# $^{18}O$-Selective Infrared Multiple Photon Decomposition of Natural and $^{18}O$-Enriched Diisopropyl Ethers

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$^{18}O$-Selective infrared multiple photon decomposition of diisopropyl ether has been studied in detail using samples with $^{18}O$ at oxygen atomic fractions of 0.20% (natural abundance ratio), 4.5%, and 17.3%. The 1022 $cm^{-1}$ band due to the $^{12}C-^{16}O-^{12}C$ antisymmetric stretching vibration was found to shift toward a low-energy side by 24 $cm^{-1}$ for $^{12}C-^{18}O-^{12}C$. The $^{18}O$-selectivities and yields of the main products containing oxygen, acetaldehyde, and 2-propanol were examined as functions of experimental parameters. The irradiation of a few Torr (1 Torr = 1 mmHg = 133.322 Pa) of diisopropyl ether with TEA (transversely excited atmospheric) $CO_2$ laser lines in the vicinity of 950 $cm^{-1}$ resulted in considerably high enrichment of $^{18}O$ in the products. The fluence at focus was more or less than 8 J $cm^{-2}$. Acetaldehyde and 2-propanol containing $^{18}O$ at about 20% were obtained from natural ether, and those containing more than 70% were obtained from 17.3% $^{18}O$-enriched ether. The observed results can be explained in term of the mechanism involving radical and molecular decomposition channels.

## Introduction

Infrared multiple photon decomposition (IRMPD) of ethers has been extensively studied for establishment of decomposition mechanisms or patterns of aliphatic and alicyclic compounds containing a C−O−C bond[1−8] as well as elucidation of retroene reaction mechanism of ethyl vinyl ether.[3,5,9−11] It is favorable to IRMPD studies that ethers have the intense infrared absorption band in the tunable wavelength region (900−1100 $cm^{-1}$) of a TEA (transversely excited atmospheric) $CO_2$ laser.

Naturally occurring oxygen consists of three stable isotopes with the abundance ratio of $^{16}O$:$^{17}O$:$^{18}O$ = 99.762:0.038:0.200. The intense band in ethers around 1000 $cm^{-1}$ is ascribed to the antisymmetric stretching vibration of the C−O−C bond and expected to have a large oxygen isotope shift, although the shift has not been well-established in experiment. On the other hand, $CO_2$ laser-induced IRMPD of several ethers has been found to show large isotope effects between these oxygen isotopes.[12−18] The fact is suggestive of the large shift of the band around 1000 $cm^{-1}$. Previously, we have obtained very high selectivity on $^{18}O$ in the IRMPD of natural diisopropyl ether under selected irradiation conditions.[14] The main products containing oxygen, which were 2-propanol and acetaldehyde, had considerably high atomic fractions of $^{18}O$. However, such high enrichment of $^{18}O$ in the products is only attainable in extremely low conversion of diisopropyl ether, because the reactant naturally contains only 0.200% of total oxygen as $^{18}O$. This low conversion makes the determination of isotope compositions of the products excessively hard. Therefore, we planned on the use of $^{18}O$-enriched diisopropyl ether for more certain data on isotope separation as well as the IRMPD mechanism. In addition, we consider that the efficient and high enrichment of $^{18}O$ most probably requires the two-stage laser process similarly to the case of $^{13}C$.[19−24] Generally speaking, the energy expenditure per one isotopic atom to be aimed in one-stage laser isotope separation increases more and more, as the enrichment becomes higher and higher. Therefore, the first stage preforms the laser enrichment of $^{18}O$ from natural abundance to a moderate concentration. The following second stage accomplishes high enrichment using the sample containing the isotope at the moderate concentration. Taking these requirements into consideration, we prepared diisopropyl ether enriched with $^{18}O$ and carried out the detailed examination of the IRMPD of $^{18}O$-enriched samples, together with natural ether. The results obtained with enriched samples provide useful information of the laser enrichment at the second stage.

