 (PCR) and Cl_2 (Airco Products) were used as such after several freeze-pump-thaw cycles. A synthetic $\text{C}_2\text{F}_4\text{Cl}_2$ sample was prepared by reacting C_2F_4 (PCR) with excess of Cl_2 . A strain gauge (Leybold MI 200) was employed for pressure measurement in sample preparation. Concentration of various fluorohalocarbons was monitored by IR spectrophotometry (Perkin Elmer 180/577). Gas chromatography (Shimadzu R1A) and mass spectrometry (VG Micromass 7070F) were used to identify the reaction products. A 1 m long Porapak Q column was used isothermally at 60°C with thermal conductivity detection and helium as carrier gas. The ^{13}C isotopic distribution was measured from $^{+}\text{CHF}_2$, $^{+}\text{C}_2\text{F}_3$, $^{+}\text{CFCl}_2$, $^{+}\text{C}_2\text{F}_4\text{Cl}$ ions for CHF_3 , C_2F_4 , CF_2Cl_2 , and $\text{C}_2\text{F}_4\text{Cl}_2$, respectively. The enrichment factor for a particular species, X , β_X , is defined as the ratio of ($^{13}\text{C}/^{12}\text{C}$) fraction in “X” to that at natural abundance. The extent of ^{13}C decomposition was measured from the m/e (52/51) ratio of the photolysed sample relative to that in a reference sample. All the samples containing Cl_2 were treated with KOH before GC and MS analysis.

2 Results and Discussion

The initial process in the IR MPD of CHF_3/Cl_2 mixtures is photochemical decomposition of the resonant molecule, $^{13}\text{CHF}_3$. Therefore, general features of ^{13}C separation are expected to be similar to those observed for the IR MPD of neat CHF_3 [5–7]. In the presence of Cl_2 , we obtained CF_2Cl_2 as main product which contained ^{13}C at various fractions depending on experimental conditions. Isotopic selectivities were significant when the laser was tuned to 9 R(10) line (1071.9 cm^{-1}). The excitation region corresponds to the

long-wavelength wing of the ν_2 band of CHF_3 (Q -branch peak for $^{12}\text{CHF}_3$: 1141 cm^{-1} and $^{13}\text{CHF}_3$: 1116 cm^{-1}) [9]. The decomposition yield of $^{13}\text{CHF}_3$ so obtained was an order of magnitude better for the mixture compared to that for neat case (cf. Fig. 1).

The experimental results obtained with the IR MPD of CHF_3/Cl_2 mixtures can be understood in terms of the following mechanism:



It has been established that the initial step in IR MPD of CHF_3 is the decomposition of highly vibrationally excited CHF_3 into a CF_2 radical and a HF molecule (cf. 1b) [5–7]. The activation energy E_a and the heat of reaction ΔH have been estimated to be 288 and 242 kJ mol^{-1} , respectively, from the pyrolysis of CHF_3 [10, 11]. For the photolysis of neat CHF_3 , it is not clear whether the only fate of CF_2 is the dimerization to form C_2F_4 . The importance of the recombination reaction (2) could be assessed to obtain the net decomposition yield of CHF_3 . The relative rate of formation of C_2F_4 , $R(\text{C}_2\text{F}_4)$ to that of CHF_3 , $R(\text{CHF}_3)$, can be estimated as:

$$\begin{aligned} R(\text{C}_2\text{F}_4)/R(\text{CHF}_3) &= K_3[\text{CF}_2][\text{CF}_2]/K_2[\text{CF}_2][\text{HF}] \\ &= K_3[\text{CF}_2]/K_2[\text{HF}] \geq 340[\text{CF}_2]/[\text{HF}] \end{aligned} \quad (10)$$

considering the values of $K_2 \leq 5 \times 10^7\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ [14] and $K_3^{300\text{ K}} = 1.7\text{--}2.2 \times 10^{10}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ [12, 15]. In the irradiated mixture, $[\text{CF}_2]$ would be of the same order as $[\text{HF}]$. Therefore, the formation of CHF_3 by the back reaction (2) is negligibly small compared to the formation of C_2F_4 .

In the case of CHF_3/Cl_2 mixture, a similar treatment compares the relative rate of formation of C_2F_4 with respect to that of CF_2Cl_2 :

$$\begin{aligned} R(\text{C}_2\text{F}_4)/R(\text{CF}_2\text{Cl}_2) &= K_3[\text{CF}_2][\text{CF}_2]/K_4[\text{CF}_2][\text{Cl}_2] \\ &= K_3[\text{CF}_2]/K_4[\text{Cl}_2] \end{aligned} \quad (11)$$

Assuming a temperature of 550 K in the irradiated volume, K_3 and K_4 were calculated to be $4.1\text{--}5.9 \times 10^{10}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ [12, 15] and $2.1 \times 10^9\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ [16], respectively. Under the present irradiation condition, the ratio of $[\text{CF}_2]$ to $[\text{CHF}_3]$ is typically 10^{-3} estimated from the yield per pulse and $(V_{\text{cell}}/V_{\text{irrad}})$ ratio of about 15, where V_{irrad} corresponds to

irradiated volume. Therefore, CF_2 radicals will be scavenged effectively by Cl_2 as the halogen is typically in equivalent or more in amount than CHF_3 . It is not quite possible to predict what fraction of the excited CF_2Cl_2^* is stabilized via reaction (5) considering the exothermicity of reaction (4) to be 298 kJ mol^{-1} [10] and the dissociation energy of C–Cl bond, $D(\text{CF}_2\text{Cl}-\text{Cl})$ to be 334 kJ mol^{-1} [17].

