# Oxidation of $(CD_3)_2\dot{C}X$ Radicals. I. Reaction of Propane and Isopropyl Radicals with Atomic Oxygen

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The reaction of oxygen atoms with propane-1,1,1,3,3,3-$d_6$, $(CD_3)_2CH_2$, in a fast-flow system was studied with a photoionization mass spectrometer. Isopropyl-$d_6$ radicals, $(CD_3)_2\dot{C}H$, formed by the initial hydrogen abstraction at the 2-position were detected directly.

$$(CD_3)_2CH_2 + O(^3P) \rightarrow (CD_3)_2\dot{C}H + OH \qquad (3)$$

The subsequent reaction of $(CD_3)_2\dot{C}H$ radicals with atomic oxygen proceeds by both an deuterium abstraction (61%) and an oxygen addition reaction (39%). The product in the deuterium abstraction was $CD_2CHCD_3$ and those in the oxygen addition were $(CD_3)_2CO$ (18%) and $CD_3CHO$ (21%).

$$(CD_3)_2\dot{C}H + O(^3P) \begin{array}{ll} \nearrow CD_2CHCD_3 + OD & (4a) \\ \longrightarrow (CD_3)_2CO + H & (4b) \\ \searrow CD_3CHO + CD_3 & (4c) \end{array}$$

Competition experiments show that $(CD_3)_2\dot{C}H$ radicals react (0.029 ±0.004) times as fast with $O_2$ as with $O(^3P)$. In the presence of an excess of $O_2$, $CD_2CHCD_3$ was observed in decreased yield (20%) and $(CD_3)_2CO$ and $CD_3CHO$ increased to 32 and 44%, respectively. The rate data for Reaction 3 were fitted by an Arrhenius expression:

$$k_3 = (2.0^{+1.0}_{-0.7}) \times 10^{-10} \exp[-(6086 \pm 392 \text{ cal mol}^{-1})/RT]^{\dagger}$$

$cm^3$ molecule$^{-1}$ $s^{-1}$ (381—627 K). The rate constant of Reaction 3 obtained from the yields of products was $7.9 \times 10^{-15}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ at 298K.

Reaction of alkyl radicals with atomic oxygen, $O(^3P)$, has been investigated for $t$-$C_4H_9$[1)] and *cyclo*-$C_6H_{11}$[2)] using the technique of discharge-flow-photoionization mass spectrometry. In the case of $t$-$C_4H_9$, it has been suggested[1)] that the reaction of $O(^3P)$ with $t$-$C_4H_9$ is very fast, and that the large rate constant was explained by the hydrogen abstraction from nine equivalent hydrogen atoms in the $t$-$C_4H_9$ radical (formation of isobutene was 80% of the total reaction). Formation of acetone (20%) by the addition of an oxygen atom to the radical was observed as an alternative channel. Similar results have been obtained in the reaction of *cyclo*-$C_6H_{11}$+$O(^3P)$.[2)] Formation of the two types of products (olefins by hydrogen abstraction and aldehydes or ketones by the oxygen addition reaction) has also been reported in reactions of $C_3H_7$+O,[3,4)] $t$-$C_4H_9$+O,[4—6)] and *neo*-$C_5H_{11}$+O,[6)] although Hoyerman and Sievert[7)] reported no formation of olefins.

The primary attack of ground state $O(^3P)$ atoms to propane is expected to be hydrogen abstraction producing a propyl radical:

$$O(^3P) + C_3H_8 \rightarrow C_3H_7 + OH \qquad (1)$$

Propyl radicals should react with oxygen atoms very rapidly and produce several products:

$$C_3H_7 + O(^3P) \rightarrow \text{Products} \qquad (2)$$

In the discharge-flow experiments reported previously,[3,4)] the formation of $CH_3CHO$, $(CH_3)_2CO$, $C_3H_6$, $C_2H_5CHO$, $C_2H_6$, $C_2H_4$, $CH_2O$, $CH_4$, $CO_2$, $H_2O$, and $H_2$ (including both primary and secondary products) has been reported.

In the previous O+$C_3H_8$ studies, however, it was not clear whether propyl or isopropyl radicals (or both) were produced by Reaction 1. Also it was not possible to clarify the reaction mechanism of the $O(^3P)$+$C_3H_7$ reaction. In the present study, the reaction of oxygen atoms with propane-1,1,1,3,3,3-$d_6$, $(CD_3)_2CH_2$, is studied by using a photoionization mass spectrometer[8,9)] coupled with a fast-flow reactor. In this case the primary attack of O atoms can be identified by measuring the mass number of the propyl radicals produced. Subsequent reactions of propyl radicals with atomic and molecular oxygen are then analyzed.

