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Isotopic enrichment of ^{13}C by IR laser photolysis followed by fast bimolecular reaction

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Abstract

The selective IR multiphoton decomposition of $^{12}CF_3I$ in the presence of NO_2 as radical scavenger was used to obtain isotopic enrichment of ^{13}C in a one- stage process. The $^{12}CF_3$ radicals produced by IR photolysis react with NO_2 through a fast bimolecular reaction to yield $^{12}CF_2O$ together with undissociated $^{13}CF_3I$ as the main carbon-containing products. The isotopic enrichment increases with the $[NO_2]/[CF_3I]$ ratio. The results are compared with those obtained using O_2 as scavenger.

Keywords: Isotopic enrichment; IR laser photolysis; Fast bimolecular reaction

1. Introduction

In recent years, many studies on laser carbon separation have been performed [1]. These studies have reported a large variety of results on the dependence of the selectivity on the laser pulse width and pressure. High isotopic selectivity cannot be obtained in processes involving CF_3I, mainly as a consequence of recombination processes, back reaction to CF_3I and scrambling processes. Recent studies generally agree that efficient IR-laser-induced separation of ^{13}C requires a two-stage process [2]. NO is used as a scavenger of CF_3 radicals to reduce the importance of the recombination reaction $CF_3 + I$, yielding a higher efficiency of $^{12}CF_3I$ dissociation without loss of isotopic selectivity [3]. The main problem of this technique is that it is necessary to work at pressures below 1.33 mbar in order to obtain an acceptable isotopic selectivity. This implies that only small amounts of $^{13}CF_3I$ can be obtained in a single experiment. Other workers have developed a flow method, based on the periodic elimination of the reaction products, in which an isotope can be enriched as desired even though the selectivity of photolysis may be low [4]. In this method, O_2 has been used as the scavenger of CF_3 radicals. Unfortunately, this reaction involves the participation of several intermediates through a complex mechanism, hence introducing an additional difficulty in the efficient control of the process. In addition, many studies of the IR multiphoton dissociation of CF_3I have been performed, providing a comprehensive understanding of the processes involved and accounting for the effect of pressure [5–7], laser pulse width [8] and isotopic selectivity [2,9]. The aim of this work is to apply this information, as well as the well-known fast bimolecular reaction between CF_3 and NO_2, to obtain isotopic enrichment of $^{13}CF_3I$ using an elimination process.

2. Experimental details

The experimental apparatus has been described previously [7]. Briefly, a pulsed CO_2 TEA laser was tuned to the R(14) line of the 9.6 μm band (1074 cm^{-1}), which is resonant with the ν_1 vibrational mode of $^{12}CF_3I$. The typical pulse consists of an initial spike with 100 ns full width at half- maximum (FWHM) and a 2 μs tail. The laser beam was focused at the centre of the reaction cell by a BaF_2 lens with a focal length of 30 cm, yielding a fluence, at the focal point, of approximately 12 J cm^{-2}. The photolysis cell was a Pyrex cylindrical tube (length, 25 cm; diameter, 3 cm) with NaCl windows at both ends. After irradiation, the products were analysed by IR spectroscopy with a NICOLET 55XC FT-IR spectrometer. CF_3I was obtained from PCR (better than 97%) and used without further purification. NO_2 was prepared by thermal decomposition of $Pb(NO_3)_2$ and its purity was controlled by IR spectroscopy and gas chromatography. The gas pressures were measured in the range 1.33–27 mbar using an MKS Baratron model PDR-C-18.