We define a total carbon yield, $Y(\text{C})$ as $[2Y(\text{C}_2\text{F}_4)]$ for neat CHF_3 or as $[Y(\text{CF}_2\text{Cl}_2) + 2Y(\text{C}_2\text{F}_4\text{Cl}_2)]$ for mixture MPD to obtain standard data for comparison. Figure 1 shows that there is an order of magnitude increase in the dissociation for the mixture compared to the neat case. This could be understood in terms of rotational bottleneck removal by Cl_2 in CHF_3 excitation.

For the mixture of 6.7 mbar CHF_3 and 6.7 mbar Cl_2 , $Y(\text{C})$ was found to be $6.67 \times 10^{-10}\text{ mol pulse}^{-1}$, while $Y(\text{C})$ for 6.7 mbar neat CHF_3 was only $4.92 \times 10^{-11}\text{ mol pulse}^{-1}$ at 30 J cm^{-2} fluence with 9 $R(10)$ CO_2 -laser line. The former yield is about 13 times larger than the latter. The corresponding enrichment factors were $\beta(\text{CF}_2\text{Cl}_2) = 11.6$ and $\beta(\text{C}_2\text{F}_4\text{Cl}_2) = 28$ for the mixture and $\beta(\text{C}_2\text{F}_4) = 12.3$ for neat CHF_3 . Doubling of CHF_3 pressure to 13.3 mbar in the neat case resulted in $Y(\text{C}) = 5.26 \times 10^{-10}\text{ mol pulse}^{-1}$ which is comparable to that for 1:1 mixture at the same total pressure. This is due to collision-assisted MPD via the rotational hole-filling mechanism. However, $\beta(\text{C}_2\text{F}_4)$ dropped to 3.8 in the 13.3 mbar neat case indicating the onset of

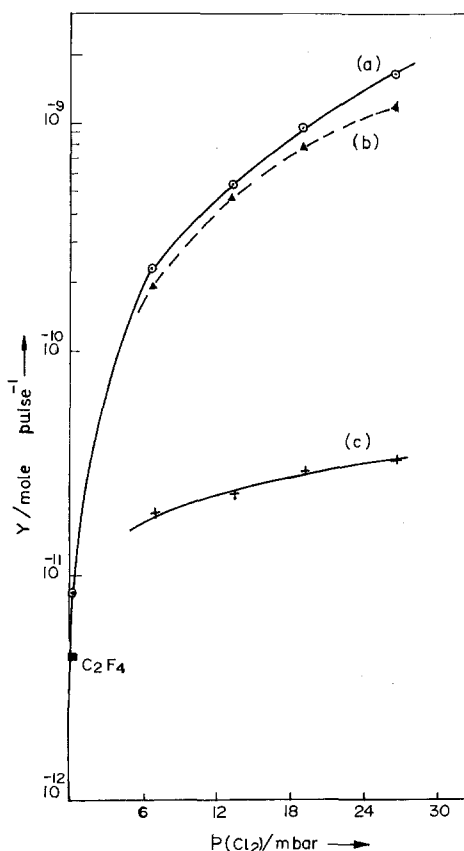


Fig. 1. Yield vs Cl_2 pressure: (a) \odot $Y(\text{C})$ for CHF_3 decomposition; (b) \blacktriangle $Y(\text{CF}_2\text{Cl}_2)$ for CF_2Cl_2 formation; (c) $+$ $Y(\text{C}_2\text{F}_4\text{Cl}_2)$ for $\text{C}_2\text{F}_4\text{Cl}_2$ formation, \blacksquare $Y(\text{C}_2\text{F}_4)$ for C_2F_4 formation. $p_{\text{CHF}_3} = 6.7\text{ mbar}$, 9 $R(10)$ line, fluence = 9 J cm^{-2}

non-selective, intermolecular energy-transfer processes. The selectivities obtained in these investigations for the neat system are similar to those reported in the literature [7].

Fluence effects on yields and enrichment factor were examined for a 1:1 mixture at 13.3 mbar total pressure in the range of 9–30 J cm⁻². For example, $Y(\text{C})$, $\beta(\text{CF}_2\text{Cl}_2)$ and $\beta(\text{C}_2\text{F}_4\text{Cl}_2)$ at 9 J cm⁻² were 2.34×10^{-10} mol pulse⁻¹, 15.1 and 33.7, respectively, while those at 30 J cm⁻² were 6.67×10^{-10} mol pulse⁻¹, 11.6 and 28, respectively. $Y(\text{C}_2\text{F}_4)$ was below the detection limit at either of the fluence. Therefore, an increase in fluence enhances the product yield, but reduces the enrichment factors.