## Experimental Section

**Preparation.** $^{18}O$-Enriched diisopropyl ether was prepared using sodium metal, isopropyl iodide, and $^{18}O$-enriched water on the basis of a series of following reactions: $Na + H_2{}^{18}O \rightarrow Na^{18}OH + {}^1/_2H_2$; $Na^{18}OH + i\text{-}C_3H_7I \rightarrow i\text{-}C_3H_7{}^{18}OH + NaI$; $i\text{-}C_3H_7{}^{18}OH + Na \rightarrow i\text{-}C_3H_7{}^{18}ONa + {}^1/_2H_2$; $i\text{-}C_3H_7{}^{18}ONa + i\text{-}C_3H_7I \rightarrow (i\text{-}C_3H_7)_2{}^{18}O + NaI$. The water used here contained $^{18}O$ at about 25%. Several byproducts such as $H_2$, $C_3H_6$, and $(CH_3)_2CO$ were formed in the series of reactions. However, the $^{18}O$-enriched diisopropyl ether finally obtained was isolated from other byproducts in preparative gas chromatography. The oxygen

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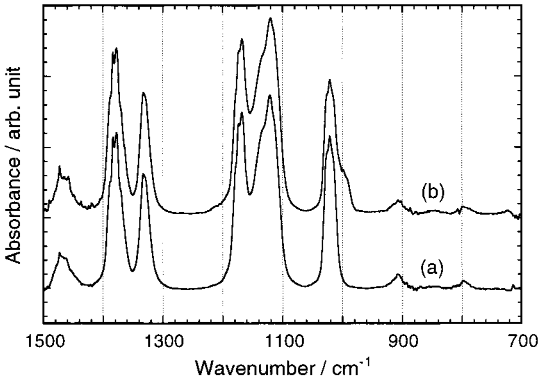

**Figure 1.** Infrared absorption spectra for natural and $^{18}$O-enriched diisopropyl ether in the wavelength region between 700 and 1500 cm$^{-1}$: $^{18}$O atomic fractions, 0.20% for natural ether (a) and 17.3% for enriched ether (b); pressures, in a vicinity of 7.0 Torr; path length, 6 cm. Spectrum b for enriched ether has been shifted upward in parallel to avoid the overlap.

isotope fractions of diisopropyl ether in the first preparation were estimated to be $^{16}$O = 95.3%, $^{17}$O ≈ 0.2%, and $^{18}$O = 4.5% from signal intensities at $m/e$ = 45, 46, and 47 for $C_2H_5O^+$ in mass spectral measurements. Some corrections were made for $^{12,12}C_3H_3{}^{18}O^+$ and $^{12,13}C_2H_5{}^{16}O^+$ because of their appreciable contributions to signals at $m/e$ = 45 and 46. Therefore, the fractions of $^{17}$O are approximate values. In the second preparation the fractions were $^{16}$O = 82%, $^{17}$O ≤ 0.7%, and $^{18}$O = 17.3%.

**Laser Irradiation.** Apparatus and procedures are the same as described previously.[23,24] The irradiation cell was a cylindrical Pyrex tube equipped with NaCl windows at both ends (length, 65 cm; total volume, 220 cm$^3$). The beam from a Lumonics model 103 TEA $CO_2$ laser was first truncated with a circular iris (diameter, 2.0 cm) and focused into a center of the irradiation cell by use of the lens with a focal length of 80 cm. The pulse energy was adjusted adequately within the region of 5−12 J cm$^{-2}$ by inserting several sheets (5−10) of polyethylene films into the beam path. The products and their isotope compositions have been determined using a gas chromatograph mass spectrometer system. The column of Gaskuropack (3 m in length) was used in the temperature range of 110−150 °C.