## Experimental

A schematic diagram of a fast-flow reactor and a photoionization mass spectrometer is shown in Fig. 1. Most of the components are as described previously[10—12)] except for two improvements; 1) three diffusion pumps (10, 4, and 6 inches in diameter for A, B, and C, respectively) with liquid nitrogen traps were used to evacuate the ionization chamber, the quadrupole mass filter, and the detector region; 2) a 0.4 mm (in diameter) Pyrex orifice was used to sample the gases into the ionization region. About $5 \times 10^4$ counts $s^{-1}$ of signal was obtained for 1 mTorr NO(1 Torr=133.322 Pa) in the flow reactor when it was ionized by a Kr lamp having a $MgF_2$ window.

Oxygen atoms were generated by a microwave discharge in a helium-oxygen mixture (0.05—2% in helium), and their concentration was determined by titration with $NO_2$ according to the reaction O+$NO_2$→NO+$O_2$. Then known partial

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[†] 1 cal=4.184 J.

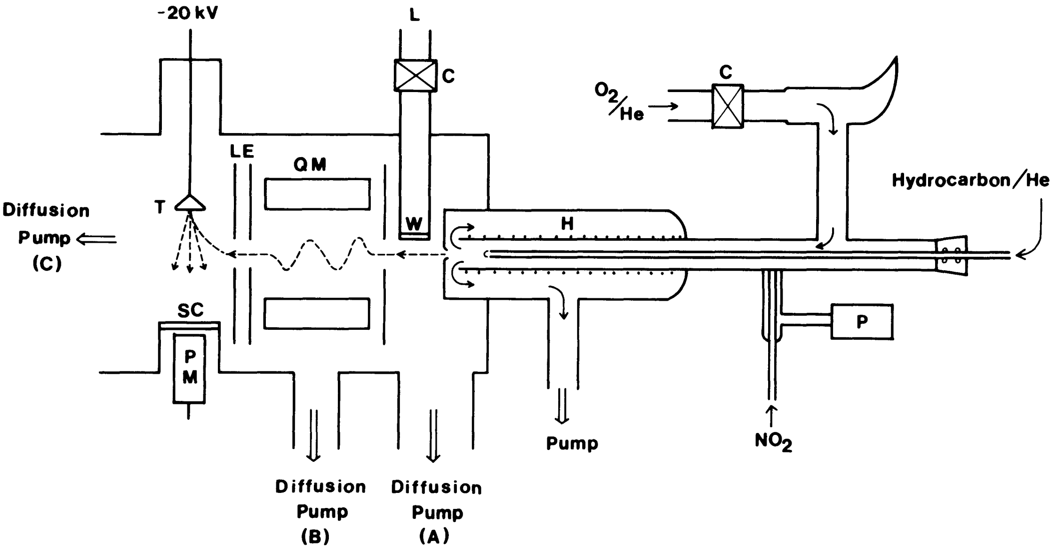

Fig. 1. Schematic diagram of the apparatus; C, microwave cavity; P, MKS Baratron pressure gauge; H, coiled Nichrome wire heater; L, VUV lamp; W, window; QM, quadrupole mass filter; LE, lens; T, Al coated Stainless steel target; SC, Al coated plastic scintillator; PM, photomultiplier.

pressures of NO were added to calibrate the instrument sensitivity. Propane-1,1,1,3,3,3-$d_6$, $(CD_3)_2CH_2$, was diluted in helium (about 10% in helium) and entered the main flow through a movable inlet with six small radially directed holes. Total and partial pressures of gases were measured by a capacitance manometer (MKS Baratron 170M-35). These pressures were converted to concentrations by using a separate calibration of the flow as a function of pressure and temperature. The linear flow velocity measured with a bubble meter was 16.5 $m\,s^{-1}$ at 2 Torr, 19.9 $m\,s^{-1}$ at 4 Torr, and 21.4 $m\,s^{-1}$ at 6 Torr at 298K. The various photoionization lamps used to ionize radicals and molecules were powered by a microwave discharge. Most of the measurements were done at room temperature, 298±3K. Some experiments were carried out at high temperature, 420—630K. The reaction zone was heated with a coiled Nichrome wire heater. Temperature was measured with a pair of Alumel Chromel thermocouples suspended in the central reactant-inlet tube. Temperature uniformity was ±2K.

