ISOTOPIC SELECTIVITY CONTROLLED BY RADICAL REACTIONS AFTER CO$_2$ LASER PHOTOLYSIS OF CF$_3$CDCl$_2$

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Summary

In deuterium separation by multiphoton dissociation of 2,2-dichloro-1,1,1-trifluoroethane using a CO$_2$ laser, radical reactions are known to decrease the isotopic selectivity. A series of experiments utilizing a tightly focused beam geometry for reaction analysis by a simple threshold model is reported. Gas chromatographic analysis suggests that the radical reactions take place in the photolysis zone before diffusion becomes significant. A mathematical model of the effect of the chlorine radical scavenger is found to give a satisfactory description of the experimental results.

1. Introduction

Recently chemical applications of lasers have been attracting attention for such practical goals as isotope separation [1 - 3] and the production of ultrapure substances [4]. In particular, the attempt to enrich deuterium by IR multiphoton dissociation has been found to give very high enrichment factors at high operating pressures.

For the laser-induced separation of hydrogen isotopes, a working substance is partially deuterated by contact with natural water, the deuterium feed stock, and only the deuterated working substance is dissociated by laser irradiation. The deuterium-containing product is separated from the unreacted material by conventional methods and the deuterium-depleted working substance is recirculated for further deuteration. Such a scheme has been discussed in detail by Marling and Herman [5]. A CF$_3$CDCl$_2$–CF$_3$CHCl$_2$ mixture (2,2-dichloro-1,1,1-trifluoroethane) is a candidate for such a working substance [6].

The selectivity S is an important factor in laser isotope separation since it gives the upper limit of the enrichment factor for the product. For 2,2-dichloro-1,1,1-trifluoroethane it is known that the selectivity is controlled

by the radical reactions (scrambling) after photolysis. Therefore the role of the radical reactions in laser isotope separation using this molecule can be best studied by means of selectivity measurements.

It is also known that CF_3CDCl_2 has two photolytic channels, *i.e.* the molecular elimination of DCl and the fission of the C—Cl bond. Such a mechanism is also best studied by revealing the effects of radical reactions.

2. Experimental details

Figure 1 shows a schematic diagram of the experimental set-up used. A transversely excited atmospheric pressure CO_2 laser (Lumonics 821) with a gas mixing ratio $He:CO_2:N_2$ of 83:17:0 was employed. The energy per pulse was held constant at 0.035 J. The laser line was selected to the peak P(28) of the 10.6 μm band at 936 cm^{-1}, which is in resonance with the C—D bending mode of CF_3CDCl_2. The pulse energy was measured with a pyroelectric detector (Lumonics 20D) calibrated to a disc calorimeter (Scientech 364) as a standard. The laser beam was collimated by a metal aperture and then focused onto the centre of a Pyrex glass cell (10 cm long for irradiation and 5 cm long for IR spectroscopy analysis) by a BaF_2 lens (focal length, 7.5 cm).

The protonated sample (CF_3CHCl_2; purity, 98.5%) was obtained from Daikin Kogyo Co. Ltd., and the deuterated sample was prepared by a standard procedure [7]. The impurity was mostly $CF_2ClCHFCl$, the isomer of CF_3CHCl_2. For the product analysis, a gas chromatograph with a flame ionization detector equipped with a stainless steel Porapak Q column 3 mm in diameter and 3 m long was used at 150 °C for analysis of CF_2CFD (or CF_2CFH), CF_2CFCl, CF_3CDCl_2 (or CF_3CHCl_2) and CF_3CCl_3. After irradiation by the laser beam the sample was completely recovered in the sample loop by liquid nitrogen condensation and was then introduced to the gas chromatograph. An IR spectrophotometer (JASCO A102) was used for measurement of the isotopic selectivities.
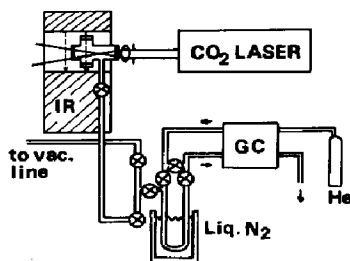

Fig. 1. Schematic diagram of the experimental set-up for product analysis and selectivity measurement.

