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CO_2-Laser Isotope Separation of Tritium with Pentafluoroethane-T (C_2TF_5)

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Abstract. Isotope separation of tritium by CO_2 laser-induced multiphoton dissociation (MPD) of C_2TF_5 is reported for the first time. The MPD spectrum obtained for C_2TF_5 comprised a broad peak at about 940 cm^{-1} where C_2HF_5 was nearly transparent. The unimolecular dissociation of C_2TF_5 was induced with much lower laser fluence than that for CTF_3, another working molecule we proposed for laser isotope separation of tritium. The mechanisms and kinetics of the dissociation of C_2TF_5 and C_2HF_5 were investigated under various experimental conditions: laser frequency, pulse energy, pulse duration, tritium concentration, sample pressure, buffer gas pressure and irradiation geometry. Single-step separation factors exceeding 500 were achieved with the most efficient $P(20)$ line in $00^\circ1$–$10^\circ0$ transition at 944.2 cm^{-1}.

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While remarkable capabilities of laser isotope separation (LIS) have been shown of many isotopes during last several years [1–4], the attempt for separation of radioactive isotopes by means of infrared lasers has been limited only to uranium [5, 6]. Since the energy used for LIS is, in principle, concentrated in the intended isotope, this new method can be most eligible for radioisotope separation because molar concentrations of radioisotopes are very low in most cases even if they are highly radioactive.

A novel isotope separation technique for tritium is needed with the development of nuclear fuel reprocessing plants in Japan. We have reported for the first time a successful isotope separation of tritium by CO_2 laser induced multiphoton dissociation (MPD) of trifluoromethane-T (CTF_3) [7] which proved to be the best compound among the tritiated halomethanes we surveyed. Later Herman and Marling reported the infrared (ir) spectrum of synthesized CTF_3 [8] which was in substantial agreement with our MPD spectrum of CTF_3 [7, 9] considering the red-shift of the peak in MPD.

After the first successful attempt, we have investigated systematically the dependency of the dissociation rates of CTF_3 and CHF_3 on laser frequency, pulse energy, pulse duration, irradiation geometry, tritium concentration, sample pressure, and buffer gas pressure [9]; isotopic selectivity exceeding 500 was attained by the addition of argon buffer gas under mildly-focused geometry. The effect of the irradiation geometry was studied in detail by using a newly developed deconvolution method for obtaining the correlation between laser fluence and fractional conversion per pulse [10]. By cooling the sample mixture at dry ice temperature during the irradiation, high selectivity was attained at higher operating pressures [11]. Selectivities above 500

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have been obtained at desirably high pressures such as 100 Torr. We also reported the separation of CDF_3 from CTF_3 [12].

In search of other candidates for the working molecule in tritium isotope separation, we have extended our survey to halogenated ethanes for which far lower threshold fluence for MPD is expected as compared with trifluoromethane-T. Among these, pentafluoroethane-T (C_2TF_5) has been found to dissociate most efficiently by CO_2 laser irradiation at 10.6 μm band where C_2HF_5 is transparent. In this paper, we report the dependency of MDP rates of C_2TF_5 and C_2HF_5 and isotopic selectivity on the laser frequency, pulse number, pulse energy, pulse duration, tritium concentration, sample pressure, buffer gas pressure and irradiation geometry.

1. Experimental

Pentafluoroethane (C_2HF_5, boiling point: $-48.5\,°C$) was purchased from PCR, Inc. (USA) and purified by trap-to-trap distillation before use. Pentafluoroethane-T was prepared by the hydrogen isotope exchange of C_2HF_5 with HTO in the presence of sodium hydroxide and dimethylsulfoxide: about 40 ml (STP) of C_2HF_5 gas was introduced into a mixture of tritiated water (1 ml, 1 mCi), NaOH (100 mg) and $(CH_3)_2SO$ (1 ml) in a flask connected to the vacuum line. The mixture was agitated for several hours at 50°–70 °C. The tritium labeled pentafluoroethane was purified by passing through a cold trap at dry ice temperature. The typical concentration of C_2TF_5 in C_2HF_5 thus obtained was 0.2 ppm (≈ 0.3 μCi/ml).