The gases $O_2$ (Nippon Sanso, 99.99%), He (Nippon Sanso, 99.9999%), NO (Matheson, 99.0%), $NO_2$ (Matheson, 99.5%) were used without further purification. The propane-1,1,1,3,3,3-$d_6$, $(CD_3)_2CH_2$, (98%) was from Merck Sharp & Dohme. Part of the $(CD_3)_2CH_2$ used was synthesized[13] in this laboratory from $(CD_3)_2CO$. Both $(CD_3)_2CH_2$ from Merck Sharp & Dohme and the synthesized material contained 1—2% of olefins (mostly $CD_2CHCD_3$). These were removed by passing the sample through a solution of $KMnO_4$ and drying on a column of $CaCl_2$. After this purification, the $CD_2CHCD_3$ contained in the $(CD_3)_2CH_2$ was less than 0.005%. Oxygen-18($^{36}O_2$ about 20%) from Merk Sharp & Dohme was analyzed by the mass spectrometer, and the $^{36}O_2$ content was determined to be 19.2±0.7%. All measurements were done under the condition $[O]>0.5[(CD_3)_2CH_2]$.[14]

## Results

### A. Radicals and Molecules Detected in the Reaction of $(CD_3)_2CH_2+O(^3P)$.

Preliminarily, the measurement of radicals and molecules produced in the reaction of $C_3H_8+O$ was investigated. A signal at $m/z=43$ was detected by using a Xe resonance lamp with a sapphire window (8.44 eV) as a photoionization light source. When a Kr lamp with a $CaF_2$ window (10.03 eV) was used, signal at $m/z=42$ and 58 were also observed. The signal at $m/z=44$ was observed in addition to the above signals when a Kr lamp with a $MgF_2$ window (10.03 and 10.64 eV) was used. Mass spectra of these signals are shown in Fig. 2. Ionization potentials together with values of heats of formation for possible radicals and molecules are listed in Table 1. The signal at $m/z=43$ shown in Fig. 2c should be from $C_3H_7$ radicals produced in the reaction of $C_3H_8+O$.[29] However, it was not possible to identify the radical as either an *n*-propyl or an isopropyl radical. The signal at $m/z=42$ might be from $C_3H_6$ and/or $CH_2CO$ and at $m/z=58$ from $(CH_3)_2CO$ and/or $C_2H_5CHO$ produced by the reaction of propyl radicals with the excess of oxygen atoms.[29] The signal at $m/z=44$ shown in Fig. 2a should be from $CH_3CHO$.[29] In addition to the signals shown in Fig. 2, signals for $CH_3$ (Kr lamp), $C_2H_4$ (Ar lamp), and $CH_2O$ (Ar lamp) were observed at $m/z=15$, 28, and 30, respectively. Although the radicals and molecules were observed as expected, the kinetic analysis of the reaction is not possible because of the failure to determine the branching ratio for the formation of *n*-propyl and isopropyl radicals.

Isopropyl-$d_6$ radicals, $(CD_3)_2\dot{C}H$ were observed at $m/z=49$ when oxygen atoms reacted with propane-1,1,1,3,3,3-$d_6$, $(CD_3)_2CH_2$. The radical was detected by using a Xe resonance lamp with a sapphire window (8.44 eV). The mass spectra are shown in Fig. 3. No significant signal of propyl-1,1,3,3,3-$d_5$ radicals, $\cdot CD_2CH_2CD_3$, was observed at $m/z=48$. Other prod-