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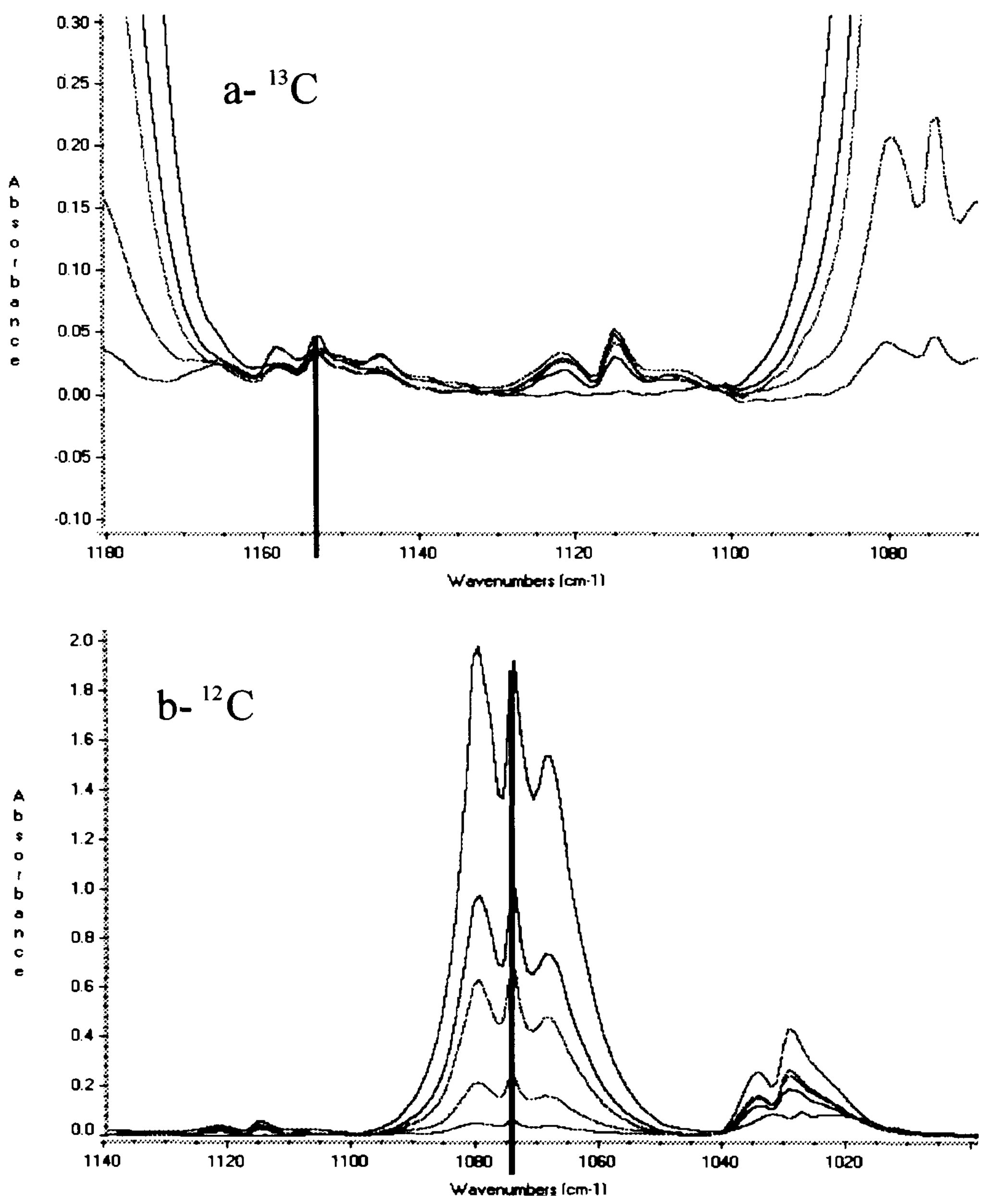

Fig. 1. IR absorption spectra of $^{13}CF_3I$ and $^{12}CF_3I$ for samples photolysed at 1074 cm^{-1} with different numbers of pulses: (a) absorption band of $^{13}CF_3I$ centred at 1154 cm^{-1}; (b) absorption band of $^{12}CF_3I$ centred at 1074 cm^{-1}. The numbers of pulses are 0, 100, 200, 300 and 800 from bottom to top in (a) and from top to botttom in (b).