3. Radical reaction mechanisms

3.1. Results

Figure 2 shows the changes in the fractional conversions X with the number t of pulses for neat CF_3CDCl_2 and CF_3CHCl_2. Unlike the results for CDF_3, the plot of $-\ln(1-X)$ *versus* t is non-linear probably because of the existence of secondary thermal reactions. However, when the conversion is low, the pseudo-first-order reaction treatment may be applicable as stated elsewhere [8]. We focus our attention on this low conversion range. The selectivity S for the photolysis of neat isotopic compounds which is given by the ratio of the slopes at $t = 0$ in Fig. 2 was greater than 300. Figure 3 shows similar results for an equimolar mixture of CF_3CDCl_2 and CF_3CHCl_2 (0.67 kPa each). The selectivity S for the mixture was drastically reduced to 1.9 compared with S for photolysis of the neat compounds. The reason for such a decrease is our main interest.
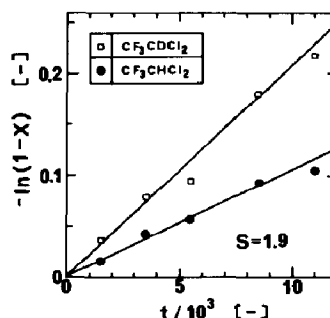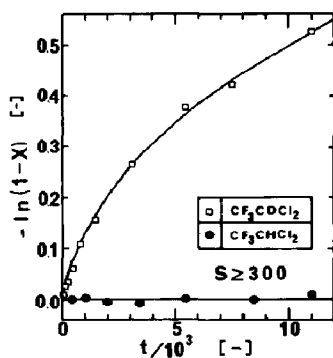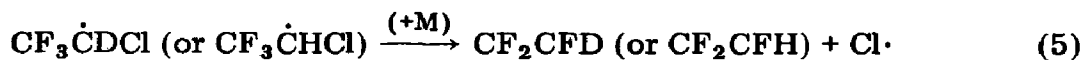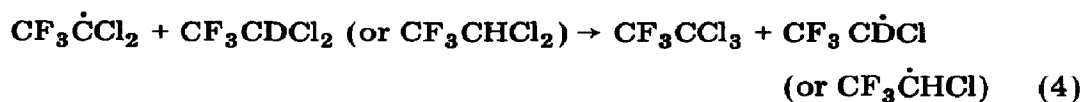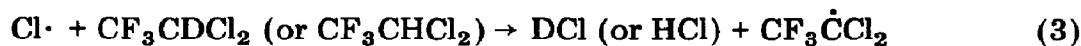

Fig. 2. Determination of the selectivity for neat CF_3CDCl_2 and CF_3CHCl_2 (0.67 kPa).

Fig. 3. Determination of the selectivity for the $CF_3CDCl_2-CF_3CHCl_2$ mixture (0.67 kPa each).

Marling and Herman [6] have suggested that radical reactions by Cl· contributed to this decrease. They postulated the reaction scheme

$$CF_3CDCl_2 \xrightarrow{nh\nu} CF_2CFD + 2Cl· \tag{1}$$

$$CF_3CDCl_2 \xrightarrow{mh\nu} CF_2CFCl + DCl \tag{2}$$

$$Cl· + CF_3CDCl_2 \text{ (or } CF_3CHCl_2) \rightarrow DCl \text{ (or HCl)} + CF_3\dot{C}Cl_2 \tag{3}$$

$$CF_3\dot{C}Cl_2 + CF_3CDCl_2 \text{ (or } CF_3CHCl_2) \rightarrow CF_3CCl_3 + CF_3\dot{C}DCl$$

$$\text{(or } CF_3\dot{C}HCl) \tag{4}$$

$$CF_3\dot{C}DCl \text{ (or } CF_3\dot{C}HCl) \xrightarrow{(+M)} CF_2CFD \text{ (or } CF_2CFH) + Cl· \tag{5}$$

$$Cl· \rightarrow \text{termination by scavenging reaction} \tag{6}$$

Reactions (3) - (6) are believed to explain the production of both CF_2CFD and CF_3CCl_3. Since no study has been reported to verify this scheme, we attempted primary qualitative and quantitative investigations by means of product analysis using gas chromatography.

