Effects of NH_3 on ^{13}C-Selective Infrared Multiple Photon Decomposition of CF_2HCl by a CO_2 Laser

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The effects of NH_3 on product yields and ^{13}C enrichment factors have been examined for the IRMPD of CF_2HCl using a CO_2 TEA laser. The IRMPD of neat CF_2HCl yields only C_2F_4 and HCl as final products. The addition of NH_3 resulted in the formation of CF_3H and NH_4Cl in addition to C_2F_4, and enhanced significantly the decomposition of CF_2HCl. The enrichment factors of ^{13}C in C_2F_4 and CF_3H decreased with increasing NH_3, but the decreases were relatively small. The mechanism of the IRMPD in the presence of NH_3 is discussed on the basis of the observed results.

It has been well-established that four-atom or larger molecules absorb numerous photons and undergo unimolecular decomposition when their resonant vibration modes are irradiated with high-fluence radiation from infrared lasers.[1] The photochemical phenomenon is called infrared multiple photon decomposition (IRMPD in abbreviation). IRMPD frequently exhibits remarkable isotope effects, reflecting the relatively large isotope shifts on infrared absorption. A number of studies have been already published on isotope separation of elements from hydrogen to uranium.[1-3] However, it is not easy to obtain practical amounts of enriched products in laser isotope separation by use of IRMPD, although selectivities are high. Recently, Kamioka et al. have succeeded in producing silicon isotopes on a practical scale using the IRMPD of Si_2F_6.[4,5]

Natural carbon consists of two isotopes, i.e., 98.9% of ^{12}C and 1.1% of ^{13}C. The IRMPD of CF_2Cl_2, CF_3X (X=Cl, Br, or I), and CF_2HCl has been extensively studied with the intention of ^{13}C separation; most of the studies have been succinctly reviewed in the introductory section of the paper by Outhouse et al.[6] The IRMPD of CF_3Br was found to produce C_2F_6 with a ^{13}C content of 80%, and that of CF_2HCl to produce C_2F_4 with 90—96% under selected irradiation conditions.[7-9] However, the enrichment of ^{13}C above 70% is attainable only with a great sacrifice of the yield. Outhouse et al. have demonstrated production rates of 0.23 g h^{-1} for 50% ^{13}C and of 0.011 g h^{-1} for 72% ^{13}C using a high power CO_2 TEA laser (10 J, 10 Hz)[6]. Therefore, there is general agreement that practical ^{13}C separation requires a two-stage process. For example, the first process is intended to increase a ^{13}C content from 1.1% to 20—50% (enrichment factor, 23—90) and the following second process is the production of ^{13}C above 90% (enrichment factor, 9—36). Since a high selectivity is not needed in each step, one can obtain a relatively large production rate of ^{13}C by such a two-stage process.

Abdushelishvili et al. have proposed the IRMPD of CF_3Br or CF_3I in the presence of NO, where NO scavenged CF_3 radicals produced from the first ^{13}C-selective IRMPD.[10] The resulting product, i.e., CF_3NO was presumed to be converted into CF_3Br or CF_3I for the second IRMPD, where the chemical conversion could be easily achieved by heating CF_3NO in Br_2 or I_2 vapor. Arai and his coworkers found that the IRMPD of C_2F_6 in the presence of Br_2 formed CF_3Br with 20—30% ^{13}C.[11] The further IRMPD of the enriched CF_3Br resulted in the production of C_2F_6 with 90% ^{13}C. On the other hand, Hackett et al. showed that the production of C_2F_4 with 95—99% ^{13}C from equimolar mixtures of 50% $^{12}CF_2HCl$ and 50% $^{13}CF_2HCl$ was very efficient in energy expenditure.[6,12] They predicted the production rate of 1.7 g h^{-1} for 99% ^{13}C, assuming that equimolar mixtures were irradiated in a flow system with 10 J pulses at a repetition rate of 10 Hz. However, enriched CF_2HCl must be provided from other enrichment process. Recently, Ma et al. proposed the two-stage IRMPD of CF_2Cl_2–HI or CF_2ClBr–HI mixtures, where the first process was the production of CF_2HCl with ^{13}C content of 30% and the second process was the further enrichment by the selective decomposition of the CF_2HCl.[13] In view of the efficient decomposition of CF_2ClBr at low fluences, the IRMPD of CF_2ClBr–HI mixtures could be one of the most effective two-stage processes to the practical enrichment of ^{13}C.