A TEA CO_2 laser (Lumonics Model 103-2) was used with a lasing gas of He and CO_2 (≈ 100 ns pulse duration) for irradiation of the sample in a Pyrex photolysis cell equipped with KCl windows. Laser pulses of 0.3–0.7 J at 1 Hz repetition rate passed through an aperture (14 mm⌀) were focused into the center of the photolysis cell (20 mm⌀, 100 mm or 450 mm long) by means of a BaF_2 lens (75 mm or 380 mm in focal length).

The irradiated sample was once condensed in an evacuated sample loop cooled at liquid nitrogen temperature, and then analyzed by radio-gas chromatography. A Porapak Q separation column (80–100 mesh, 5 mm i.d., 3 m long) was mainly used with He carrier gas (30 ml/min) at 50 °C for 16 min, then the temperature was raised linearly at 4 °C/min up to 150 °C.

The amounts of C_2HF_5 and its photolysis products were determined with a thermal conductivity detector (TCD). After mixing propane (80 ml/min) into the carrier gas helium, C_2TF_5 and its tritiated photolysis products were determined with an internal gas-flow proportional counter (PC) heated at 60 °C. While the responses of both detectors were monitored with a two-pen strip chart recorder, as shown in Fig. 1, each compound was determined quantitatively by measuring the electronically integrated TCD peak area or the total radioactivity counts for the peak [12]. The analyses of C_2HF_5 and C_2TF_5 were reproducible within 0.3 % and 1.0 %, respectively.

Since C_2TF_5 is present in trace amounts, the chemical composition or total pressure of the irradiated sample is affected only by the decomposition of C_2HF_5. Therefore, the laser pulse number for irradiation was chosen to induce 10–80 % decomposition of C_2TF_5 for obtaining better accuracy in quantitative measurements, where the decomposition of C_2HF_5 was usually kept below 10 %.

2. Results and Discussion

2.1. Hydrogen Isotope Exchange Between Pentafluoroethane and Tritiated Water

Pentafluoroethane was labeled readily with tritium in tritiated water by nearly the same method developed for the tritiation of trifluoromethane [7, 12]. Although the rate of hydrogen isotope exchange between C_2HF_5 and D_2O was negligibly slow in a sodium hydroxide aqueous solution (and similar system has been reported before [13]), it was enhanced remarkably (more than thousand times) by the addition of $(CH_3)_2SO$, which is known to increase the basicity of alkaline solution [14, 15]. Similar enhancement has been observed in the case of base-catalyzed hydrogen exchange with D_2O of $CHCl_3$ [16], H_2 [17], and CHF_3 [18]. After the tritiation (of C_2HF_5), C_2TF_5 was the only tritiated species found by radio-gas chromatographic analysis.

2.2. Chemical Change Induced by Laser Irradiation

Pentafluoroethane-T excited by ir multiphoton absorption (MPA) may decompose via two pathways as shown below (1) and (2): molecular elimination of hydrogen fluoride and C–C bond rupture.

$$C_2TF_5 \xrightarrow{nh\nu} C_2F_4 + TF\,, \qquad (1)$$

$$C_2TF_5 \xrightarrow{n'h\nu} \cdot CTF_2 + \cdot CF_3\,. \qquad (2)$$

Small amounts of tritium fluoride produced may have reacted with glass surface of the photolysis cell and were removed from the gas phase. The tritium in another tritiated product, CTF_2 radical, was found in