First, the following points were confirmed.

(1) The major products observed in the gas chromatograms were CF_2CFD (or CF_2CFH), CF_2CFCl and CF_3CCl_3. The CF_3CCl_3 content decreased as i-C_4H_{10} was added, while the CF_2CFD and CF_2CFCl contents did not. This supports the laser-induced origin of CF_2CFD and CF_2CFCl in reactions (1) and (2).

(2) The fact that S is greater than unity for the mixture shows that some scavenging mechanism exists even without radical scavengers. If the radical termination in reaction (6) does not exist, the scheme suggests that 1 mol Cl· in reaction (3) finally produces 1 mol Cl· in reaction (5), leading to $S = 1$.

Secondly, the validity of reactions (1) - (6) was quantitatively investigated by experiments with equimolar mixtures of CF_3CDCl_2 and CF_3CHCl_2 at a fixed total pressure (1.33 kPa) using i-C_4H_{10} as a radical scavenger at pressures between 0 and 0.27 kPa. The number of laser pulses was set at 500. Figure 4 shows the changes in yield per pulse when i-C_4H_{10} is added; Y_G, Y_B and Y_C denote the yields of CF_2CFCl, CF_2CFD (or CF_2CFH) and CF_3CCl_3 respectively.

Y_G and Y_B increase with the addition of i-C_4H_{10} while Y_C decreases. The increase is presumably due to collision-induced rotational hole filling which tends to increase the average number of photons absorbed by CF_3CDCl_2. Such an increase in absorbance was observed in a separate parallel beam experiment. Y_G and Y_B reach maxima when the i-C_4H_{10} pressure is about 1.1 kPa and then decrease. The decrease may be due to the collisional quenching of vibrationally excited CF_3CDCl_2. Such behaviour has also been observed for CDF_3 [9].

If the scheme is valid, 1 mol of CF_2CFD (or CF_2CFH) should be produced by scrambling for each mole of CF_3CCl_3 produced by reactions (3) - (5). The yield of CF_2CFD (or CF_2CFH) directly produced by laser irradiation is then given by $Y_B - Y_C$. Figure 5 shows that $Y_G/(Y_B - Y_C)$ is approximately independent of the i-C_4H_{10} pressure, indicating that it is equal to the intrinsic branching ratio for reactions (1) and (2). This ratio was found to be 1.1 in our case.

3.2. Simple threshold model

For an irradiation geometry of the type we adopted, it is customary to apply the simple threshold model proposed by Gauthier et al. [10]. This is illustrated in Fig. 6 where the fractional conversion is unity in the shaded reaction zone and is zero in the zone where the fluence is less than Φ_{react}. This simple threshold model is known to be justifiable [11 - 13] when the dependence of the reaction probability q on the fluence Φ is expressed as $q \propto \Phi^n$ with $n \gg 1$. Marling et al. [14] reported $n \approx 3$ for CF_3CDCl_2. The
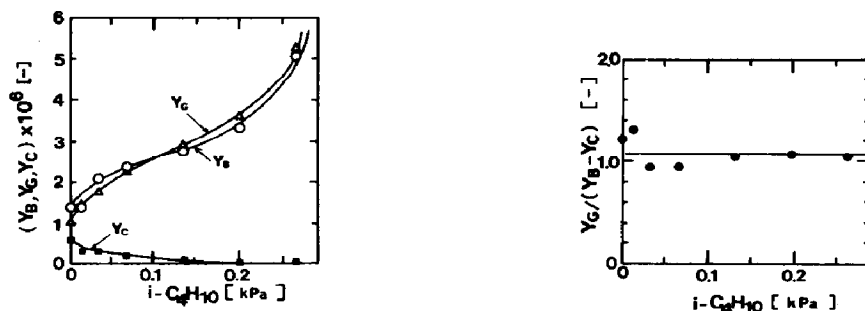
Fig. 4. Yields Y_B, Y_G and Y_C for CF_2CFD (or CF_2CFH), CF_2CFCl and CF_3CCl_3 respectively when i-C_4H_{10} is added to equimolar mixtures of CF_3CDCl_2-CF_3CHCl_2 (0.67 kPa each).