IRMPD of several fluorocarbons has been examined in our group for the development of a practical two-stage ^{13}C enrichment. In the course of the study we found that NH_3 significantly enhanced the decomposition yield in the IRMPD of CF_2HCl. The effect could be applied to an improvement of a ^{13}C yield in separation processes involving IRMPD of CF_2HCl. The present paper describes detailed experimental results and decomposition mechanisms.

Experimental

The experimental apparatus and procedures are essentially the same as were described elsewhere.[14,15]

Laser beams from a Lumonics 103-2 CO_2 TEA laser were focussed on the center of a reaction cell by a BaF_2 lens with a focal length of 60 cm, where the resulting focus area was about 0.045 cm^2. The laser was operated without nitrogen gas at a repetition rate of 0.7 Hz. A typical pulse had a half width of about 80 ns and a triangle profile without a tail.

Output energies were measured with a Scientech 362 energy power meter and a Scientech 360001 detector. The reaction cell was a 113 cm long and 2.0 cm diameter cylindrical Pyrex tube equipped with KBr windows at both ends. In addition, the cell has KBr side windows for infrared spectrophotometric analysis, where the optical path length was 5.0 cm. The total volume was 393 cm^3.

Formation amounts and isotopic compositions of products were determined by using a Shimadzu GC-7A gas chromatograph coupled with a NEVA quadrapole mass spectrometer, where a 3 mm ϕ and 3 m long VZ-10 column was mainly employed under programmed temperature variations. CF_2HCl purchased from Nitto Fluorochemical Co. was distilled repeatedly at low temperatures and the middle fractions were used as irradiation samples. We could not detect impurities such as C_2F_4 and CF_3H except for a trace amount of CF_2Cl_2. NH_3 from Suzuki Shokan Co. was also distilled repeatedly at low temperatures.

Results

The infrared absorption spectra of natural CF_2HCl and NH_3 are shown in Fig. 1. The bands centered at 1105 and 1120 cm^{-1} in CF_2HCl are assigned to CF_2 symmetric and antisymmetric stretching vibration modes, respectively. The bands at 932 and 968 cm^{-1} in NH_3 are due to degenerate symmetric deformation modes, where their R branches are extending on the higher wavenumber side. A ^{13}C isotope shift has been reported to be nearly 30 cm^{-1} for CF_2HCl.[16] In comparison to usual infrared absorption spectra, the band shapes become broader and the peaks shift to the red side in multiple-photon absorption spectra, depending on a laser fluence. The previous study of the IRMPD of CF_2HCl has shown that the decomposition probability of ^{13}C bearing molecules is considerably larger than that of ^{12}C bearing molecules in a wavenumber region from 1030 cm^{-1} to 1060 cm^{-1}.[9] Since this study was concerned with ^{13}C enrichment, we employed mainly the 9P (20) line at 1046.85 cm^{-1} and the 9P (22) line at 1045.02 cm^{-1} for irradiation of the mixtures. Although NH_3 also absorbed some of the laser radiation, neat NH_3 did not decompose at all under the present irradiation conditions, probably because of insufficient fluences for decomposition of a simple four-atom molecule.[17]

The IRMPD of neat CF_2HCl gives only C_2F_4 and HCl as stable final products; these are the same products as in homogeneous gas-phase thermolysis.[18,19] The addition of NH_3 causes the formation of a new product, which can be definitely identified as CF_3H on the basis of its retention time on gas chromatography, a peak wavenumber in infrared spectroscopy, and a cracking pattern in mass spectrometry. In addition, we observed thick deposition of a white solid on the cell walls. The element analysis of the solid showed C, 1.04; H, 7.39; N, 25.7% in weight; the composition was consistent with NH_4Cl. No fluorocarbons containing Cl, (for example, CFH_2Cl, $CFHCl_2$, $C_2F_2Cl_2$) were detected on gas chromatography.