The formation of C₂F₄Cl₂ suggests the occurrence of reaction (6a), since the compound is probably formed by the dimerization of CF₂Cl radicals. However, the possibility of laser induced IR MPD of CF₂Cl₂ via reaction (6a) will also contribute to the formation of C₂F₄Cl₂. The primary product CF₂Cl₂ has two vibrational modes: ν_1 stretch (1099 cm⁻¹) and ν_6 rock modes (922 cm⁻¹) which can be excited by CO₂-laser frequencies. The isotope shift for ¹³C is about 22 cm⁻¹ in the ν_1 mode and therefore ¹³C selective IR MPD could be effected in the range of 1030–1080 cm⁻¹ [18].

The two lowest decomposition channels and their energetics have been thoroughly studied for CF₂Cl₂ [17]:



An activation barrier exists for the reverse of reaction (13) which makes reaction (12) as the lowest MPD channel for CF₂Cl₂ with a maximum 10% yield for reaction (13). Such isotopically selective secondary photolysis of CF₂Cl₂ at the exciting laser frequency of 9 R(10) can be substantiated by looking at the different enrichments obtained in these two products. At low conversions, i.e., during the initial stage of decomposition, the ¹³C atom fraction in CF₂Cl₂ and C₂F₄Cl₂ are close to each other. However, the fraction in C₂F₄Cl₂ becomes progressively larger than that in CF₂Cl₂ as the conversion increases. If C₂F₄Cl₂ originates only from the decomposition of excited CF₂Cl₂^{*} (reaction 6a), then the β values in both CF₂Cl₂ and C₂F₄Cl₂ would be identical. Therefore, C₂F₄Cl₂ is formed via reactions (6a) and (6b) followed by dimerization of CF₂Cl₂ radicals in reaction (8). When Cl₂ is added gradually to the 6.7 mbar CHF₃ system, both $Y(\text{C})$ and $\beta(\text{CF}_2\text{Cl}_2)$, $\beta(\text{C}_2\text{F}_4\text{Cl}_2)$ are found to increase. However, with increase in Cl₂ pressure, the yield of CF₂Cl₂ relative to that of C₂F₄Cl₂ (Fig. 2) increases rapidly due to the competition between reactions (7) and (8) in addition to that between reactions (5) and (6). The apparent loss of selectivity at high pressures of Cl₂ could be due to collisional deactivation of the preferentially excited ¹³CHF₃ molecules. Therefore, the end product CF₂Cl₂ is enriched to a lesser extent and similarly lower selectivity is obtained for the C₂F₄Cl₂ arising from such CF₂Cl₂ by collisional and/or laser-induced decomposition.

In conclusion, we have demonstrated that Cl₂ addition enhance the MPD yield of CHF₃. The mechanism for such enhancement is suggested on the basis of the enrichment factors and yields of the two products, viz. CF₂Cl₂ and C₂F₄Cl₂. The enrichment in C₂F₄Cl₂ could be improved by appropriate choice of mixture composition, laser frequency

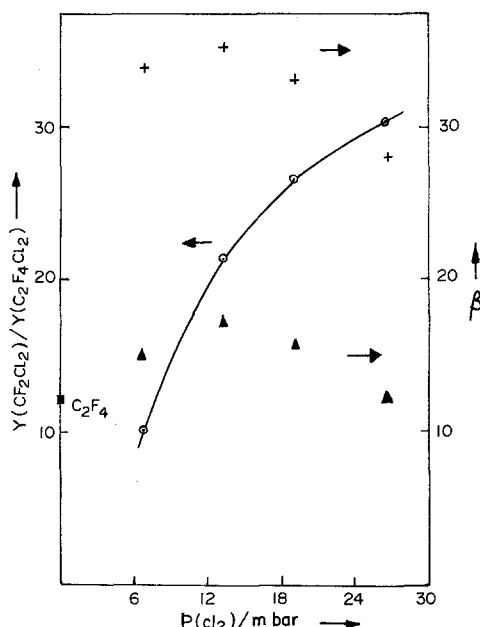


Fig. 2. Relative yield and product-enrichment factor vs Cl₂ pressure: \circ $Y(\text{CF}_2\text{Cl}_2)/Y(\text{C}_2\text{F}_4\text{Cl}_2)$; \blacktriangle $\beta(\text{CF}_2\text{Cl}_2)$; $+$ $\beta(\text{C}_2\text{F}_4\text{Cl}_2)$; \blacksquare $\beta(\text{C}_2\text{F}_4)$. Experimental conditions as in Fig. 1

and the extent of photolytic conversion. The potentiality of CHF₃/Cl₂ system for ¹³C enrichment appears to be limited in view of the relatively higher fluence requirement compared to other halocarbon systems. However, it may be useful in the tritium removal problem through efficient burning of the ¹³C isotope in a CTF₃/CHF₃ system.

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