3. Results and discussion

3.1. Mechanism

The reaction of NO_2 with CF_3, produced by the multiphoton decomposition of CF_3I, has been studied recently [10a–10e]. Under the present experimental conditions, the reaction mechanism can be represented as follows

$$^{12}CF_3I + nh\nu \longrightarrow {}^{12}CF_3I^* \qquad (1)$$

$$^{12}CF_3I^* \longrightarrow {}^{12}CF_3 + I \qquad (2)$$

$$^{12}CF_3I^* + M \longrightarrow {}^{12}CF_3I + M \qquad (3)$$

$$^{12}CF_3 + NO_2 \longrightarrow {}^{12}CF_2O + FNO \qquad (4)$$

$$^{12}CF_3I^* + {}^{13}CF_3I \longrightarrow {}^{12}CF_3I + {}^{13}CF_3I^* \qquad (5)$$

$$^{12}CF_3 + {}^{13}CF_3I \longrightarrow {}^{12}CF_3I + {}^{13}CF_3 \qquad (6)$$

$$^{12}CF_3 + NO_2 \longrightarrow {}^{12}CF_3O + NO \qquad (7)$$

$$^{12}CF_3O + NO_2 \longrightarrow {}^{12}CF_3ONO_2 \qquad (8)$$

$$^{12}CF_3 + I_2 \longrightarrow {}^{12}CF_3I + I \qquad (9)$$

$$^{12}CF_3 + I \longrightarrow {}^{12}CF_3I \qquad (10)$$

$$^{12}CF_3 + {}^{12}CF_3 \longrightarrow {}^{12}C_2F_6 \qquad (11)$$

where M is any colliding species, which in this work is mainly NO_2. The $^{13}CF_3I^*$ and $^{13}CF_3$ radicals, produced by steps (5) and (6) respectively, can undergo the same reactions as the corresponding ^{12}C species.

In order to determine the efficiency of isotopic enrichment, two different sets of experiments were performed. In one set, the pressure of CF_3I was varied between 1.28 and 2.88 mbar with a constant pressure of NO_2 of 3.33 mbar, whereas in the other set, the NO_2 pressure was varied between 3.33 and 9.60 mbar and the CF_3I pressure was kept constant at 2.88 mbar.

The reaction yield was determined by IR spectroscopy following the absorption lines of 1074 cm^{-1} for $^{12}CF_3I$, 1153 cm^{-1} for $^{13}CF_3I$ and 1950 cm^{-1} for $^{12}CF_2O$. A typical result, displayed in Fig. 1, shows a decrease in the absorption intensity of $^{12}CF_3I$ after irradiation with increasing numbers of laser pulses, whereas the absorption intensity of $^{13}CF_3I$ remains nearly constant. The fractions of $^{12}CF_3I$ and $^{13}CF_3I$ remaining (without dissociation) as a function of the number of laser pulses are presented in Fig. 2 for different initial pressures of NO_2 and CF_3I. From the experimental results, we conclude that steps (5)–(11) can be neglected in agreement with Ref. [10]. In contrast, the fraction of CF_3I dissociated per pulse is nearly independent of the pressure of NO_2 and CF_3I (Figs. 3 and 4) implying that, at the pressure of the experiments, the rotational bottlenecks to absorption have been removed, and also the rate of step (3) is negligible in comparison with that of step (2). This is in agreement with the results of Ref. [11], which report a rate for the unimolecular dissociation of CF_3I higher than 10^9 s^{-1} at fluences much lower than in our experiments. In addition, the fractional yield per pulse is independent of the number of laser pulses, indicating that the reaction is free from side complications originating from IR absorption by the reaction products.