## Results and Discussion

**Infrared Spectroscopy.** Figure 1 presents the infrared absorption spectra for natural and $^{18}$O-enriched diisopropyl ethers, where the latter contains $^{18}$O at 17.3%, $^{17}$O at about 0.7% or less, and $^{16}$O at 82.0%. The pressures of both ethers were in a vicinity of 7 Torr (1 Torr = 1 mmHg = 133.322 Pa), and the optical path length was 6 cm in the measurements. The peaks of intense infrared absorption bands in natural diisopropyl ethers are located at 800, 910, 1020, 1170, 1330, 1380, and 1470 cm$^{-1}$. On the other hand, a clear shoulder can be observed at a lower wavelength side of the 1020 cm$^{-1}$ band in the enriched ether, although there is no other noticeable difference between both spectra. Figure 2 presents the enlarged spectra with regard to the horizontal axis in the region of 970−1060 cm$^{-1}$. Neglecting the absorption due to $(i\text{-}C_3H_7)_2{}^{17}O$ and taking the net amounts of $(i\text{-}C_3H_7)_2{}^{16}O$ of both ethers into consideration, the subtraction method in essence gives the spectrum for pure $(i\text{-}C_3H_7)_2{}^{18}O$, as also shown in the same figure. The peak wavenumbers are 1022 cm$^{-1}$ for $(i\text{-}C_3H_7)_2{}^{16}O$ and 988 cm$^{-1}$ for $(i\text{-}C_3H_7)_2{}^{18}O$. The isotope shift of about 24 cm$^{-1}$ agrees well with the value of 24 cm$^{-1}$ calculated from the simplest diatomic oscillator model of $^{12}C{-}^{16}O$ or $^{12}C{-}^{18}O$. The same isotope shift of 24 cm$^{-1}$ has been reported of the antisymmetric C−O−C stretching vibration of $^{16}$O- and $^{18}$O-bearing 2,4,6-triphenylanisol.[25,26]

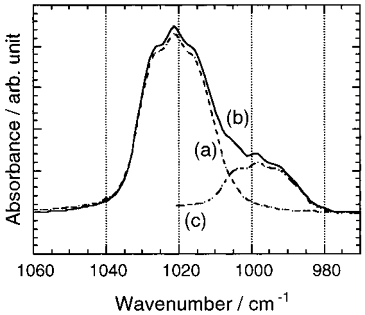

**Figure 2.** Enlarged spectra for natural and $^{18}$O-enriched diisopropyl ether in the region between 970 and 1060 cm$^{-1}$ and spectrum estimated for pure $^{18}$O-bearing diisopropyl ether: (a) natural, (b) $^{18}$O-enriched, (c) difference, i.e., $^{18}$O diisopropyl ether.

**IRMPD.** The main products of the IRMPD of diisopropyl ether have been found to be propylene, isobutane, acetaldehyde, acetone, and 2-propanol, while minor ones were ethane and propane. We did not analyze methane quantitatively in each run, although it was detected in the present gas chromatography. The peak of propane appeared almost at the same retention time as propylene in GC, but the main signal of $m/e$ = 44 for propane was not observed to a meaningful extent in the corresponding mass spectrogram. For example, relative amounts of products in the IRMPD of natural diisopropyl ether were ethane (0.071), propylene (1.0), propane (≤0.05), isobutane (0.26), acetaldehyde (0.26), acetone (0.19), and 2-propanol (1.0). The material balance among O, C, and H is in reasonable accordance with O:C:H = 1:3:14 for diisopropyl ether.

The selectivity or enrichment factor of $^{18}$O is defined as $\alpha_{18}$ = {($^{18}$O/$^{16}$O) in photolysis product}/{($^{18}$O/$^{16}$O) in natural or $^{18}$O-enriched ether}. We determine ($^{18}$O/$^{16}$O) in acetaldehyde from signal heights at $m/e$ = 44 and 46 and the same ratio in 2-propanol from those at $m/e$ = 45 and 47. However, the selectivity of $^{17}$O in the IRMPD has not been examined in the present experiment because the possible occurrence of $^{13}$C enrichment is expected to disturb the accurate and meaningful determination of $\alpha_{17}$. We are concerned here with $^{18}$O selectivities $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) and yields $Y$(RCHO) and $Y$(R′OH) for acetaldehyde (RCHO) and 2-propanol (R′OH) as functions of several experimental parameters such as pulse number, pressure, laser fluence, and laser wavenumber. The symbols $y$(RCHO) and $y$(R′OH) stand for the yields of both products per one laser pulse.

