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Isotopic Selectivity in Infrared Multiphoton Dissociation of $CF_3CH(D)BrCl$

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The infrared multiphoton dissociation of $CF_3CDBrCl$ in the presence of equimolar $CF_3CHBrCl$ was investigated with attention to the isotopic selectivity of the reaction. Large selectivity was found at pressures lower than 3 Torr [1 Torr = (101 325/760) Pa]. Several products were obtained, and the molar fraction of deuterium-containing species (deuterium fraction) of each product was measured. The products were classified into two groups with respect to the pressure and fluence dependences of the deuterium fraction. A reaction scheme, consistent with the experimental results, is proposed.

Among various methods, laser isotope separation (LIS) tends to give very high separation factors. As for hydrogen isotopes, extensive research has been performed for tritium separation in the field of nuclear technology[1–4] and for deuterium separation towards the aim of heavy water production.[5–11] In most of the previous studies in this field, halogenated methanes, such as chloroform and fluoroform, were chosen as test molecules, while a few studies have dealt with haloethanes, such as $CF_3CTF_2^3$ and $CF_3CDCl_2^7$.

The isotope separation process involves several steps. The most important steps are isotope transfer to working molecules from water by a hydrogen exchange reaction and a selective reaction using laser irradiation. The working molecules must achieve rapid isotope exchange with water and require a high separation factor in the laser radiation. Infrared multiphoton dissociation (IRMPD) of fluoroform was examined, because it has attractive spectroscopic features,[6] but it has been reported that the exchange reaction is rather slow compared with that of chloroform.[1,5–9] While chloroform shows a higher rate of the exchange reaction, the reaction becomes sluggish with increasing reaction time because of the consumption of the base catalyst by the products of the hydrolysis reaction.[12]

We have studied the exchange and hydrolysis reactions of various haloethanes,[13–15] and have found that $CF_3CHBrCl$ (2-bromo-2-chloro-1,1,1-trifluoroethane; halothane) satisfies the requirements for the exchange reaction. Unlike chloroform and fluoroform, halothane shows good resistance against the hydrolysis reaction.[13] Therefore, halothane can be a candidate for the LIS working molecule, if the isotopic selectivity in the laser dissociation is high enough.

In this work, an equimolar mixture of $CF_3CDBrCl$ and $CF_3CHBrCl$ was irradiated by a TEA CO_2 laser. The compounds studied previously have been found to give mainly one hydrogen (or deuterium) containing product, and the isotopic selectivity was examined simply for such a product or for the parent molecule.[5–11] In the present study, however, many H (or D) containing products were found. Furthermore, some products showed a molar fraction of the deuterium-containing isotopomer (deuterium fraction, hereafter) different from that of the other products. The deuterium fraction of several major products was quantified and it was found that the products were classified into two groups on the basis of the dependence of the deuterium fraction upon sample pressure and incident laser energy fluence. The reaction scheme, which is consistent with the difference between the two groups, is discussed.

Experimental

The sample was prepared by mixing $CF_3CHBrCl$ with $CF_3CDBrCl$. After mixing the isotopomers in nearly equal weight proportions in the liquid phase, the deuterium fraction in the vapour phase was measured with GC–MS. The liquid phase composition was carefully adjusted, so that the vapour-phase deuterium fraction becomes 0.5 ± 0.05. $CF_3CHBrCl$ was purchased from Hoechst Japan Ltd. and used without further purification. No appreciable impurity was detected by GC–MS analysis. $CF_3CDBrCl$ was prepared by the hydrogen-exchange reaction of $CF_3CHBrCl$ and D_2O in the presence of alkali-metal catalysis.[13]

A multimode pulsed TEA CO_2 laser (Lumonics model 101-2) was used for the irradiation. The laser beam was partially focused with a 1000 mm focal length concave mirror. The beam cross-section was regulated with an aperture of 12 mm in diameter. The incident fluence was measured with a Joule meter (Gentec ED-500). The fluence at the focal point was calculated by using the beam cross-section measured preliminarily, and was *ca.* 4.3 J cm^{-2} for the pressure dependence measurements. For all the experimental runs, the irradiation was performed with 1000 shots of the laser pulses using the 10.6 μm-R(14) line (971.9 cm^{-1} or 10.29 μm). The laser line was confirmed by a CO_2 laser spectrum analyser (Optical Engineering model 16A). At this wavelength $CF_3CDBrCl$ has a large absorbance, while $CF_3CHBrCl$ is transparent.[13]