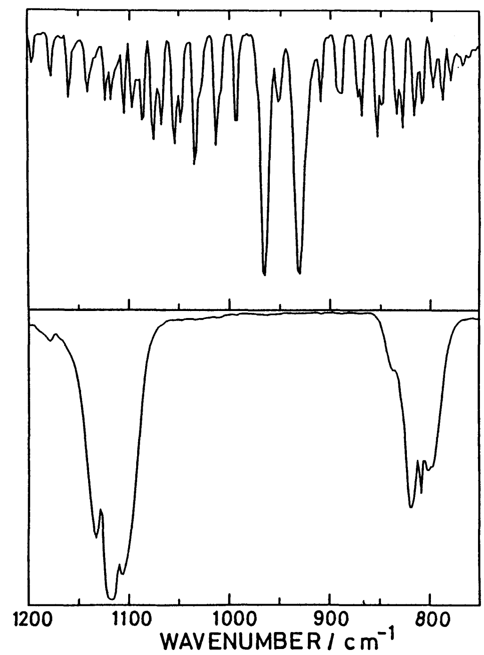

Fig. 1. Infrared absorption spectra of CF_2HCl (lower) and NH_3 (upper).

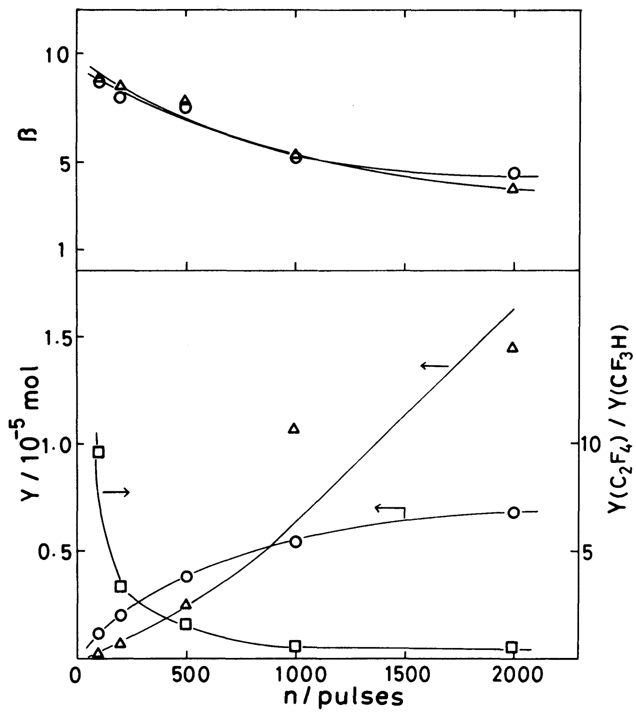

Fig. 2. Effects of pulse number n on yields Y (lower) and enrichment factors β (upper) for IRMPD of CF_2HCl–NH_3 mixtures at 5 Torr and 5 Torr. ○, $Y(C_2F_4)$ or $\beta(C_2F_4)$; △, $Y(CF_3H)$ or $\beta(CF_3H)$; □, $Y(C_2F_4)/Y(CF_3H)$. Laser wavenumber, 1046.85 cm^{-1}; laser fluence at focus, about 27 J cm^{-2}.

Figure 2 shows the effects of pulse number on yields and enrichment factors for the IRMPD of CF_2HCl–NH_3 mixtures at 5 Torr plus 5 Torr (1 Torr=133.322 Pa). The yield for C_2F_4, $Y(C_2F_4)$ is defined as a total amount of C_2F_4 produced, while that for CF_3H,

$Y(CF_3H)$ has a similar definition. The enrichment factors for C_2F_4 and CF_3H are as follows.

$$\beta(C_2F_4) = \{[^{13}C]/[^{12}C] \text{ in } C_2F_4\}/\{[^{13}C]/[^{12}C] \text{ in natural}\}$$

$$\beta(CF_3H) = \{[^{13}C]/[^{12}C] \text{ in } CF_3H\}/\{[^{13}C]/[^{12}C] \text{ in natural}\}$$