**IRMPD of Natural Diisopropyl Ether.** The IRMPD of natural diisopropyl ether under selected irradiation conditions results in considerably high enrichment of $^{18}$O in acetaldehyde and 2-propanol. Figure 3 shows dependences of selectivities $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) and yields $Y$(RCHO) and $Y$(R′OH) on number of laser pulses, where the wavenumber of laser is 954.55 cm$^{-1}$, the pressure of diisopropyl ether is 5.5 Torr, and the laser fluence is in a vicinity of 8 J cm$^{-2}$. Selectivities for acetaldehyde and 2-propanol appear to be almost constant below 2500 pulses. The diminishing concentration of $^{18}$O seems not to affect the selectivities appreciably at this pressure after 2500 pulses. The yields of both products increase linearly with increasing pulse number up to 1500 pulses and appear to level off beyond. Figure 4 presents laser fluence dependences of $\alpha_{18}$(RCHO), $\alpha_{18}$(R′OH), $y$(RCHO), and $y$(R′OH) in the range of 8−12 J cm$^{-2}$, where irradiation conditions are described in the figure captions. As observed generally for isotope-selective

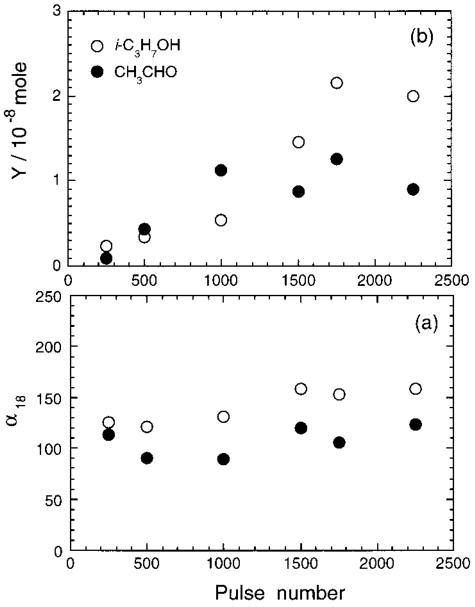

**Figure 3.** Dependences of selectivities $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on pulse number (a) and dependences of yields *Y*(RCHO) and *Y*(R′OH) on pulse number (b) in the IRMPD of natural diisopropyl ether: ○, 2-propanol R′OH; ●, acetaldehyde RCHO; pressure, 5.5 Torr; laser wavenumber, 954.55 cm$^{-1}$; fluence, approximately 8 J cm$^{-2}$.

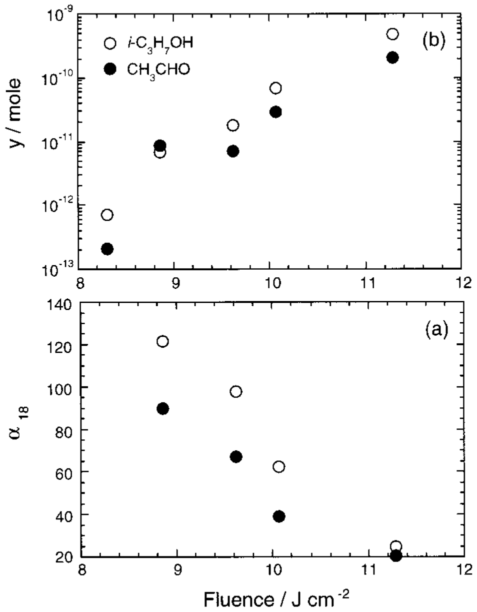

**Figure 4.** Dependences of $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on fluence (a) and dependences of *y*(RCHO) and *y*(R′OH) on fluence (b) in the IRMPD of natural diisopropyl ether: pressure, 5.5 Torr; laser wavenumber, 954.55 cm$^{-1}$.

IRMPD, selectivities decrease and yields increase with increasing fluence in both products.

The dependences of $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on pressure have maxima at about 5 Torr, as shown in Figure 5a. The relation between isotope selectivity and reactant pressure is complicated, depending on the intrinsic feature of the reactant itself. For example, the $^{13}$C selectivity in the IRMPD of $CHClF_2$ increases with an increase in pressure, unless the pressure is over 80 Torr.[19−24] Contrarily, the isotope selectivity on $^{30}$Si decreases rapidly with increasing pressure in the IRMPD of $Si_2F_6$.[27] The difference in excitation and deactivation rates between isotopic molecules under various conditions decides the selectivity in IRMPD, but a number of parameters such as