The reaction cell comprised a Pyrex cylinder (400 mm in length and 35.5 mm in inner diameter) equipped with KBr windows at both ends. NaCl windows were used for the experiments to determine the fluence dependence of the yield. The sample pressure was measured with a diaphragm pressure gauge (Baratron, MKS Inc.). The fluence dependence of the yield was investigated at constant initial reactant pressure (2.0 Torr).

After the irradiation, the reaction cell was connected to a buffer line, which can be evacuated and to which the pressure gauge is attached. Then the sample was released to the line and the pressure was measured. The pressure in the reaction cell after the irradiation was estimated from the final pressure. The products were collected using a liquid-N_2 trap. Ethene was than added until the pressure becomes slightly greater than atmospheric pressure. The addition of ethene enables analysis of the halogen molecules, which react with ethene to produce dihaloethanes. Preliminary tests showed that the addition of ethene did not bring about any secondary reactions. Analysis was performed with gas chromatograph–mass spectrometer (GC–MS) (Shimadzu, model QP-1000) equipped with a Porapak-Q column.

Results

Most of the obtained products were halogenated C_2 and C_4 hydrocarbons and Br_2. They are given in Table 1. Qualitative analysis of the products was performed using the mass spectra. Some of the products obtained here were also observed by CW CO_2 laser photosensitized decomposition of halothane.[16] Major products of the present experiments were $CBrF_2CHBrF$ (E1), $C_4H_2Cl_2F_6$ (B1) and its structural isomer (B1′), and other minor products were CF_2CHF (E2), $CF_3CHCHCF_3$ (B2), $CF_3CHCClCF_3$ (B3), CF_3CHCl_2 (E3), Br_2 and further minor products. We could not specify the structure of the products B1 and B1′, because the fragmentation pattern is very complicated. It is only suggested that both the products have one or two CF_3— groups.

The deuterium fraction (X_D) of each product is defined as

$$X_D \equiv \frac{I_D}{I_H + I_D}$$

where I_H and I_D are the amount of H-, and D-containing isotopomers, respectively. They were determined from the peak areas of chromatogram of a specified mass number.

The pressure dependence of the deuterium fraction X_D for various products is shown in Fig. 1. The product E2 was obtained only at low pressures as shown in the figure. The deuterium fraction of every product was nearly unity in the low-pressure region. As the sample pressure becomes high, X_D decreases, and finally the isotopic selectivity disappears. The products B1 and B1′ showed a smaller X_D value than E1 and E2 in the middle pressure region. Other minor products B2, B3 and E3 also showed smaller X_D values.

Fluence dependence of the product yield was examined with a constant sample pressure. The results were given in Fig. 2. The yields of the D- and H-containing products, respectively, were calculated as follows;

$$Y_D = X_D r_i p_0$$

$$Y_H = (1 - X_D) r_i p_0$$

where r_i is the relative intensity of the GC peak of the product i, and p_0 is the initial sample pressure. The relative sensitivity of each GC peak was not taken into consideration, and p_0 was used instead of a final pressure, because the conversion was very low. The yield of every product increased with increasing fluence, regardless of the hydrogen isotope. However, the increase for $CBrF_2CDBrF$ is very steep in comparison with the others.

Discussion

In the present study various products were obtained. This may be due to the use of the focused high-intensity beams.