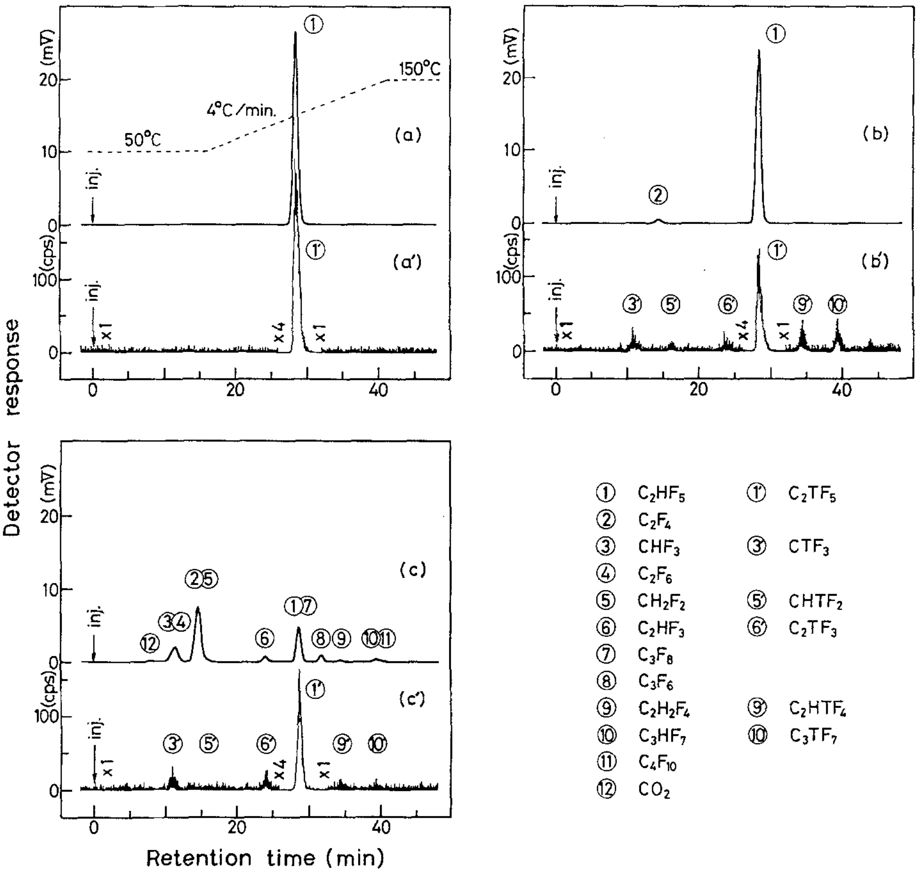

Fig. 1. (a) and (a′) gas chromatogram (TCD) and radio-gas chromatogram (proportional counter), respectively, of non-irradiated reference sample (C_2TF_5/C_2HF_5, 0.2 ppm); broken line indicates temperature programming of analytical column (Porapak Q); (b) and (b′) chromatograms of the sample irradiated at 944.2 cm^{-1} for 1100 pulses; (c) and (c′) chromatograms of the sample irradiated at 1078.6 cm^{-1} for 960 pulses

chemical forms such as CTF_3, $CHTF_2$, C_2TF_3, C_2HTF_4, and C_3TF_7 (Fig. 1b′).

When the major component C_2HF_5 was decomposed, CHF_3, CH_2F_2, C_2F_4, C_2F_6, C_2HF_3, $C_2H_2F_4$, C_3F_6, C_3F_8, C_3HF_7, C_4F_{10}, and CO_2 (from COF_2) were detected with TCD as the products (Fig. 1c). SiF_4 was also observed in ir spectrum as a reaction product of HF with the glass surface.

The identification of each peak in radio-gas chromatogram was confirmed by comparison with the known sample or estimation on the basis of the correlation between atomic composition of halogenated hydrocarbons and retention time in gas chromatography [19, 20]. The other separation columns such as Porapak T were also used for identification.

The overall distribution of gaseous tritiated products can be explained as the consequence of the following reactions of tritiated CTF_2 radical with other radicals derived from C_2HF_5:

$$\cdot CTF_2 + \cdot CF_3 \longrightarrow :CF_2 + \cdot CTF_3 \tag{3}$$

$$\longrightarrow [C_2TF_5]^* \longrightarrow C_2F_4 + TF \tag{4}$$

$$\xrightarrow{M} C_2TF_5 \tag{5}$$

$$\cdot CTF_2 + \cdot CHF_2 \longrightarrow :CF_2 + CHTF_2 \tag{6}$$

$$\longrightarrow [C_2HTF_4]^* \longrightarrow C_2TF_3 + HF \tag{7}$$

$$\xrightarrow{M} C_2HTF_4 \tag{8}$$

$$\cdot CTF_2 + \cdot C_2F_5 \longrightarrow [C_3TF_7]^* \longrightarrow C_3F_6 + TF \tag{9}$$

$$\xrightarrow{M} C_3TF_7. \tag{10}$$

On the other hand, the decomposition of the major component C_2HF_5 produces radicals in much higher concentrations:

$$C_2HF_5 \xrightarrow{mh\nu} C_2F_4 + HF \tag{11}$$

$$C_2HF_5 \xrightarrow{m'h\nu} \cdot CHF_2 + \cdot CF_3 . \tag{12}$$

Then these reactions are followed by radical-radical reactions:

$$\cdot CF_3 + \cdot CF_3 \longrightarrow C_2F_6 \tag{13}$$

$$\cdot CHF_2 + \cdot CF_3 \longrightarrow :CF_2 + CHF_3 \tag{14}$$

$$\longrightarrow [C_2HF_5]^* \longrightarrow C_2F_4 + HF \tag{15}$$

$$\xrightarrow{M} C_2HF_5 \tag{16}$$

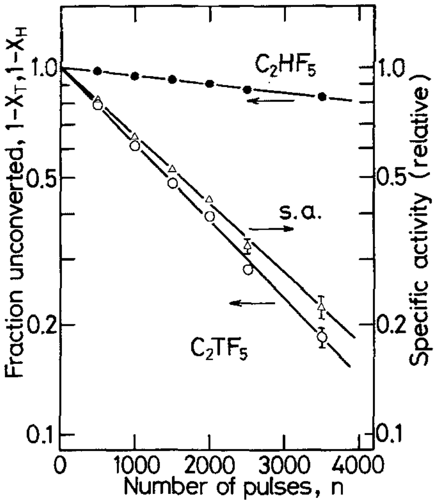

Fig. 2. Pseudo-first-order decay plots of C_2TF_5 (○) and C_2HF_5 (●), and specific activity of residual gas (△) by the CO_2 laser irradiation at $P(20)$, 944.2 cm^{-1}. $E_0 = 0.6$ J. Sample: 2 Torr C_2HF_5 containing 0.2 ppm C_2TF_5 (0.3 µCi/ml). X_T and X_H: fraction decomposed

$$\cdot CHF_2 + \cdot CHF_2 \longrightarrow :CF_2 + CH_2F_2 \qquad (17)$$

$$\longrightarrow [C_2H_2F_4]^* \longrightarrow C_2HF_3 + HF \qquad (18)$$

$$\xrightarrow{M} C_2H_2F_4 \qquad (19)$$

$$\cdot CF_3 + :CF_2 \longrightarrow \cdot C_2F_5 \qquad (20)$$

$$\cdot CF_3 + \cdot C_2F_5 \longrightarrow C_3F_8 \qquad (21)$$

$$\cdot CHF_2 + \cdot C_2F_5 \longrightarrow [C_3HF_7]^* \longrightarrow C_3F_6 + HF \qquad (22)$$

$$\xrightarrow{M} C_3HF_7 \qquad (23)$$

$$\cdot C_2F_5 + \cdot C_2F_5 \longrightarrow C_4F_{10}. \qquad (24)$$

Shock-wave pyrolysis of C_2HF_5 has been studied by Tschuikow-Roux et al. [21]. While they proposed mechanisms similar to (13)–(24) for the radical reactions following the primary dissociation processes (11) and (12), they suggested that CHF_3 and CH_2F_2 are mainly supplied from the reactions of fluoromethyl radicals with the parent molecule C_2HF_5 [(25) and (26)] but not from H abstraction reactions between radicals (14) and (17):

$$\cdot CF_3 + C_2HF_5 \longrightarrow CHF_3 + \cdot C_2F_5 \qquad (25)$$

$$\cdot CHF_2 + C_2HF_5 \longrightarrow CH_2F_2 + \cdot C_2F_5. \qquad (26)$$

However the attack of the CF_3, CHF_2 or CTF_2 radicals on the pentafluoroethane (C_2HF_5 and C_2TF_5) shown in (25)–(29) was considered to be unimportant in our MPD experimental conditions,

$$\cdot CF_3 + C_2TF_5 \longrightarrow CTF_3 + \cdot C_2F_5 \qquad (27)$$

$$\cdot CHF_2 + C_2TF_5 \longrightarrow CHTF_2 + \cdot C_2F_5 \qquad (28)$$

$$\cdot CTF_2 + C_2HF_5 \longrightarrow CHTF_2 + \cdot C_2F_5 \qquad (29)$$

because of the following experimental results:

(i) the specific activity of the trifluoromethane in the products was found to be more than ten times higher than that of reactant pentafluoroethane; these two values should be equal if the reactions (25) and (27) are the main sources of the trifluoromethane. The specific activity ratio of trifluoromethane and original pentafluoroethane was rather close to the isotopic selectivity in the dissociation of C_2TF_5 and C_2HF_5.