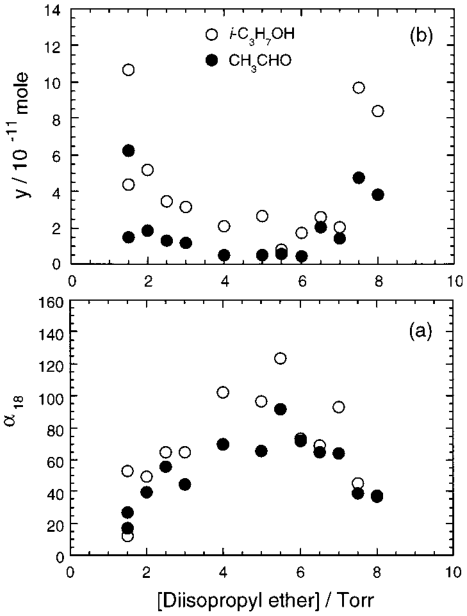

**Figure 5.** Dependences of $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on pressure (a) and dependences of *y*(RCHO) and *y*(R′OH) on pressure (b) in the IRMPD of natural diisopropyl ether: laser wavenumber, 954.55 cm$^{-1}$; fluence, approximately 8 J cm$^{-2}$.

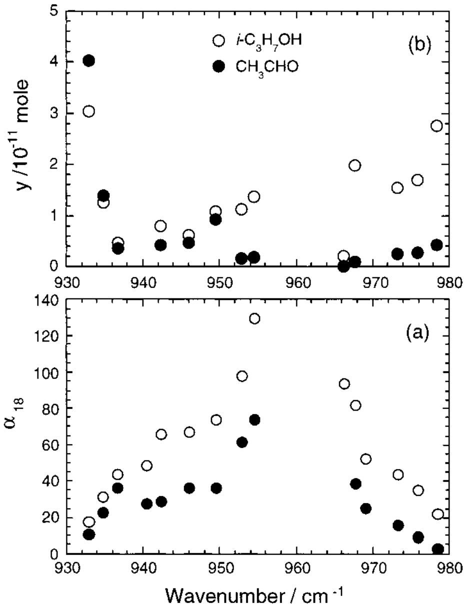

**Figure 6.** Dependences of $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on laser wavenumber (a) and dependences of *y*(RCHO) and *y*(R′OH) on laser wavenumber (b) in the IRMPD of natural diisopropyl ether: pressure, 0.9 Torr; fluence, approximately 8 J cm$^{-2}$.

pressure, fluence, optical cross section, and collisional cross section affect the rates. Both *y*(RCHO) and *y*(R′OH) decrease rapidly, pass minima, and increase, as the pressure of diisopropyl ether is increased up to 8 Torr, as shown in Figure 5b. The initial rapid decreases of both yields with an increase in pressure below 5 Torr must be due to collisional deactivation of excited molecules by surrounding nonresonant molecules. On the other hand, we consider that the thermal decomposition probably occurs at higher pressures than 6 Torr. As a result, selectivities decrease and yields increase. The laser line dependences of $\alpha_{18}$(RCHO), $\alpha_{18}$(R′OH), *y*(RCHO), and *y*(R′OH) are shown in Figure 6. The maxima in selectivity appear to be located in the region of 950−970 cm$^{-1}$ where intense lines are not available in a $CO_2$ laser. In contrast, both yields seem to increase below

940 cm$^{-1}$ or above 970 cm$^{-1}$; such increases are due to increasing absorption of laser photons by a molecule, because diisopropyl ether has infrared bands at 910 and 1022 or 998 cm$^{-1}$.

The initial step of the IRMPD leading to the formation of acetaldehyde or 2-propanol may be the scission of one of C−O bonds in a parent molecule to form isopropoxyl radical and isopropyl radical:

$$(CH_3)_2CHOCH(CH_3)_2 + nh\nu \rightarrow (CH_3)_2CHO + (CH_3)_2CH \quad (1)$$

The multiple photon process is, of course, isotope-selective. The C−O bond has the lowest bond dissociation energy of about 315 kJ mol$^{-1}$ in diisopropyl ether as compared to other C−C (about 350 kJ mol$^{-1}$) and C−H (about 400 kJ mol$^{-1}$) bonds. The $(CH_3)_2CHO$ radical produced here may abstract a hydrogen atom from diisopropyl ether to form 2-propanol. The abstraction reaction

$$(CH_3)_2CHO + (CH_3)_2CHOCH(CH_3)_2 \rightarrow (CH_3)_2CHOH + (CH_3)_2COCH(CH_3)_2 \quad (2)$$

is exothermic, since the bond dissociation energy of the O−H bond of 2-propanol is about 428 kJ mol$^{-1}$ and that of the $H-C(CH_3)_2OCH(CH_3)_2$ bond may be almost the same as that of the $H-C(CH_3)_3$ bond, i.e., 387 kJ mol$^{-1}$.