Fig. 5. Branching ratio of photochemically produced CF_2CFD (as given by $Y_B - Y_C$) to CF_2CFCl (as given by Y_G) where B denotes CF_2CFD or CF_2CFH, G denotes CF_2CFCl and C denotes CF_3CCl_3.

pseudo-first-order specific reaction rate b ($b \equiv -\ln(1 - X)/t$) is related to q by $b = qU/V$ where V is the total volume of the cell and U is the volume of the photolysis zone. As long as this model is applicable, a change in b means simply a change in Φ_{react}.

One of our primary interests with respect to geometry is whether reactions (3) - (6) take place homogeneously all over the cell or locally in the photolysis zone only.

The product analyses for neat CF_3CDCl_2 (0.67 kPa) and the CF_3CDCl_2-CF_3CHCl_2 mixture (0.67 kPa each) were performed to answer this question. Figure 7 shows that, compared with the case for the mixture, the $Cl\cdot$ produced after the photolysis of neat CF_3CDCl_2 is very effectively scavenged by the small amount of i-C_4H_{10}. The simple threshold model suggests that there
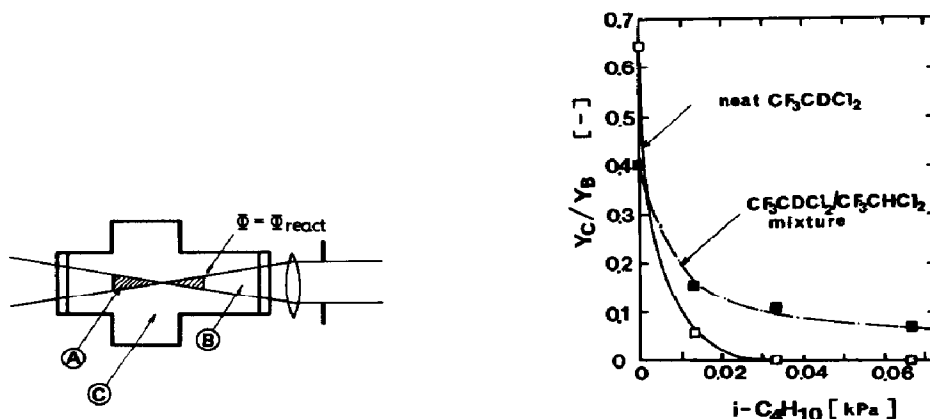

Fig. 6. Schematic diagram of the simple threshold model when $b_A \propto \Phi^n$ and $n > 1$; $q = 1$ for region A and $q = 0$ for regions B and C.

Fig. 7. Comparison of the effects of i-C_4H_{10} to suppress the production of CF_3CCl_3 for neat CF_3CDCl_2 and for the CF_3CDCl_2-CF_3CHCl_2 mixture.

is no CF_3CDCl_2 in the photolysis zone for neat CF_3CDCl_2 after irradiation since it is completely reacted. Therefore either $Cl\cdot$ or CF_3CDCl_2 has to diffuse across the photolysis boundary in order to react for scrambling before the $Cl\cdot$ is scavenged by i-C_4H_{10} in the photolysis zone.

In contrast, the case for the mixture is quite different. While CF_3CDCl_2 is completely reacted as in the previous case, both the unreacted CF_3CHCl_2 and i-C_4H_{10} exist in the photolysis zone. This results in competing reactions of the $Cl\cdot$ radical with CF_3CHCl_2 and i-C_4H_{10}. If the scrambling reaction is homogeneous, there should be no such drastic difference as is shown in Fig. 6. Consequently, Fig. 7 is good evidence that reactions (3) - (6) take place mostly in the reaction zone.