Ratios of $[^{13}C]$ to $[^{12}C]$ in C_2F_4 were determined from ion intensities of $^{12}CF_2^+$ at m/z=50 and those of $^{13}CF_2^+$ at m/z=51 for the C_2F_4 peak in GC-MS. On the other hand, we obtained similar ratios in CF_3H from ion intensities at m/z=50 ($^{12}CF_2^+$), m/z=51 ($^{12}CF_2H^+$ and $^{13}CF_2^+$), and m/z=52 ($^{13}CF_2H^+$), taking the cracking pattern of CF_3H into consideration. Figure 2 includes plots of $Y(C_2F_4)/Y(CF_3H)$ vs. number of pulses. $Y(C_2F_4)$ predominates over $Y(CF_3H)$ at small pulse numbers, but $Y(C_2F_4)$ decreases to about a half of $Y(CF_3H)$ at 2000 pulses. For pulse numbers less than 1000, logarithmic plots of $[CF_2HCl]_n/[CF_2HCl]_0$ vs. number of pulses give a good straight line, as shown in Fig. 3, where $[CF_2HCl]_0$ and $[CF_2HCl]_n$ are the amounts of CF_2HCl before and after n-pulse irradiation, respectively. The slope corresponds to a so-called specific decomposition rate in IRMPD, which is 2.1×10^{-4} pulse^{-1} in this case.

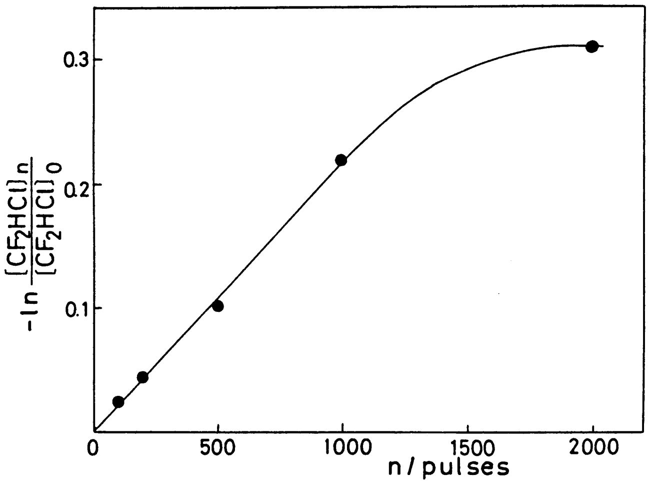

Fig. 3. Logarithmic plots of $[CF_2HCl]_n/[CF_2HCl]_0$ vs. number of pulses for IRMPD of CF_2HCl–NH_3 mixtures at 5 Torr and 5 Torr. $[CF_2HCl]_n$ and $[CF_2HCl]_0$, see text. Laser wavenumber, 1046.85 cm^{-1}; laser fluence at focus, about 27 J cm^{-2}.

Figure 4 shows the laser line dependences of yields and enrichment factors for the IRMPD of 10 Torr CF_2HCl and 10 Torr NH_3, where the number of laser pulses is 1000 at each line. In these irradiations, fluences at the focus were adjusted to fall within 20.8±2.8 J cm^{-2} by inserting polyethylene films into the beam path. However, that for the 9P(34) line at 1033.49 cm^{-1} was 12.5 J cm^{-2} at a maximum output. Although $Y(C_2F_4)$ and $Y(CF_3H)$ decrease with decreasing wavenumber, $\beta(C_2F_4)$ and $\beta(CF_3H)$ have maxima at the 9P (26) line, i.e., 1041.28 cm^{-1} and the 9P (30) line, i.e., 1037.43 cm^{-1}. In addition, the parallel relations between C_2F_4 and CF_3H in yield and enrichment factor suggest that both compounds have the same origin, which must be a CF_2 radical produced in the ^{13}C selective IRMPD of mixtures. There seems to be a structure in the wavenumber dependences of $\beta(C_2F_4)$ and $\beta(CF_3H)$. The structure may originate from the nar-