When the fragment $(CH_3)_2CHO$ in reaction 1 has enough internal energy to undergo further decomposition, acetaldehyde is produced in the following decomposition reaction:

$$(CH_3)_2CHO \rightarrow CH_3CHO + CH_3 \quad (3)$$

However, the reaction requires, at least, 29 kJ mol$^{-1}$ on the basis of $\Delta H_f(CH_3) = 142$ kJ mol$^{-1}$, $\Delta H_f(CH_3CHO) = -166$ kJ mol$^{-1}$, and $\Delta H_f((CH_3)_2CHO) = -53$ kJ mol$^{-1}$. A part acetaldehyde may result from the secondary IRMPD of $(CH_3)_2CHO$ during each laser pulse:

$$(CH_3)_2CHO + mh\nu \rightarrow CH_3CHO + CH_3 \quad (4)$$

Daly and Stimson[28] have demonstrated that propylene and 2-propanol (70−90%) and propane and acetone (30−10%) are the major products in the thermal decomposition of diisopropyl ether at 423−487 °C. Only a trace quantity of acetaldehyde is produced. The scission of the C−O bond is also the initial step in the thermal decomposition. They suggested that a radical chain reaction is the source of propane and acetone, but propylene and 2-propanol are produced in either a radical-chain or a molecular process. The facts that propane is a minor product, acetone is not enriched with $^{18}$O, and the $^{18}$O selectivities of acetaldehyde and 2-propanol are significantly high indicate that a chain reaction does not occur to a meaningful extent in the present IRMPD. Considering large quantities of 2-propanol and propylene among products, we propose the following molecular and isotope-selective decomposition process in addition to reactions 1−4 in the IRMPD:

$$(CH_3)_2CHOCH(CH_3)_2 + lh\nu \rightarrow (CH_3)_2CHOH + C_3H_6 \quad (5)$$

The decomposition of diisopropyl ether into 2-propanol and propylene is endothermic by 67 kJ mol$^{-1}$ and energetically preferable to the scission of the C−O bond (313 kJ mol$^{-1}$). The IRMPD of ethyl vinyl ether $C_2H_5OC_2H_3$ has been found to occur through two decomposition channels: $C_2H_5OC_2H_3 \rightarrow CH_3CHO + C_2H_4$ and $C_2H_5OC_2H_3 \rightarrow CH_2CHO + C_2H_5$.[11] The branching ratio increases in favor of the higher energy radical producing channel as the laser fluence is increased. Similarly, the molecular decomposition of diisopropyl ether probably occurs at lower fluences, but the other channel, i.e., C−O scission, becomes predominant with increasing fluence. The preexponential factor of reaction 1 may be much larger than that of reaction 5, although there is a large difference in activation energy between these unimolecular decomposition reactions.

TABLE 1: Results Obtained with the IRMPD[a] of $^{18}$O-Enriched Diisopropyl Ether at Atomic Fraction of 4.5%

| pressure (Torr) | fluence (J cm$^{-2}$) | pulse number | $\alpha_{18}$-(RCHO) | Y(RCHO) (nmol) | $\alpha_{18}$-(R′OH)[b] | Y(R′OH) (nmol) |
|---|---|---|---|---|---|---|
| 0.9 | 10.0 | 1000 | 16 | 81 | 14 | 265 |
| 0.9 | 8.4 | 2000 | 17 | 60 | 14 | 209 |
| 0.9 | 7.3 | 2000 | 16 | 42 | 15 | 227 |
| 0.5 | 6.4 | 2000 | 17 | 11 | 14 | 75 |

[a] Laser line, 10P(8) at 954.55 cm$^{-1}$. [b] Values of 14, 15, 16, and 17 in α correspond to $^{18}$O atomic fractions of about 40%, 41%, 43%, and 45% in acetaldehyde or 2-propanol.