(ii) CF_3 radicals produced in the presence of C_2HF_5 did not react with C_2HF_5: when a mixture of hexafluoroacetone [$(CF_3)_2CO$] and C_2HF_5 in a photolysis cell was irradiated by the CO_2 laser at 970 cm^{-1} which corresponds to the maximal MPD of $(CF_3)_2CO$ [22], neither decrease of C_2HF_5 nor formation of CHF_3 was observed after 60% of $(CF_3)_2CO$ had decomposed. In the meantime, C_2F_6 was produced by the recombination of CF_3 radicals. Accordingly the radical attack on the parent molecule (radical scrambling), which often reduces isotopic selectivity [23], can be neglected in the pentafluoroethane system.

Although Hackett et al. have reported the ir laser-induced MPD of C_2HF_5 at 1078 cm^{-1} and proposed mechanisms similar to (13)–(18) for the radical reactions [24], they have not mentioned the formation of $C_2H_2F_4$, C_3HF_7, C_3F_6, C_3F_8, and C_4F_{10}. Since tritium in the MPD products other than TF was found mostly in $C_2H_2F_4$ and C_3HF_7 fractions as C_2HTF_4 and C_3TF_7 (Fig. 1b'), the formation of such compounds can not be ignored to elucidate the overall reaction scheme.

By the addition of oxygen, however, all the primary radical products were scavenged and were detected as COF_2 (in ir measurements) or as CO_2 after the gas chromatographic separation. Since the dissociation rates of C_2TF_5 and C_2HF_5 were not affected substantially by the radical products although the distribution of the products is dependent on the secondary processes, we will mainly discuss in this paper the dissociation of C_2TF_5 and C_2HF_5 and the selectivity in dissociation between the isotopically substituted molecules.

2.3. Dependence of Dissociated Fraction and Specific Activity on Number of Laser Pulses

When the sample mixture ($C_2TF_5 + C_2HF_5$) was irradiated with $P(20)$ line at 944.2 cm^{-1}, the unchanged fractions of C_2TF_5 ($1-X_T$) and of C_2HF_5 ($1-X_H$) both decreased exponentially with the increase in pulse number n (Fig. 2), indicating pseudo-first order decays over a fairly wide range of conversion (X_T and X_H),

$$1 - X_T = \exp(-d_T n),$$

$$1 - X_H = \exp(-d_H n),$$

where d_T and d_H correspond to the slopes and are named the apparent dissociation rate constants for

C_2TF_5 and C_2HF_5, respectively:

$$d_T = -(1/n)\ln(1 - X_T),$$

$$d_H = -(1/n)\ln(1 - X_H).$$

Since d_T and d_H values remained constant, it is not likely that the dissociation of C_2TF_5 and C_2HF_5 is affected by the reaction products in these conversion ranges.

The ratio of these dissociation rate constants gives the selectivity ($S_{T/H}$) between the two isotopic molecules:

$$S_{T/H} = d_T/d_H.$$

Under the experimental conditions shown in Fig. 2, the $S_{T/H}$ value was obtained as 9.0.

The specific activity of the residual gas was also decreased exponentially (Fig. 2), demonstrating that tritium is removed from the mixture selectively – that is exactly what the radioactive-waste treatment aims at.

2.4. Frequency Dependence of Dissociation Rates for C_2TF_5 *and* C_2HF_5 *and Isotopic Selectivity*

The effect of laser frequency on the MPD rates for C_2TF_5 (d_T) and for C_2HF_5 (d_H) was measured over the CO_2 laser emission region: 9–11 µm (Fig. 3).

As is expected from the ir spectrum of C_2HF_5 with a strong *a'* fundamental absorption band at 1111 cm^{-1} [25, 26], d_H showed large values at higher frequency region (>1060 cm^{-1}). However it decreased sharply toward lower frequency and resulted in very small values over the wide frequency range (from 1030 to 940 cm^{-1}). It increased again slightly toward much lower frequency corresponding to a weak combination band observed at 936 cm^{-1}. The red-shift in MPD spectrum can be reasonably explained in terms of the anharmonic shift of the vibrational levels of excited molecules [27–29], which favors the excitation by lower frequency laser lines.