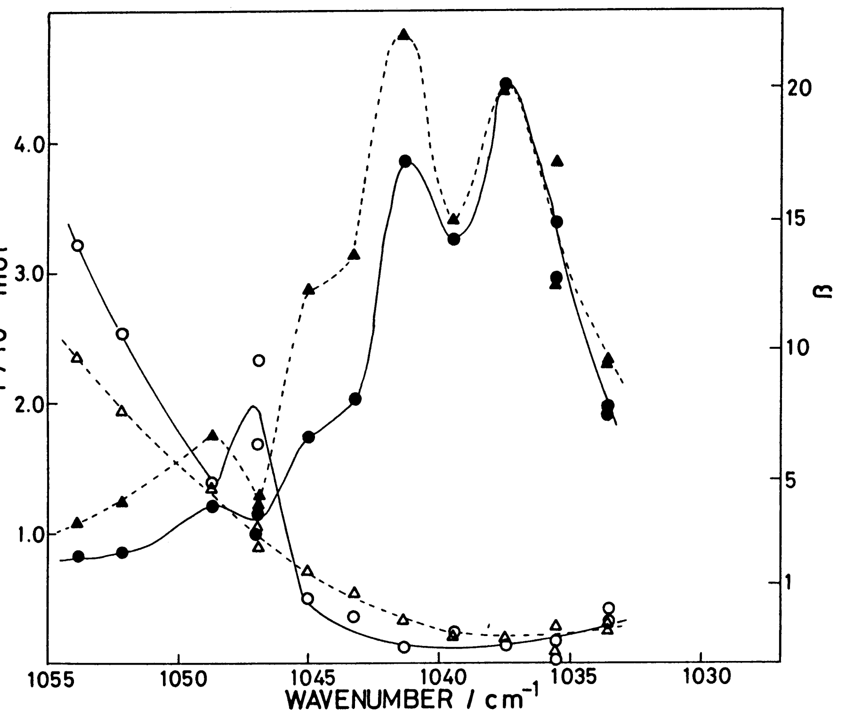

Fig. 4. Laser line dependences of yields Y and enrichment factors β for IRMPD of CF_2HCl–NH_3 mixtures at 10 Torr and 10 Torr. ○, $Y(C_2F_4)$; △, $Y(CF_3H)$; ●, $\beta(C_2F_4)$; ▲, $\beta(CF_3H)$; pulse number, 1000. Fluences, see text.

row resonance of the laser radiation with rotation-vibration transition energy in the discrete energy-level region.[1] In the IRMPD of neat CF_2HCl for different irradiation frequencies at 1053.92, 1046.85, 1041.28, and 1035.47 cm^{-1}, the enrichment factor increased rapidly with decreasing wavenumber. We consider that a non-selective thermal process may contributes to the formation of both C_2F_4 and CF_3H in mixtures of 10 Torr CF_2HCl and 10 Torr NH_3. The contribution becomes more significant with decreasing wavenumber, resulting in a rapid decrease in $\beta(C_2F_4)$ or $\beta(CF_3H)$ below 1035 cm^{-1}.

In order to obtain standard data for comparison, we examined briefly the IRMPD of neat CF_2HCl under the same experimental conditions as the CF_2HCl-NH_3 mixtures. Figure 5 shows the pressure dependences of $Y(C_2F_4)$ and $\beta(C_2F_4)$, where the laser was adjusted to the 9P (22) line and the fluences were set at about 30 $J\,cm^{-2}$. As NH_3 is added to 1.0 Torr CF_2HCl, $Y(C_2F_4)$ decreases rapidly and, after passing through a minimum, increases gradually with increasing NH_3 (see Fig. 6). $Y(CF_3H)$ increases simply with increasing NH_3, while both $\beta(C_2F_4)$ and $\beta(CF_3H)$ decrease. Hereafter, we define a total carbon yield, $Y(C)$ as 2 $Y(C_2F_4)$ for neat CF_2HCl or $Y(CF_3H)+2\ Y(C_2F_4)$ for

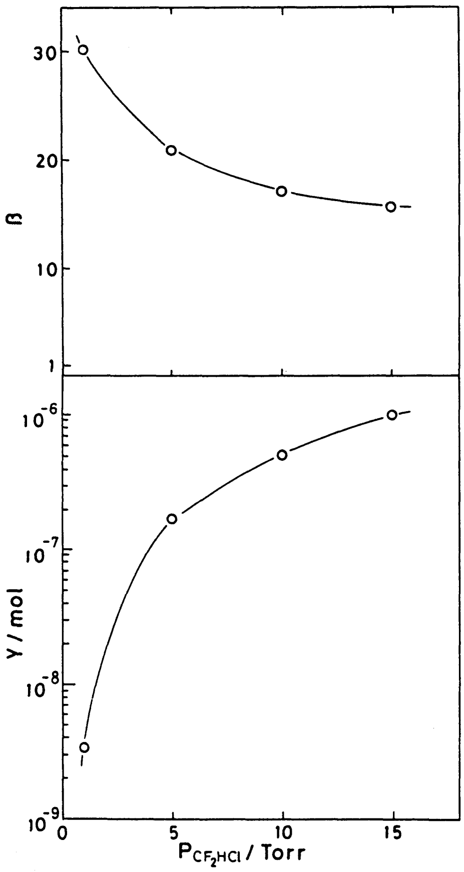

Fig. 5. Pressure dependences of $Y(C_2F_4)$ and $\beta(C_2F_4)$ for IRMPD of neat CF_2HCl. Laser wavenumber, 1045.02 cm^{-1}; laser fluence at focus, about 29 $J\,cm^{-2}$; pulse number, 1000.