The formation of methane, ethane, propane, propylene in part, and isobutane may be due to various reactions of methyl and isopropyl radicals such as abstraction, combination, and disproportionation. We did not observe significant enrichment of $^{18}$O in acetone. Therefore, acetone is probably formed in the decomposition of excited $(CH_3)_2COCH(CH_3)_2$ radicals:

$$(CH_3)_2COCH(CH_3)_2 \rightarrow (CH_3)_2CO + (CH_3)_2CH \quad (6)$$

The $(CH_3)_2COCH(CH_3)_2$ radicals originate from the hydrogen abstraction due to the fragment $(CH_3)_2CHO$ or $CH_3$ from nonresonant $(CH_3)_2CH^{16}OCH(CH_3)_2$. Subsequently, the resulting radicals may be excited collisionally or through multiple photon absorption prior to decomposition.

**IRMPD of $^{18}$O-Enriched Diisopropyl Ether.** We have used diisopropyl ether enriched with $^{18}$O at atomic fractions of 4.5% and 17.3%. We could not change experimental parameters so widely because of limited quantities of the enriched samples prepared here. Pressures have been mostly adjusted to 1 Torr or less than 1 Torr. Table 1 tabulates the results for the IRMPD of 4.5% $^{18}$O ether, together with experimental conditions used. The selectivities did not differ appreciably among the runs. Acetaldehyde and 2-propanol were found to contain $^{18}$O at 40−45%.

The results for another enriched ether ($^{18}$O = 17.3%) are shown in Figure 7 as a function of pulse number. Roughly speaking, $\alpha_{18}$(RCHO) does not change significantly, but $\alpha_{18}$-(R′OH) tends to increase with increasing pulse number. The infrared absorption spectrum of $i$-$C_3H_7{}^{16}OH$ has the intense band with a peak at 953 cm$^{-1}$, while $CH_3CH^{16}O$ shows the absorption maximum at 1113 cm$^{-1}$ due to the C−C stretching vibration. The band of the latter is too far to be resonating with the laser pulses in the present irradiation. On the other hand, the selective IRMPD of $i$-$C_3H_7{}^{16}OH$ is likely to occur at 954.55 cm$^{-1}$ for the 10P(8) line and possibly increases $\alpha_{18}$(R′OH) with increasing number of pulses. The yields of acetaldehyde and 2-propanol are apparently saturated with increasing number of pulses. This fact suggests that the optical absorption of laser pulse radiation due to an accumulating product, which may be $i$-$C_3H_7{}^{16}OH$ reduces the IRMPD of the parent diisopropyl ether.

The maxima of $\alpha_{18}$'s appear to be in the region between 940 and 950 cm$^{-1}$, although the selectivities for both products distribute rather broadly over laser wavenumber, as shown in Figure 8a. On the other hand, the yields of both products seem

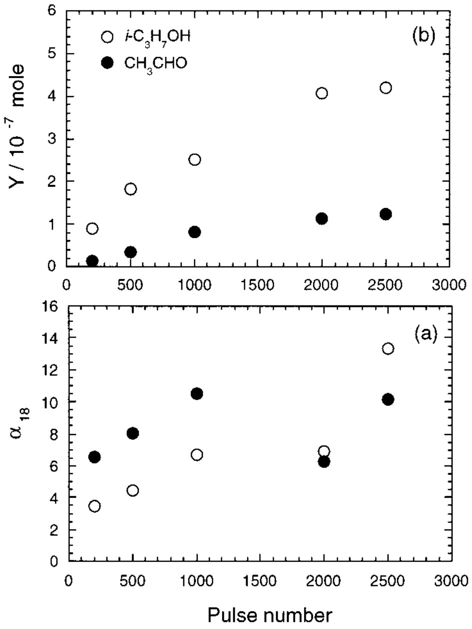

**Figure 7.** Dependences of $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on pulse number (a) and dependences of *Y*(RCHO) and *Y*(R′OH) on pulse number (b) in the IRMPD of $^{18}$O-enriched (17.3%) diisopropyl ether: pressure, 0.9 Torr; laser wavenumber, 954.55 cm$^{-1}$; fluence, approximately 6 J cm$^{-2}$.