3.2. Isotopic selectivity

The enrichment factor β is defined as [12]

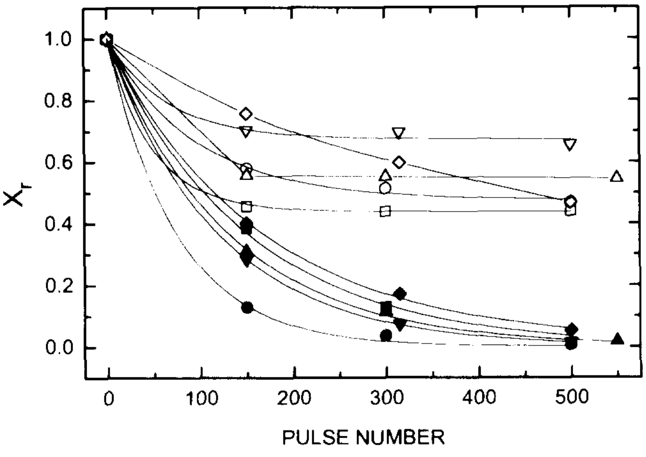

Fig. 2. Fraction of $^{13}CF_3I$ (open symbols) and $^{12}CF_3I$ (filled symbols) remaining (without dissociation) as a function of the number of laser pulses for different initial pressures (mbar) of CF_3I and NO_2 respectively: ▼, ▽, 1.24 and 2.93; ▲, △, 2.88 and 3.33; ■, □, 2.88 and 7.47; ●, ○, 2.88 and 7.20; ◆, ◇, 2.88 mbar of CF_3I and 7.47 mbar of O_2.

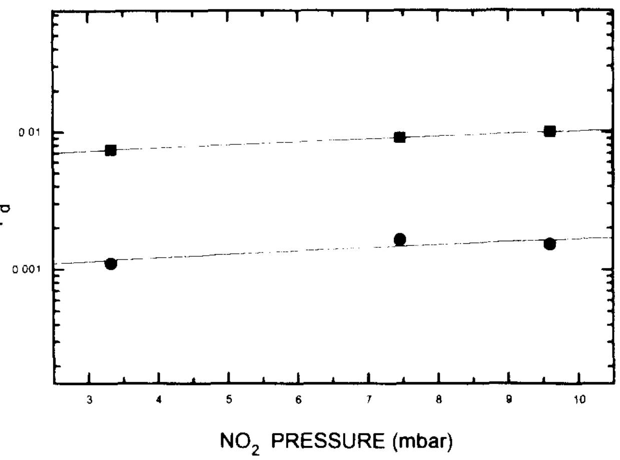

Fig. 3. Fraction of CF_3I dissociated per pulse at 2.88 mbar as a function of the NO_2 pressure: ■, $^{12}CF_3I$; ●, $^{13}CF_3I$.

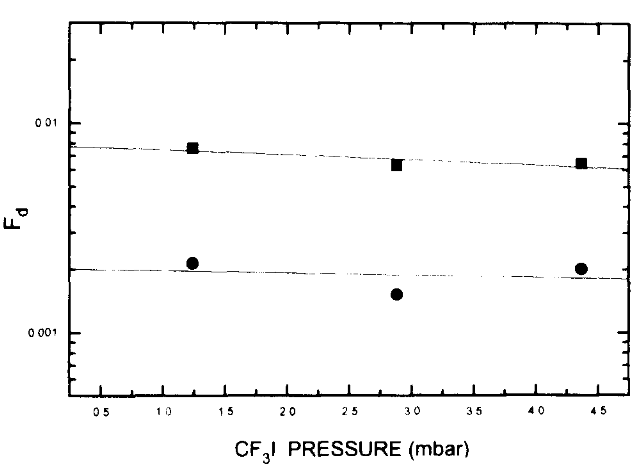

Fig. 4. Fraction of CF_3I dissociated per pulse at 5.33 mbar of NO_2 as a function of the CF_3I pressure: ■, $^{12}CF_3I$; ●, $^{13}CF_3I$.

$$\beta = R/R_0 \qquad (12)$$

where R_0 is the natural abundance isotope ratio and R is the isotope ratio of the reactant remaining after irradiation. Also, following Ref. [12], the selectivity factor α is defined as

$$\frac{dn_1}{dn_2} = \alpha \frac{n_1}{n_2} \qquad (13)$$

where n_1 and n_2 are the concentrations of the two isotopic species $^{12}CF_3I$ and $^{13}CF_3I$ respectively. Therefore α measures the degree of selectivity of the process, while β indicates the extent of enrichment that may be produced in any given stage.