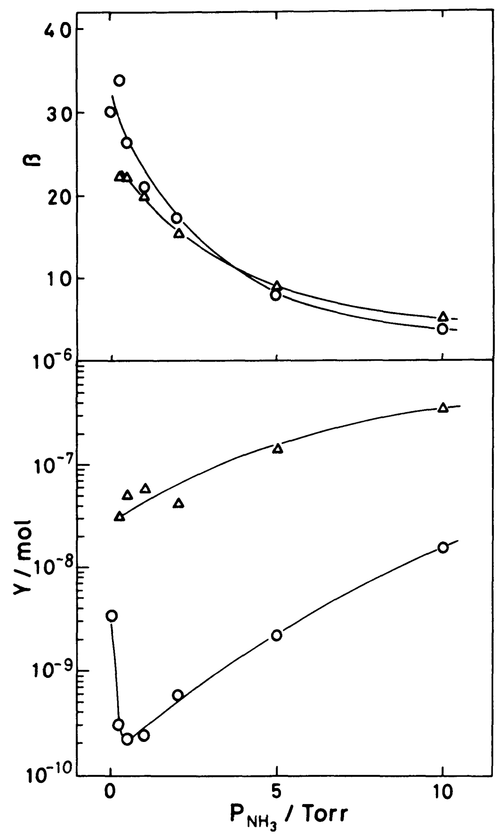

Fig. 6. Effects of NH_3 pressure on yields Y and enrichment factors β for IRMPD of CF_2HCl (1.0 Torr)-NH_3 mixtures. ○, $Y(C_2F_4)$ or $\beta(C_2F_4)$; △, $Y(CF_3H)$ or $\beta(CF_3H)$. Laser wavenumber, 1045.02 cm^{-1}; laser fluence at focus, about 29 $J\,cm^{-2}$; pulse number, 1000.

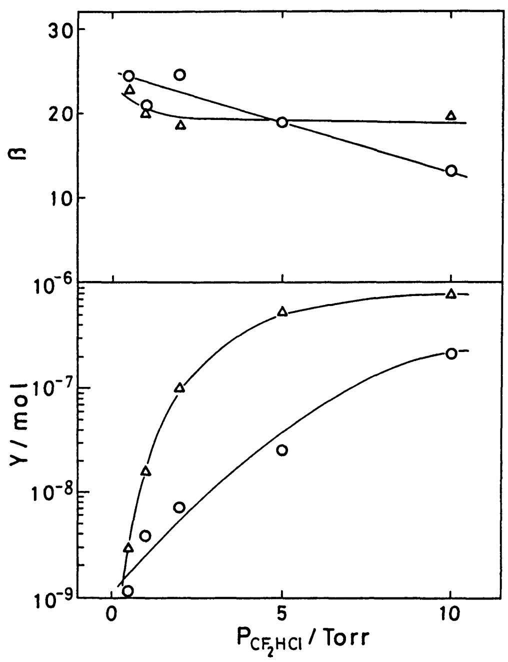

Fig. 7. Effects of CF_2HCl pressure on yields Y and enrichment factors β for IRMPD of CF_2HCl-NH_3 (1.0 Torr) mixtures. ○, $Y(C_2F_4)$ or $\beta(C_2F_4)$; △, $Y(CF_3H)$ or $\beta(CF_3H)$. Laser wavenumber, 1045.02 cm^{-1}; laser fluence at focus, about 29 $J\,cm^{-2}$; pulse number, 1000.