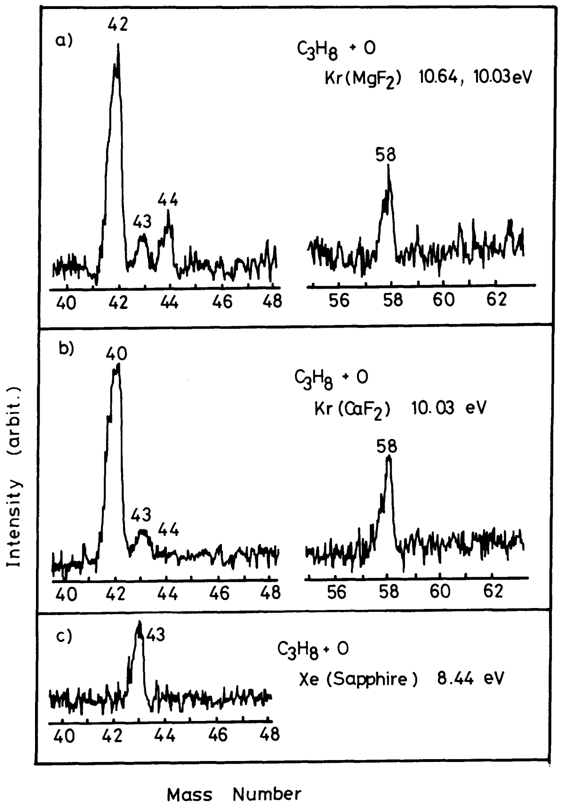

Fig. 2. Mass spectra of the reaction products produced in $O+C_3H_8$. Kr lamps having a $MgF_2$ window (10.64 and 10.03 eV) and a $CaF_2$ window (10.03 eV), and a Xe lamp having a sapphire window (8.44 eV) were used. The conditions: $[O]_0=3.6$ mTorr; $[C_3H_8]_0=1.4$ mTorr; reaction time 4.5 ms; total pressure 4.3 Torr.

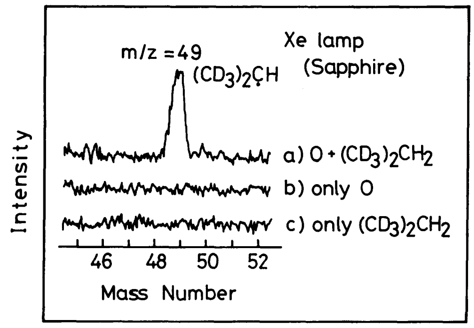

Fig. 3. Mass spectra of the $(CD_3)_2\dot{C}H$ radical produced in $O+(CD_3)_2CH_2$. A Xe lamp with a sapphire window (8.44 eV) was used for the photoionization. The conditions: partial pressure (mTorr), $[O]_0=3.7$, $[(CD_3)_2CH_2]=1.5$; reaction time=4.5 ms; total pressure=4.3 Torr.

ucts produced by subsequent reactions and the parent molecule were not photoionized by this lamp.

$$(CD_3)_2CH_2+O(^3P)\rightarrow(CD_3)_2\dot{C}H\ (m/z=49)+OH \qquad (3)$$

From the ratio of the signal at $m/z$=49 to the back ground noise at $m/z$=48, it was concluded that more than 95% of the total reaction of $(CD_3)_2CH_2+O$ forms $(CD_3)_2\dot{C}H$ radicals by abstraction of the 2-hydrogen from $(CD_3)_2CH_2$.

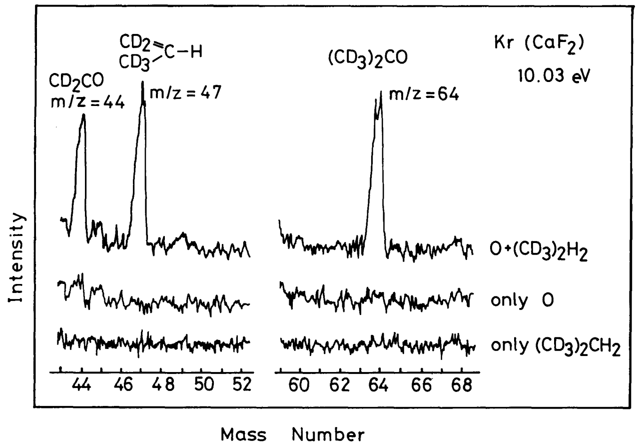

Fig. 4. Mass spectra of the reaction products produced in $O+(CD_3)_2CH_2$. A Kr lamp having a $CaF_2$ window (10.03 eV) was used for the photoionization. The conditions: partial pressure (mTorr), $[O]_0=3.5$, $[(CD_3)_2CH_2]=0.7$; reaction time=4.5 ms; total pressure=4.3 Torr.