Table 1 Products of the IRMPD of $CF_3CHBrCl$

product	abbreviation	GC analysis	isotope selectivity
$CBrF_2CHBrF$	E1	major	high
CF_2CHF	E2	minor	high
CF_3CHCl_2	E3	minor	low
$C_4H_2Cl_2F_6$	B1	major	low
$C_4H_2Cl_2F_6$ isomer	B1′	major	low
$CF_3CHCHCF_3$	B2	minor	low
$CF_3CHCClCF_3$	B3	minor	low

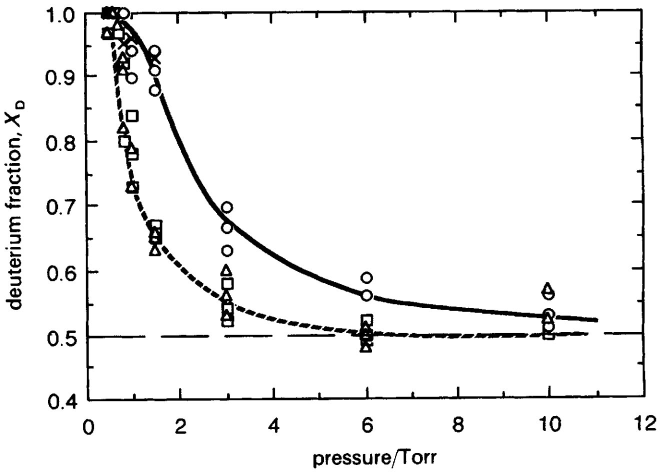


Fig. 1 Pressure dependence of the deuterium fraction. ○, $CBrF_2CH(D)BrF$ (E1); ×, $CF_2CH(D)F$ (E2); □, $C_4H(D)_2Cl_2F_6$ (B1); △, $C_4H(D)_2Cl_2F_6$ isomer (B1′). The laser energy fluence was 4.33 J cm^{-2}

The variety of the products seems to make it difficult to elucidate the reaction scheme. However, we can show that the measurement of the hydrogen isotope content in each product provides useful information in the verification of the reaction scheme. We specified the reaction scheme of the IRMPD of halothane, so that it explains the observed difference in deuterium concentration between the two product groups (one including the products E1 and E2, and the other the products B1 and B1′).

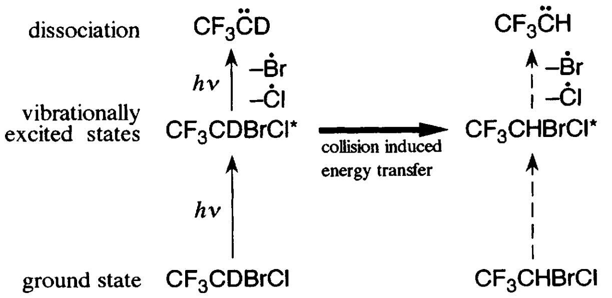
The reaction scheme which explains the experimental results consistently is presented in Scheme 1 for the relatively high deuterium fraction products E1 and E2. The laser radiation is selectively absorbed by $CF_3CDBrCl$, leading to successive vibrational excitation, and finally to dissociation. $CF_3CHBrCl$ cannot obtain energy directly from the laser radiation, while it can be excited by the collision-induced vibrational energy transfer from the excited $CF_3CDBrCl$ molecules. The frequency of the collisions between $CF_3CDBrCl$ and $CF_3CHBrCl$ increases with increasing sample pressure, and hence, the isotopic selectivity disappears at high pressures.

The products E1 and E2 are obtained from a carbene intermediate produced by the successive or molecular elimination of Br and Cl followed by the reactions;

$$CF_3\ddot{C}D \rightarrow CF_2CDF \text{ (E2) (rearrangement)} \quad (1)$$

$$CF_2CDF \text{ (E2)} + Br_2 \rightarrow CBrF_2CDBrF \text{ (E1)} \quad (2)$$

The species E1 and E2 are stable final products and do not take part in further reactions with any other hydrogenated hydrocarbons. Although the reaction of the $CF_3\ddot{C}H$ carbene