Although the ir spectrum of pure C_2TF_5 has not been measured yet because of its high radioactivity, the result of the MPD of C_2TF_5 showed a characteristic MPD spectrum composed of a broad peak at around 940 cm^{-1} (Fig. 3). The selectivity $S_{T/H}$, or the ratio of d_T to d_H, has a maximum at about 950 cm^{-1}, as shown in the upper part of Fig. 3. On the other hand, selectivities become less than unity in 9 µm band, indicating that C_2HF_5 dissociates more readily than C_2TF_5 in this frequency region. When dielectric breakdown was induced intentionally by increasing either sample pressure or pulse energy, the selectivity between the two isotopic molecules disappeared. It ensures that the analytical procedure has not been isotopically biased and the selectivities obtained at different lines are an evidence for the real isotope-selective phenomena.

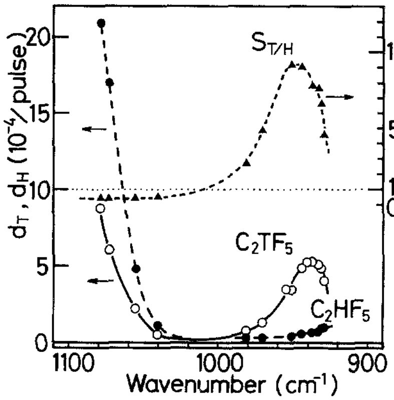

Fig. 3. Frequency dependence of dissociation rate constants for C_2TF_5 (○) and C_2HF_5 (●) and of selectivity $S_{T/H}$ (▲). Sample: 2 Torr C_2HF_5 containing 0.2 ppm C_2TF_5. $E_0 = 0.6$ J

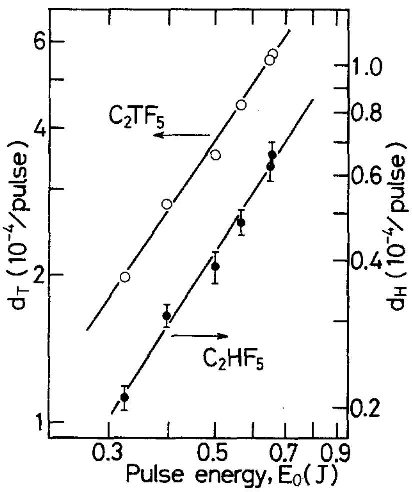

Fig. 4. Dependence of dissociation rate constants for C_2TF_5 (○) and C_2HF_5 (●) upon laser pulse energy

The laser line used for irradiations in all the other experiments was fixed at 00°1–10°0 transition $P(20)$ (944.2 cm^{-1}) for the following reasons: *(i)* the value of $S_{T/H}$ at 944 cm^{-1} is very close to the maximum value; *(ii)* the dissociation rate of C_2TF_5 (d_T) at 944 cm^{-1} is only 10% below the d_T value at the maximum; *(iii)* TEA CO_2 lasers can emit $P(20)$ line most efficiently in all the emission lines, and $P(20)$ is the only line which is emitted spontaneously even without line tuning.

2.5. Effect of Pulse Energy and Pulse Duration on Dissociation Rates

The dependence of the dissociation rates (d_T and d_H) on laser pulse energy (E_0) was investigated under tightly-focused geometry by using a 75 mm focal length (f.l.) lens. As is shown in Fig. 4, both $\log d_T$ and $\log d_H$ were correlated linearly with $\log E_0$ (in the range of 0.3–0.7 J)

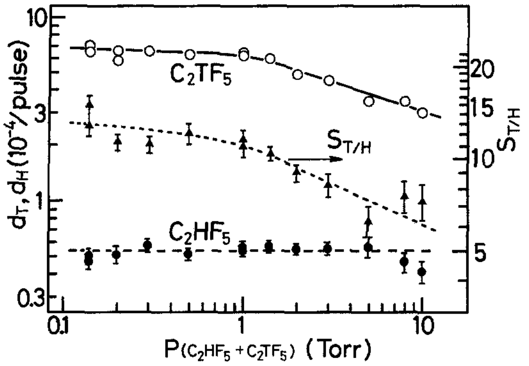

Fig. 5. Pressure dependence of dissociation rate constants for C_2TF_5 (○) and C_2HF_5 (●) and of selectivity $S_{T/H}$ (▲)

with slopes very close to 1.5 ($d_T \propto E_0^{1.45 \pm 0.05}$ and $d_H \propto E_0^{1.54 \pm 0.09}$).