Addition of the radical scavenger affects not only the selectivity S for the mixture but also the total laser-induced yield $Y_G + (Y_B - Y_C)$. However, it should be pointed out that the simple threshold model assumption means constant $Cl\cdot$ concentration (0.63 kPa) in the reaction zone immediately after the laser pulse because of the value of 1.1 obtained for the branching ratio for reactions (1) and (2) with the initial CF_3CDCl_2 (0.67 kPa) completely reacted, irrespective of the value of the photolysis zone volume or b.

4. The effect of radical scavengers on selectivity

4.1. Model description

In this section a model is introduced to describe the effect of the addition of radical scavengers.

First, we assume that the $Cl\cdot$ concentration decays in the form

$$\frac{dD}{d\theta} = -k_2D = -(k_4 + k_5P_s)D \tag{7}$$

where D and P_s denote the concentration of the chlorine radical and the pressure of the scavenger respectively. The rate constants k_5 and k_4 correspond to the scavenging mechanisms with and without a radical scavenger.

In the photolysis zone only CF_3CHCl_2 is subject to radical scrambling since CF_3CDCl_2 is completely reacted after laser irradiation. The decay of CF_3CHCl_2 in the reaction zone by scrambling is assumed to be given by

$$\frac{dA}{d\theta} = -k_3AD \tag{8}$$

where A denotes the concentration of CF_3CHCl_2. The solutions of eqns. (7) and (8) are

$$D = D_0 \exp(-k_2\theta) \tag{9}$$

$$\ln A = \ln A_0 - \frac{k_3D_0}{k_2}\{1 - \exp(-k_2\theta)\} \tag{10}$$

By allowing θ to approach infinity, A_∞ is obtained as

$$A_\infty = A_0 \exp\left(-\frac{k_3 D_0}{k_2}\right) \tag{11}$$

where A_∞ is the final concentration after one pulse. The selectivity S is given by

$$S = \frac{A_0' U / A_0' V}{(A_0 - A_\infty) U / A_0 V} \tag{12}$$

where A_0, A_0', U and V denote the initial concentration of CF_3CHCl_2, the initial concentration of CF_3CDCl_2, the volume of the photolysis zone and the cell volume respectively. Substitution of eqn. (11) into eqn. (12) gives

$$S = \frac{1}{1 - \exp(-k_3 D_0 / k_2)} \tag{13}$$

$$-\frac{1}{\ln(1 - 1/S)} = \frac{k_2}{k_3 D_0}$$

$$= \frac{1}{k_3 D_0}(k_4 + k_5 P_s) \tag{14}$$

For $S \gg 1$, this is approximated by

$$S \approx \frac{1}{k_3 D_0}(k_4 + k_5 P_s) \tag{15}$$

4.2. Results and discussion of isotope separation

Figure 8 shows the effects of the radical scavengers i-C_4H_{10}, NO and C_2F_4. The selectivity S was determined by IR spectroscopy measurements utilizing absorption peaks at about 940 cm^{-1} and 850 cm^{-1} for CF_3CDCl_2 and CF_3CHCl_2 respectively. The full straight lines are the best-fit theoretical lines based on eqn. (14). The intercept and the slopes in Fig. 8 give the values of k_4/k_3 and k_5/k_3 respectively.
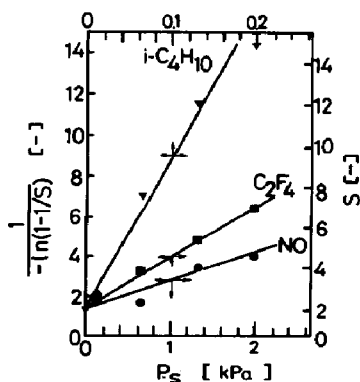

Fig. 8. The effect of radical scavengers on the selectivity S.