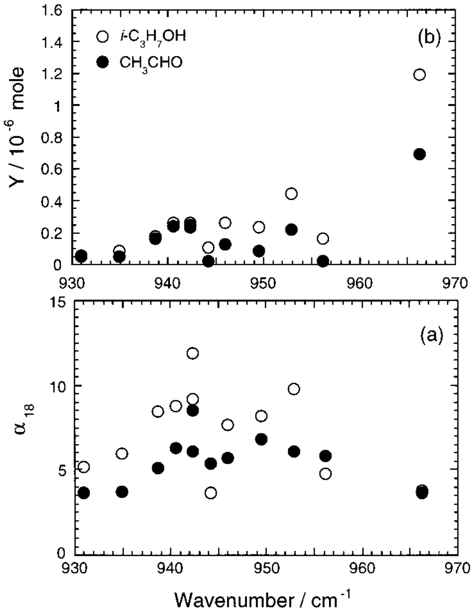

**Figure 8.** Dependences of $\alpha_{18}$(RCHO) and $\alpha_{18}$(R′OH) on laser wavenumber (a) and dependences of *Y*(RCHO) and *Y*(R′OH) on laser wavenumber (b) in the IRMPD of $^{18}$O-enriched (17.3%) diisopropyl ether: pressure, 0.9 Torr; pulse number, 10 000; fluence, approximately 10 J cm$^{-2}$.

to increase as the irradiation wavenumber approaches the intense band of diisopropyl ether, as shown in Figure 8b.

Selectivities and yields have been also examined as a function of fluence in the region between 5 and 10 J cm$^{-2}$. Although data were spread widely, observed selectivities and yields did not show meaningful changes in the fluence region.

Selectivities obtained with three kinds of diisopropyl ethers are 100−200 ($^{18}$O in product, 15−30%) for natural, 15 ($^{18}$O in product, 40%) for 4.5% $^{18}$O, and 10−12 ($^{18}$O in product, about 70%) for 17.3% $^{18}$O samples under selected conditions. Such variation in selectivity that $\alpha_{18}$ decreases with increasing concentration of $^{18}$O in ether is generally observed for laser isotope separation such as deuterium and $^{13}$C by IRMPD. The present study has demonstrated that 2-propanol containing $^{18}$O over 17% can be directly obtained with the IRMPD of natural diisopropyl ether. The 2-propanol is converted to diisopropyl ether in chemical transformation. The further enrichment of $^{18}$O over 70% is accomplished in the IRMPD of diisopropyl ether containing $^{18}$O over 17%.

## Conclusions

Diisopropyl ether enriched with $^{18}$O was prepared for isotope-selective IRMPD experiments. The atomic fractions of $^{18}$O were 4.5% and 17.3%. The peak at 1022 cm$^{-1}$ for natural diisopropyl ether ($^{18}$O = 0.2%) shifts to 998 cm$^{-1}$ in $^{18}$O-bearing molecules. The ethers containing $^{18}$O at 0.2% (natural), 4.5%, and 17.3% were irradiated with TEA $CO_2$ laser lines in the fluence range of 6−12 J cm$^{-2}$. Pressures were below several Torr. The observed products can be explained in terms of the mechanism including the following radical and molecular decomposition channels: $(CH_3)_2CHOCH(CH_3)_2 \rightarrow (CH_3)_2CHO + (CH_3)_2CH$ and $(CH_3)_2CHOCH(CH_3)_2 \rightarrow (CH_3)_2CHOH + C_3H_6$. Acetaldehyde and 2-propanol were considerably enriched with $^{18}$O under irradiation conditions used here. Maxima in selectivities appeared to be in the region between 950 and 970 cm$^{-1}$ for natural diisopropyl ether and, although broad, in the region between 940 and 950 cm$^{-1}$ for the enriched one (17.3%). We successfully obtained 2-propanol containing $^{18}$O beyond 20% in the IRMPD of natural diisopropyl ether and 2-propanol containing $^{18}$O at 70% in the IRMPD of 17.3% $^{18}$O-enriched diisopropyl ether. The present results give confidence in high enrichment of $^{18}$O by the two-stage laser process. Therefore, this process has the potential to provide the practical technique for mass production of marketable $^{18}$O-enriched compounds having $^{18}$O atom concentrations of more than 90%.

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