Table 1. Ionization Potentials and Heat of Formations of Radicals and Molecules[a)]

| $m/z$ | Molecule | I.P. eV | $\Delta H^0_{f298}$ (g) kcal mol$^{-1}$ |
|---|---|---|---|
| 42 | $C_3H_6$ | 9.7 | 4.88 |
| 42 | $CH_2CO$ | 9.6 | −14.6 |
| 43 | $n$-$C_3H_7$ | 8.1 | 20.7 |
| 43 | $i$-$C_3H_7$ | 7.5 | 17.6 |
| 44 | $C_3H_8$ | 11.0 | −24.8 |
| 44 | $CH_3CHO$ | 10.2 | −39.7 |
| 48 | $(CH_3)_2CO$ | 9.7 | −52.0 |
| 58 | $C_2H_5CHO$ | 9.9 | −45.9 |

a) Quoted from Ref. 28.

Possible products produced by the reaction of $O+(CD_3)_2\dot{C}H$ are as follows:

$$(CD_3)_2\dot{C}H+O \begin{array}{ll} \nearrow CD_2CHCD_3\ (m/z=47)+OD & (4a) \\ \longrightarrow (CD_3)_2CO\ (m/z=64)+H & (4b) \\ \searrow CD_3CHO\ (m/z=47)+CD_3 & (4c) \end{array}$$

where Reaction 4a is deuterium abstraction, 4b and 4c result from the addition reaction of an oxygen atom to carbon. Signals at $m/z$=44, 47, and 64 were observed when the Kr lamp having a $CaF_2$ window (10.03 eV) was used (see Fig. 4). Among the signals observed, the signal at $m/z$=64 should be from $(CD_3)_2CO$. The signal at $m/z$=47 should be from $CD_2CHCD_3$ not from $CD_3CHO$, since as shown in Table 1, the ionization potential of propene is 9.7 eV, while that of acetaldehyde is 10.2 eV. The signal at $m/z$=44 would be from ketene, $CD_2CO$, produced in the secondary reaction of $CD_3CHO+O$.[29)]

As mentioned before, since acetaldehyde was observed in the reaction of $O+C_3H_8$, $CD_3CHO$ ($m/z$=47) should be observed in the present case when the Kr lamp having a $MgF_2$ window (10.03 and 10.64 eV) was used. However, it is difficult to distinguish $CD_2$-$CHCD_3$ and $CD_3CHO$, because these have the same mass number. In order to distinguish between these two molecules, $(CD_3)_2CH_2$ was reacted with $^{18}O$ (19.2% of $^{36}O_2$ in $^{32}O_2$ was diluted in helium and discharged by microwave). Mass spectra observed in the region from $m/z=43$ to 53 by using the Kr lamp with the $MgF_2$ window are shown in Fig. 5. Possible molecules corresponding to the significant signals observed are listed in Table 2. Signals of ketene, $CD_2CO$, propene, $CD_2CHCD_3$, and acetaldehyde, $CD_3CHO$ was observed as expected. In addition, the signal of $CD_3CDO$ was observed. $CD_3CDO$ might be a secondary product in the reaction of $CD_2CHCD_3+O$ (reaction mechanisms will be discussed later). Among the above signals, the signal at $m/z=49$ ($CD_3CH^{18}O$) can be used to monitor the concentration of acetaldehyde produced in Reaction 4c because, as will be described later, the concentration of $(CD_3)_2\dot{C}H$ radicals is in the steady-state concentration under the present experimental conditions (the signal intensity of $(CD_3)_2\dot{C}H$ is independent of the reaction time), while the concentration of $CD_3CH^{18}O$ increases linearly with reaction time. In this way the signals from $CD_3C^{18}O$ and $(CD_3)_2\dot{C}H$ can be distinguished.

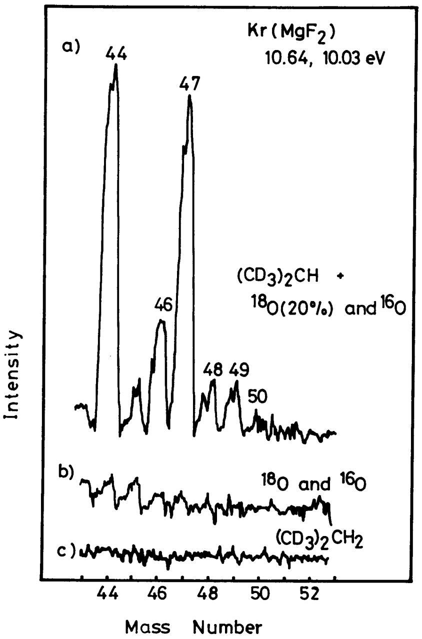

Fig. 5. Mass spectra of the reaction products produced in $(CD_3)_2CH_2+^{18}O(20\%)+^{16}O(80\%)$. A Kr lamp with a $MgF_2$ window (10.64 and 10.03 eV) was used to photoionize molecules. The conditions: partial pressure (mTorr), $[O]_0=3.4$, $[(CD_3)_2CH_2]=0.9$; reaction time=4.5 ms; total pressure=4.3 Torr.