Scheme 1 Reaction scheme related to the products which have relatively high deuterium concentrations. The symbol * denotes a vibrationally excited state

is known to give a dimerization product as well as the isomerization product,[17] most $CF_3\ddot{C}D$ should have isomerized to CF_2CDF in the present experiment, since the dimerization product was very minor. This means that the energy transfer from $CF_3CDBrCl$ to $CF_3CHBrCl$ before the elimination of Br and Cl is the only cause of the decrease in the isotopic selectivity, and that the higher D-concentration in the products E1 and E2 reflects the preference in the formation of $CF_3\ddot{C}D$ carbene with respect to $CF_3\ddot{C}H$. The migration of fluorine atom after the carbene formation has been reported in the decomposition of CF_3CHCl_2[7] and CF_3CH_2Cl,[17] and after N_2 elimination from CF_3CHN_2.[18] The addition of Br_2 [eqn. (2)] was confirmed by the absence of the product E1, when halothane (2–3 Torr) was irradiated in the presence of ethene or NO as a Br trap.

The reaction scheme for the lower deuterium fraction products, B1 and B1′, is presented in Scheme 2. In this case, the initial $\dot{\mathrm{B}}\mathrm{r}$ radical elimination will give an intermediate $CF_3\dot{C}DCl$ radical in an isotopically selective way. However, this radical may have a lifetime longer than that of $CF_3\ddot{C}D$ and, hence, the conversion from $CF_3\dot{C}DCl$ to $CF_3\dot{C}HCl$ by the following $\dot{\mathrm{B}}\mathrm{r}$ extraction reaction occurs;

$$CF_3\dot{C}DCl + CF_3CHBrCl \rightarrow CF_3CDBrCl + CF_3\dot{C}HCl \quad (3)$$

The products B1 and B1′ are obtained by the coupling of these intermediate haloethyl radicals;

$$CF_3\dot{C}D(H)Cl + CF_3\dot{C}D(H)Cl \rightarrow C_4D(H)_2Cl_2F_6 \text{ (B1, B1′)} \quad (4)$$

Because of the additional lowering in the isotopic selectivity by eqn. (3), the deuterium fraction of the products B1 and B1′ is lower than the products E1 and E2. Other low deuterium fraction C_4 products, $CF_3CD(H)CD(H)CF_3$ and $CF_3CD(H)CClCF_3$, can be produced from B1 and B1′;

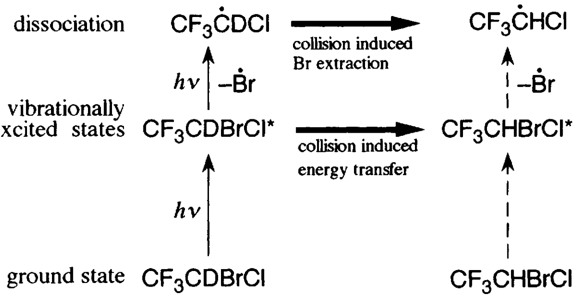
$$C_4D(H)_2Cl_2F_6 \text{ (B1, B1′)} \rightarrow CF_3CD(H)CD(H)CF_3 + Cl_2 \quad (5)$$

$$\rightarrow CF_3CD(H)CClCF_3 + D(H)Cl \quad (6)$$

These reactions were induced possibly by the excess energy in the radical coupling, or by the laser reaction of the products B1 and B1′. The production of CF_3CHCl_2 (E3), which is classified in the lower deuterium fraction group, can be explained by the $\dot{\mathrm{C}}\mathrm{l}$ extraction by $CF_3\dot{C}H(D)Cl$ from halothane, *i.e.*,

$$CF_3\dot{C}D(H)Cl + CF_3CD(H)BrCl \rightarrow CF_3CD(H)Cl_2 + CF_3\dot{C}D(H)Br \quad (7)$$

Because the isotopic selectivity is lowered for $CF_3\dot{C}H(D)Cl$ radical as shown above in eqn. (3), the deuterium fraction of the product E3 becomes lower.