Eq. (13) can be integrated for constant α to obtain

$$\ln\left(\frac{n_1}{n_{1\,(0)}}\right) = \alpha \ln\left(\frac{n_2}{n_{2\,(0)}}\right) \qquad (14)$$

where $n_1/n_{1(0)} = X_{r12}$ and $n_2/n_{2(0)} = X_{r13}$ are the fractions of $^{12}CF_3I$ and $^{13}CF_3I$ that remain without being dissociated after n pulses. Considering that the dissociation cross-section σ_{diss} is related to the fraction of undissociated $^{12}CF_3I$ according to [13]

$$\ln X_{r_{12}} = -\frac{\sigma_{\text{diss}}}{h\nu} I \qquad (15)$$

where I is the intensity of the laser pulse of frequency ν, and that σ_{diss} is proportional to the laser absorption cross-section σ_{L}, we obtain the following expression for the selectivity

$$\alpha = \frac{\sigma_{\text{diss}}{}^{12}}{\sigma_{\text{diss}}{}^{13}} = \frac{\sigma_{\text{L}}{}^{12}}{\sigma_{\text{L}}{}^{13}} \qquad (16)$$

Since σ_{L} decreases as the laser fluence increases [7], Eq. (16) implies that the maximum value of α is given by the ratio of the conventional IR absorption cross-sections of the isotopes at the irradiation frequency. In this case, a value of 248 was calculated from the IR spectral data. The α factor depends only on the optical properties of the irradiated molecules, and thus must be independent of the scavenger, provided that the bimolecular reaction rate is fast enough to allow the scrambling (steps (5) and (6)) and recombination (steps (9) and (10)) reactions to be neglected.

Fig. 5 shows the β factor as a function of the number of laser pulses for different pressures of CF_3I and NO_2. It can be seen that the β factor increases with increasing pressure of NO_2 when the pressure of CF_3I remains constant, whereas β decreases with increasing pressure of CF_3I at constant NO_2 pressure. Indeed, β seems to depend linearly on the $[NO_2]/[CF_3I]$ ratio (Fig. 6). The values of α obtained from the data on the undissociated fraction are shown in Table 1. In order to optimize the value of α, it is necessary to find the laser fluence that yields the maximum value of σ_{diss} for $^{12}CF_3I$ and the minimum value of σ_{diss} for $^{13}CF_3I$. In this respect, Quack et al. [11] found a value of 0.6 J cm^{-2} for $^{12}CF_3I$. However, our experiments were performed at a higher fluence, because otherwise step (3) could not be neglected [7], producing lower values of β.

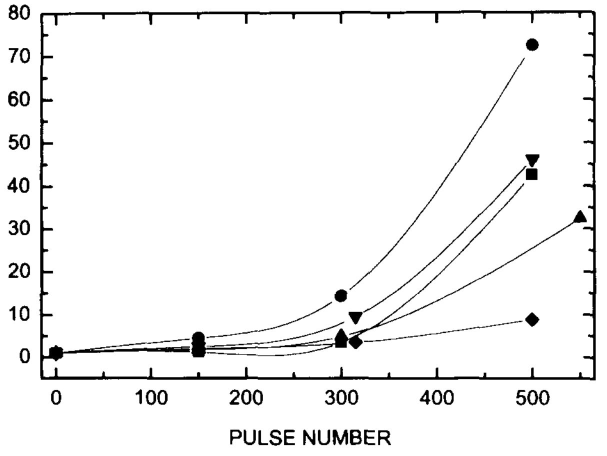

Fig. 5. β factor as a function of the number of laser pulses for different pressures of scavengers and CF_3I. The symbols are the same as in Fig. 2.