Since d_T corresponds to the fractional volume of the dissociation zone (V) where the laser fluence (Φ) exceeds the critical value for dissociation of C_2TF_5 (Φ_c), this 3/2-power dependency of d_T on E_0 only suggests that the reaction zone in this relatively large E_0 range can be approximated simply by a "double cone" geometry [30, 31], where the contribution of diffraction zone due to the beam divergence is neglected. According to a simple threshold model [30, 31] which assumes that the fractional dissociation probability (q) is unity (or complete decomposition) inside the zone where $\Phi \geqq \Phi_c$ but negligible outside the zone, the value of Φ_c for C_2TF_5 was calculated as 19 J/cm^2 at 2 Torr sample pressure. Since the value of Φ_c for CTF_3 in the same conditions has been estimated to be as high as 80 J/cm^2 (2 Torr $CTF_3 + CHF_3$ mixture at 1075 cm^{-1}) [9], the MPD in C_2TF_5 is suggested to be much more efficient than that in CTF_3.

The reaction zone for C_2HF_5 can also be approximated by the double-cone geometry and the Φ_c value for C_2HF_5 under the same conditions was estimated at 80 J/cm^2 in the same manner.

When a more accurate geometrical expression is adopted and the value of q is expressed more realistically as $q = 1$ for $\Phi \geqq \Phi_c$ and $q = (\Phi/\Phi_c)^{n'}$ for $\Phi < \Phi_c$ ($n' = 3 \sim 6$ depending on compound and irradiation condition), the values of Φ_c should be somewhat higher [10, 31].

By the addition of nitrogen to the lasing gas ($He : CO_2 : N_2 = 0.88 : 0.10 : 0.02$), the pulse energy increased by the contribution of 1 µs tail following the 100 ns spike peak. When the dissociation rates for C_2TF_5 and C_2HF_5 with such longer pulses were compared with those for 100 ns pulses (without N_2 in the lasing gas), d_T and d_H decreased to about half and two-thirds, respectively, for the same pulse energy. The $S_{T/H}$ value also decreased as the result.

Multiphoton dissociation rate has been recognized to be primarily determined by overall energy fluence [27, 32, 33]. The decrease in the dissociation rate observed for C_2TF_5 and C_2HF_5 with 1 µs pulses may be attributed (as minor effects) to the lowering of peak intensity with the same fluence and/or to the increase in the probability of collisional deexcitation of partially activated molecules during the long laser pulse.

2.6. Sample Composition and Pressure Effect

When the tritium concentration in pentafluoroethane was changed over a wide range (0.01 ppm – 2 ppm) at a constant C_2HF_5 pressure, the value of d_T remained unchanged, which is quite reasonable since there is no chance of collision between C_2TF_5 molecules due to its extremely low partial pressure (≈ 1 µTorr). The d_H value also remained constant throughout the concentration range and was in good agreement with the d_H value in neat C_2HF_5, indicating that the dissociation of non-resonant C_2HF_5 molecules takes place independently of C_2TF_5. Hence it is obvious that decomposition of C_2HF_5 was not induced by the energy transfer from an excited resonant molecule C_2TF_5 to non-resonant C_2HF_5, but rather by multiphoton absorption of C_2HF_5 itself; the isotopic selectivity will be increased most efficiently by controlling the latter mechanism.

Figure 5 shows the pressure dependence of the dissociation rates of C_2TF_5 and C_2HF_5 and the isotopic selectivity. As the pressure of $C_2TF_5 + C_2HF_5$ mixture was increased from 0.1 to 10 Torr, the d_T value gradually decreased at above 1 Torr. The collision frequency of C_2TF_5 with C_2HF_5 molecules is estimated to be about 10^7 s^{-1} at 1 Torr from the simple gas kinetic theory [34], which corresponds to one collision per Torr within the duration of laser pulse (≈ 100 ns): this suggests that the excited C_2TF_5 molecules suffer vibrational quenching via collision with non-resonant C_2HF_5 at above 1 Torr. The decrease in the reaction probability of resonant molecules due to collisional deexcitation is often observed in most polyatomic molecules [27, 35, 36].

In the case of trifluoromethane, on the other hand, the dissociation rate of resonant CTF_3 molecule increased with the increase in the sample pressure [9], indicating the collisional relaxation of the rotational bottlenecking during the multiphoton excitation. The bottleneck condition is observed particularly in small molecules due to lower density of vibrational states [27, 28, 37]. Since higher density of vibrational-rotational states is expected in large molecules and the quasicontinuum starts at relatively low vibrational levels, C_2TF_5 seems to be free from the rotational bottlenecking in its MPD.