TABLE 1

Values obtained for k_4/k_3 and k_5/k_3

| | Scavenger | | |
	i-C_4H_{10}	NO	C_2F_4
k_5/k_3	48.5	0.76	2.07
k_4/k_3 (kPa)		0.82	

TABLE 2

Comparison of k_{5I}/k_{5N} values from thermal reaction data and from this work (I denotes i-C_4H_{10} and N denotes NO)

	20 °C	200 °C	500 °C	1000 °C
$k_{5I} \times 10^{-12}$, thermal [a] $(cm^3\ mol^{-1}\ s^{-1})$	1.8	3.5	5.5	7.2
$k_{5N} \times 10^{-12}$, thermal [b] $(cm^3\ mol^{-1}\ s^{-1})$	170	170	170	170
k_{5I}/k_{5N}, thermal	94	49	31	24
k_{5I}/k_{5N}, this work		64		

[a]From ref. 15.
[b]From ref. 16.

Unfortunately, there is no accurate way of determining the temperature of the reaction zone at the time of radical scrambling because the vibrational excitation is eventually reduced to thermal energy leading to temperature rise. However, such a radical reaction has a very low activation energy and is almost temperature independent.

The values obtained for k_4/k_3 and k_5/k_3 are summarized in Table 1. The second and third rows in Table 2 show the thermal reaction rates of i-C_4H_{10} and NO with Cl· radicals. The rates for C_2F_4 were not available. The value for k_5/k_3 in Table 1 shows that i-C_4H_{10} is 64 times more effective in scavenging than NO is. The ratio of k_5 for i-C_4H_{10} to k_5 for NO at 140 °C is roughly in agreement with our value.

5. Conclusion

In order to investigate the role of radical scavengers in isotope separation by IR lasers, experiments were performed on the photolysis of 2,2-dichloro-1,1,1-trifluoroethane.

Product analysis by gas chromatography revealed that the primary photoproducts were CF_2CFD and CF_2CFCl and that scrambling as described by the simple threshold model took place in the photolysis zone. The model

relating the radical reaction rates to the selectivity was found to be useful in predicting the performance of the radical scavengers.

Acknowledgment

References

1 V. S. Letokhov, *Phys. Today, 30* (May 1977) 24.
2 S. Kimel and S. Speiser, *Chem. Rev., 77* (1977) 437.
3 C. B. Moore (ed.), *Chemical and Biochemical Applications of Lasers*, Academic Press, New York, 1977.
4 J. H. Clark and R. G. Anderson, *Appl. Phys. Lett., 32* (1978) 46.
5 J. B. Marling and I. P. Herman, *Proc. Electro-optics/Laser '78, Int. Conf. Expo., 1978*, p. 116.
6 J. B. Marling and I. P. Herman, *Appl. Phys. Lett., 34* (1979) 439.
7 J. Hine, R. Wiesboeck and R. G. Ghirardelli, *J. Am. Chem. Soc., 83* (1961) 1219.
8 K. Takeuchi, O. Kurihara and R. Nakane, *J. Chem. Eng. Jpn., 13* (1980) 246.
9 I. P. Herman and J. B. Marling, *Chem. Phys. Lett., 64* (1979) 75.
10 M. Gauthier, P. A. Hackett and C. Willis, *Chem. Phys., 45* (1980) 39.
11 J. L. Lyman, S. D. Rockwood and S. M. Freund, *J. Chem. Phys., 67* (1977) 4545.
12 S. Speiser and J. Jortner, *Chem. Phys. Lett., 44* (1976) 399.
13 W. Fuss and T. P. Cotter, *Appl. Phys., 12* (1977) 265.
14 J. B. Marling, I. P. Herman and S. J. Thomas, *J. Chem. Phys., 72* (1980) 5603.
15 J. H. Knox and R. L. Nelson, *Trans. Faraday Soc., 55* (1959) 937.
16 F. Kaufman, *Prog. Reaction Kinet., 1* (1961) 1.