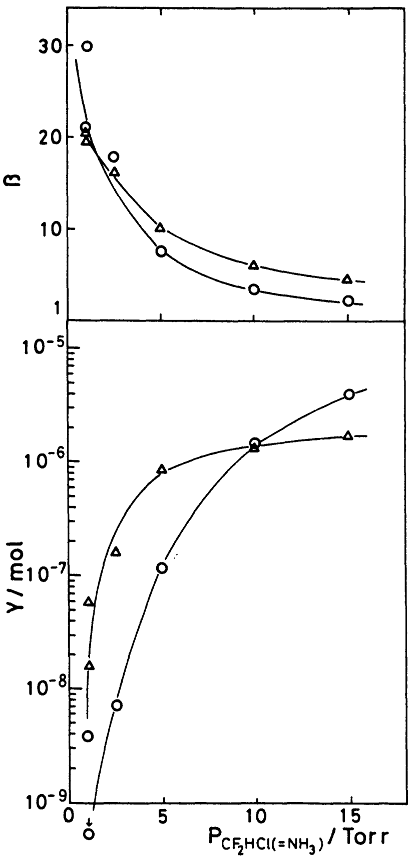

Fig. 8. Effects of total pressure on yields Y and enrichment factors β for IRMPD of equimolar CF_2HCl-NH_3 mixtures. ○, $Y(C_2F_4)$ or $\beta(C_2F_4)$; Δ, $Y(CF_3H)$ or $\beta(CF_3H)$. Laser wavenumber, 1045.02 cm^{-1}; laser fluence at focus, about 28 J cm^{-2}; pulse number, 1000.

mixtures. Y(C) for the mixture of 1.0 Torr CF_2HCl and 1.0 Torr NH_3 was found to be 5.8×10^{-7} mol, while Y(C) for 1.0 Torr neat CF_2HCl was only 6.8×10^{-8} mol; the former yield is about 8 times as large as the latter. The corresponding enrichment factors were $\beta(CF_3H)$= 20 for the mixture and $\beta(C_2F_4)$=30 for the neat CF_2HCl.

Fluence effects on yields and enrichment factors were examined for mixtures of 1.0 Torr CF_2HCl and 5.0 Torr NH_3 in the range from 12 to 30 J cm^{-2}. For examples, $Y(CF_3H)$ and β (CF_3H) at 12 J cm^{-2} were 1.96×10^{-7} mol and 26, respectively, while those at 30 J cm^{-2} were 1.40×10^{-6} mol and 9.0, respectively. $Y(C_2F_4)$ was much less than $Y(CF_3H)$ at either fluence. An increase in fluence enhances product yields and reduces enrichment factors. When CF_2HCl was added to 1.0 Torr NH_3, we observed an increase in $Y(C_2F_4)$ or $Y(CF_3H)$ and a decrease in $\beta(C_2F_4)$ or $\beta(CF_3H)$ with increasing CF_2HCl, as shown in Fig. 7. Similar results were also obtained with total pressure effects on equimolar mixtures of CF_2HCl and NH_3, as shown in Fig. 8.

Discussion

The IRMPD of neat CF_2HCl has been explained satisfactorily in terms of the initial photochemical decomposition of CF_2HCl into CF_2 and HCl, and the subsequent combination between two carbene radicals.[9,18)]

$$CF_2HCl + nh\nu \rightarrow CF_2 + HCl \qquad (1)$$

$$2\,CF_2 \rightarrow C_2F_4 \qquad (2)$$

The same products, i.e., C_2F_4 and HCl have been obtained with the thermal decomposition of CF_2HCl, and the activation energy for the initial decomposition has been found to be 56 kcal mol^{-1} (1 cal=4.184 J) at pressures above 100 Torr.[19)] Since the addition of HCl results in a decrease in decomposition rate, the following back reaction is considered to occur in thermolysis.

$$HCl + CF_2 \rightarrow CF_2HCl \qquad (3)$$

The heat of formation for CF_2, $\Delta H_f(CF_2)$ show large divergence among several determinations.[19,20)] The enthalpy change of the initial decomposition is calculated to be 41 kcal mol^{-1} on the basis of $\Delta H_f(CF_2)$= -49.5 kcal mol^{-1}.[19)]

In the presence of NH_3, one can consider the following bimolecular decomposition with an enthalpy change much less than that of Reaction 1.

$$CF_2HCl + nh\nu \rightarrow CF_2HCl^* \qquad (4)$$

$$CF_2HCl^* + NH_3 \rightarrow CF_2 + NH_4Cl \quad \Delta H = -1 \text{ kcal mol}^{-1} \qquad (5)$$

Therefore, the activation energy of Reaction 5 may be considerably smaller than the 56 kcal mol^{-1} observed for Reaction 1. The reduction in activation energy means that a certain fraction of the excited molecules, which cannot decompose without NH_3, undergo Reaction 5 in the IRMPD of mixtures, where excited CF_2HCl originates from ^{13}C-selective multiple-photon absorption. We conclude that the observed large increases in product yields are caused by the contribution of such excited parent molecules into laser-induced decomposition via Reaction 5.