Scheme 2 Reaction scheme related to the products which have relatively low deuterium concentrations. The symbol * denotes a vibrationally excited state

The deuterium fractions of all the products, including those classified as lower deuterium fraction products, were nearly unity at very low pressures, namely <1 Torr. C_4 products were still observed at such low pressures, which suggests that haloethyl radicals are present. This seems inconsistent with the observed deuterium fractions at the low pressures, because haloethyl radicals result in the lowering of the deuterium fraction, as shown above. We will give one possible explanation for this from the point of view of the reactivity of vibrationally excited molecules. The number of vibrationally excited $CF_3CHBrCl$ molecules decreases with decreasing pressure, because of the suppression of collision-induced vibrational energy transfer from $CF_3CDBrCl$ to $CF_3CHBrCl$ due to the lowering of collision frequency. At low pressures only a few $CF_3CHBrCl$ molecules are vibrationally excited in contrast to $CF_3CDBrCl$. The vibrationally excited species are expected to have higher reaction rates than those at the ground state.[19] Thus $CF_3\dot{C}DCl$ radicals extract, at low pressures, Br atoms more efficiently from $CF_3CDBrCl$ than from $CF_3CHBrCl$. This means that the energy transfer from D-containing compounds to H-containing compounds rarely occurs at low pressures. Hence, the deuterium fraction in the products becomes unity at the low pressures. As the pressure and the collision frequency increase, the excitation of $CF_3CHBrCl$ through collision and the Br extraction from the thus excited $CF_3CHBrCl$ are accelerated.

Fig. 2 shows that the observed increase of the yield of $CBrF_2CDBrF$ with increasing fluence is much steeper than that of $CBrF_2CHBrF$, whereas the isotopomers of the products B1 showed a similar feature. This means that the deuterium fraction for the product E1 increases with increasing fluence while that for the product B1 is nearly constant. This can be explained as follows. When the fluence becomes higher, the subsequent laser pumping of the already vibrationally excited halothane proceeds more rapidly, *i.e.*, the $CF_3CDBrCl^*$ molecule has a shorter lifetime. This leads to a decrease in the collision frequency of $CF_3CDBrCl^*$, and as a result, leads to a higher selectivity in the reaction. In the case of the formation of the product E1 this works very effectively, because the following reaction steps proceed without any collisions [eqn. (1)]. On the other hand, for the case of the formation of the product B1, the reaction intermediate $CF_3\dot{C}DCl$ has a longer lifetime than $CF_3\ddot{C}D$, and therefore,

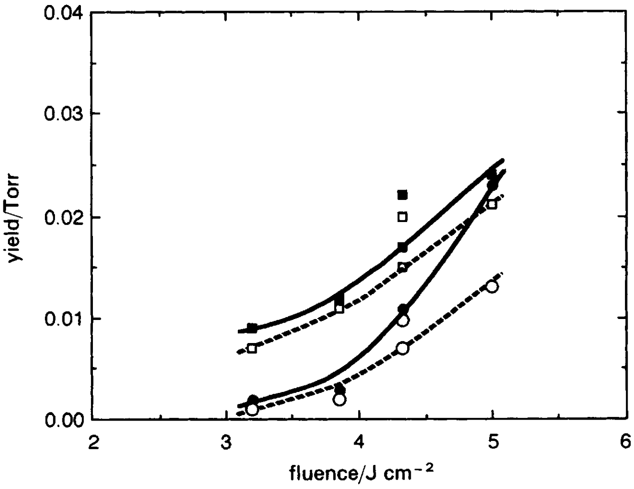


Fig. 2 Fluence dependence of the product yields, Y_H and Y_D (see Results section). ●, Y_D of $CBrF_2CDBrF$ (E1-d); ○, Y_H of $CBrF_2CHBrF$ (E1-h); ■, Y_D of $C_4H(D)_2Cl_2F_6$ (B1-d); □, Y_H of $C_4H(D)_2Cl_2F_6$ (B1-h). The initial sample pressure was 2.0 Torr.

the collisions of this intermediate cause degradation in the selectivity. The difference in behaviour between the products E1 and B1 may result from this step.

Finally, note that although the data for the isotope concentrations in the reaction products of IRMPD under irradiation conditions give considerable information on the reaction pathway and enable detailed analysis of the mechanism of the reaction, such information is not uniquely available from the present experiments. Further information about the reaction mechanism may be obtained from molecular beam experiments, but they do not take into account the complicated collision effects involved in the cell experiments.

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