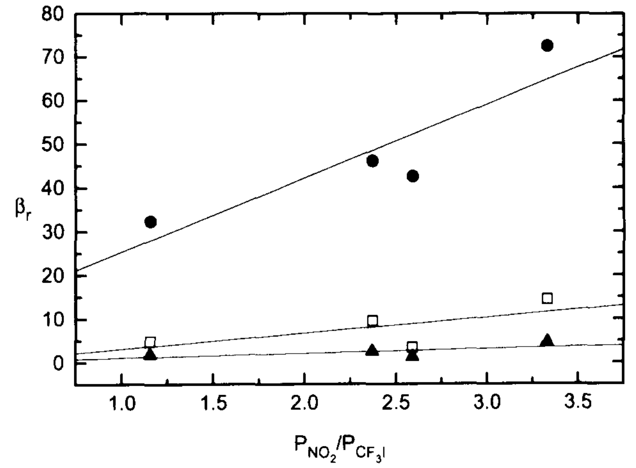

Fig. 6. β factor as a function of the relation $[NO_2]/[CF_3I]$ for different numbers of laser pulses: ▲, 150; □, 300; ●, 500.

Table 1
Selectivity factor α for different pressures of CF_3I and scavenger (NO_2 and O_2)

Scavenger	Pressure of CF_3I (mbar)	Pressure of scavenger (mbar)	[Scavenger]/[CF_3I]	α (at 500 pulses)
NO_2	2.88	3.33	1.16	146
NO_2	1.24	3.33	2.69	22
NO_2	2.88	7.47	2.89	4.61
NO_2	2.88	9.6	3.33	11
O_2	2.88	7.47	2.89	5.3

A few experiments were also performed with O_2 as scavenger of the CF_3 radicals, in order to compare the efficiency and selectivity with the results obtained with NO_2 under the same experimental conditions. The main reaction product was CF_2O, together with other unidentified products. As expected, the α factor with O_2 as scavenger is equal to that with NO_2 as scavenger within experimental error (see Table 1). However, as shown in Fig. 5, the experiments performed using 2.88 mbar of CF_3I and 7.47 mbar of O_2 yield β factors which increase with increasing number of pulses more slowly than with NO_2 as scavenger under similar conditions, and after 500 pulses produce a lower extent of isotopic enrichment. This result can be rationalized by considering that the rate constant for reaction of CF_3 with NO_2 is 1.6×10^{-11} cm^3 molecule^{-1} s^{-1} [10a] which is 60% larger than that with O_2 (1×10^{-11} cm^3 molecule^{-1} s^{-1}) [14]. Indeed, the rate constant for NO_2 is the largest of all the reactions used for isotopic enrichment, such as CF_3 with Cl_2 (4.47×10^{-12} cm^3 molecule^{-1} s^{-1}) [15], CF_3 with Br_2 (1.79×10^{-12} cm^3 molecule^{-1} s^{-1}) [16], CF_3 with IH (8.88×10^{-13} cm^3 molecule^{-1} s^{-1}) [17] and CF_3 with NO ($(0.8–4)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} in the pressure range 1–10 mbar) [18]. The high rate of reaction is a determining factor, because the pressure of scavenger needed to eliminate the recombination reactions can be proportionally reduced. This reduces the problem of collisional quenching of vibrationally excited CF_3I, so that the rate of step (2) can be larger than that of step (3) at lower laser fluences. Since the selectivity depends on the relative value of the absorption cross-section (Eq.

(16)), which increases as the fluence decreases, a better isotopic separation can be obtained.

4. Conclusions

The IR multiphoton decomposition of CF_3I in the presence of NO_2 provides a direct method to obtain isotopically enriched ^{13}C, because the main reaction products are $^{12}CF_2O$ and unreacted $^{13}CF_3I$ which can be easily separated by simple processes such as gas chromatography or trap to trap distillation. Although the reaction of CF_3 with O_2 is also adequate, the rate of isotopic selectivity is not as high as that obtained with NO_2 due to the lower reaction rate and a more complicated chemistry [19]. Additional advantages over other processes are that there is no need to work at reduced temperature [9] or to use a silver grid [3] to obtain a good dissociation fraction.

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