The formation of C_2F_4 is explained simply by dimerization of two CF_2 radicals in mixtures. However, the rapid decrease of $Y(C_2F_4)$ by adding NH_3 suggests that CF_2 radicals react directly with NH_3 to form a key product, which is responsible for the formation of CF_3H via some subsequent process. The reaction and subsequent process may be as follows.

$$CF_2 + NH_3 \rightarrow HCF_2NH_2 \qquad (6)$$

$$CF_2 + HCF_2NH_2 \rightarrow CF_3H + HCFNH \qquad (7)$$

A further reaction of CF_2 with HCFNH will give CF_3H and HCN.

$$CF_2 + HCFNH \rightarrow CF_3H + HCN$$

The relative yield of CF_3H to the yield of C_2F_4 tends to increase with increasing pulse number, as shown in

Table 1. IRMPD of CF_2HCl-NH_3 Mixtures

CF_2HCl Torr	NH_3 torr	Pulse number	Fluence[a] $J\,cm^{-2}$	$Y(C_2F_4)$	$Y(CF_3H)$	$\beta(C_2F_4)$	$\beta(CF_3H)$	$Y(C)$ per pulse
1.0	0	1000	31	3.4×10^{-8}	0	30	—	6.8×10^{-11}
1.0	1.0	200	25	4.2×10^{-8}	Small	19	b)	4.2×10^{-10}
5.0	0	1000	30	1.7×10^{-6}	0	21	—	3.4×10^{-9}
5.0	5.0	100	28	4.0×10^{-7}	3.5×10^{-8}	18	b)	8.4×10^{-9}
10.0	0	1000	26	5.0×10^{-6}	0	17	—	1.0×10^{-8}
10.0	10.0	30	19	4.9×10^{-7}	2.6×10^{-7}	12	9	4.2×10^{-8}
10.0	10.0	100	26	2.1×10^{-6}	9.8×10^{-7}	8	8	5.1×10^{-8}
10.0	10.0	200	27	3.9×10^{-6}	2.1×10^{-6}	7	8	5.0×10^{-8}

a) Fluence at focus. b) Selectivity could not be determined because of a small yield of CF_3H.

Fig. 2. This fact seems to indicate that the accumulation of a certain compound during pulse irradiation causes the observed preferential formation of CF_3H in a late period. However, we failed to detect directly HCF_2NH_2 by gas chromatography.

CF_2HCl is one of the most promising working molecules in ^{13}C separation by IRMPD. Gauthier et al. have reported that the irradiation of 100 Torr natural CF_2HCl with the CO_2 laser radiation at 1046.9 cm^{-1} and 3.5 $J\,cm^{-2}$ yields C_2F_4 containing 50% ^{13}C at the efficiency that an absorption of 140 photons produces one carbon atom.[9] Therefore, a 100-watt CO_2 TEA laser can produce carbon at rate of 1.3 $g\,h^{-1}$, if 50% of the laser radiation is absorbed by CF_2HCl. Although the production rate is sufficiently high in their experiment, the ^{13}C content must be increased to 90% or higher for practical purposes. In the previous paper we have proposed the two-stage IRMPD separation of ^{13}C using CF_2Cl_2-HI and CF_2ClBr-HI mixtures, where the first IRMPD gives CF_2HCl with a ^{13}C content of about 30% and the second IRMPD of the CF_2HCl is expected to result in the production of highly enriched ^{13}C. Since CF_2ClBr decomposes at low laser fluences, one can obtain a relatively high yield of CF_2HCl in the CF_2ClBr-HI mixture. The production of 90% ^{13}C from the CF_2HCl with a ^{13}C content of about 30% corresponds to a separation process with an enrichment factor of only 21.

Table 1 tabulates yields and enrichment factors for the IRMPD of CF_2HCl in the presence of NH_3. The results clearly demonstrate that a total carbon yield per pulse increases significantly by adding NH_3 without a large loss of selectivity. The effect may be useful for the second stage in the IRMPD separation of ^{13}C using a CF_2ClBr-HI mixture.

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