By the addition of argon (or nitrogen) buffer gas no enhancement of dissociation rate was observed for

C_2TF_5, but d_T decreased gradually, indicating the same collisional deexcitation effect.

The reaction rate of C_2HF_5 (d_H) is scarcely changed by increasing the sample pressure over this range while it slightly decreased at higher pressure near 10 Torr or with addition of buffer gas. Besides the collisional-quenching, enhancement of the dissociation of C_2HF_5 may be taking place at above 1 Torr C_2HF_5 pressure: *(i)* collision-induced energy disproportionation between slightly-excited C_2HF_5 molecules in the early stage of excitation, followed by non-selective laser light absorption leading to the dissociation, and/or *(ii)* collision-induced dissociation between C_2HF_5 molecules which are excited but not sufficiently to spontaneous unimolecular dissociation.

The isotopic selectivity $S_{T/H}$ also decreased with the sample pressure above 1 Torr, as shown in Fig. 5. Since this trend is due to collisional effect and not due to secondary reactions, however, the introduction of a CO_2 laser with shorter pulse duration such as 2 ns [38, 39] will increase the pressure range free from collisional effect without sacrificing the selectivity.

2.7. *Effect of Irradiation Geometry*

Tightly-focused geometry was adopted in the first series of experiment since C_2TF_5 was not decomposed with unfocused beam due to the limited laser power. This irradiation geometry is simple and convenient for obtaining the approximated values of critical fluence for dissociation of C_2TF_5 and C_2HF_5 molecules. It is also useful to normalize the observed values of dissociation rates to the same laser pulse energy according to the 3/2-power dependency described in Sect. 2.5. However, the energy fluence at beam waist (around the focal point) is estimated to be as high as one thousand joules per square centimeter for a 75 mm f.l. lens (based on the laser beam divergence of 3.5 m rad), and is too high for dissociation of resonant C_2TF_5. Even non-resonant C_2HF_5 is decomposed completely near the focal region and the isotopic selectivity is lost in this region, resulting in the selectivity value as low as 9 as the total.

As indicated in Sect. 2.5, if we lower the maximum fluence at the waist to between the Φ_c values for C_2HF_5 (80 J/cm^2) and for C_2TF_5 (19 J/cm^2) by using longer f.l. lenses, the isotopic selectivity should increase substantially. Furthermore, Rayleigh range is prolonged and the reaction volume for C_2TF_5 should increase at the same time. Consequently a 380 mm f.l. lens was used in another experiment, with a larger photolysis cell (450 mm long, 170 ml volume) considering the damage threshold fluence for KCl windows of 3–6 J/cm^2. The fluence at the focal point decreases to about 30 J/cm^2 (at 0.6 J pulse), and the reaction volume of C_2TF_5 above 19 J/cm^2 increases considerably. As the result, d_T increased ($\approx 1.0 \times 10^{-3}$), d_H decreased ($\approx 2.0 \times 10^{-6}$), and thus $S_{T/H}$ increased remarkably to ≈ 500.

By using a lens with much longer focal length (e.g. 520 mm f.l.), selectivities far beyond 500 have been attained, while improvement of the analytical setup or introduction of a new analytical method is necessary to determine these values exactly under such highly selective conditions and extremely low conversion of C_2HF_5.

4. Concluding Remarks

The tritium isotope separation by CO_2 laser-induced MPD of C_2TF_5 in C_2HF_5 was achieved for the first time with the selectivity above 500. Since the critical fluence needed for MPD of C_2TF_5 is far lower than that for CTF_3 and the optimal laser line was $P(20)$ at 10.6 µm which is most efficiently emitted by TEA CO_2 lasers, pentafluoroethane may be one of the most feasible compounds as the working molecule for LIS of tritium.

Since the selectivity was found to be increased most effectively by suppressing the light absorption of non-resonant C_2HF_5 molecule, this method will be further improved by cooling the sample mixture as well as by optimizing the irradiation geometry. While the dissociation of resonant C_2TF_5 is hampered at higher pressure by collisional deexcitation, the pressure range giving the high selectivity will be extended by short pulse CO_2 lasers.

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