Table 2. Signals Observed and Possible Molecules in the Reaction of $^{18}O+(CD_3)_2CH_2$ (19.2%) and $^{16}O+(CD_3)_2CH_2$ (80.8%) over the Mass Number Region from 43 to 53. The Kr Lamp with a $MgF_2$ Window Was Used as a Photoionization Light Source

| $m/z$ | Possible molecule |
|---|---|
| 44 | $CD_2CO$ |
| 45 | Isotope ($^{13}C$) signal of $m/z=44$ |
| 46 | $CD_2C^{18}O$ |
| 47 | $CD_2CHCD_3$, $CD_3CHO$ |
| 48 | $CD_3CDO$, isotope ($^{13}C$) signal of $m/z=47$ |
| 49 | $CD_3CH^{18}O$, $(CD_3)_2CH$ radical |
| 50 | $CD_3CD^{18}O$ |

**B. Competition between $O(^3P)$ and $O_2$ for $(CD_3)_2\dot{C}H$.** The time dependence of the $(CD_3)_2\dot{C}H$ radical signal was measured by changing the reaction time of $(CD_3)_2CH_2$ and oxygen atom. No significant change of signal was observed for the conditions of 3—6 mTorr of oxygen atoms, 1 mTorr of $(CD_3)_2CH_2$, and 0.5—10 ms of reaction time. When the concentration of $(CD_3)_2CH_2$ was increased, the signal for $(CD_3)_2\dot{C}H$ increased in proportion to the $(CD_3)_2CH_2$ concentration. This means that Reaction 4 is very rapid and that $(CD_3)_2\dot{C}H$ radicals are in their steady-state concentration

$$[\text{2-pr}]_{ss} = \frac{k_3}{k_4}[P]. \tag{5}$$

Here $[\text{2-pr}]_{ss}$ and $[P]$ represent the steady-state concentration of $(CD_3)_2\dot{C}H$ radicals and the initial concentration of $(CD_3)_2CH_2$, respectively. When molecular oxygen was added to the system, the steady-state concentration of $(CD_3)_2\dot{C}H$ decreased. This decrease is caused by the competition between $O(^3P)$ and $O_2$ for $(CD_3)_2\dot{C}H$ radicals and the competition results in a Stern-Volmer-type of equation.

$$\frac{[\text{2-pr}]^0_{ss}}{[\text{2-pr}]_{ss}} = 1 + \frac{k_7[O_2]}{k_4[\bar{O}]}, \tag{6}$$

where the superscript zero refers to the conditions in the absence of $O_2$ and $k_7$ is the effective second-order rate constant for the reaction of $(CD_3)_2\dot{C}H+O_2$.

$$(CD_3)_2\dot{C}H + O_2 \rightarrow \text{Products} \tag{7}$$

The results of the $O_2$ addition for two different conditions are presented in Fig. 6. The average concentration of oxygen atoms, $[\bar{O}]$, was calculated[36)] using a stoichiometric factor of $n=6$. The correction for oxygen-atom consumption was 0.5% or less. The concentration of $O_2$ was calculated from $[O_2]_{\text{added}}+[O_2]_0-1/2[O]_0$, where $[O_2]_0$ and $[O]_0$ refer to the original concentraiton of $O_2$ in the $O_2$/He mixture before the discharge, and the original oxygen-atom concentration produced in the $O_2$/He discharge, respectively. The value of $[O_2]_0-1/2[O]_0$ corresponds to the concentration of $O_2$ surviving from the $O_2$/He discharge. The two points shown on the left-hand side in Fig. 6 are obtained with just $[O_2]_0-1/2[O]_0$ present.

Values for $[\text{2-pr}]^0_{ss}$ were determined by plotting $([\text{2-pr}]_{ss})^{-1}$ against $[O_2]/[\bar{O}]$ and then determining $([\text{2-pr}]^0_{ss})^{-1}$ from the intercept of a least-square fit in order to remove the effect of the $O_2$ surviving from the discharge. The value for $k_7/k_4$ calculated from the slope in Fig. 6 is 0.029±0.004. Error limits due to the scattering of plots were calculated by the least square with

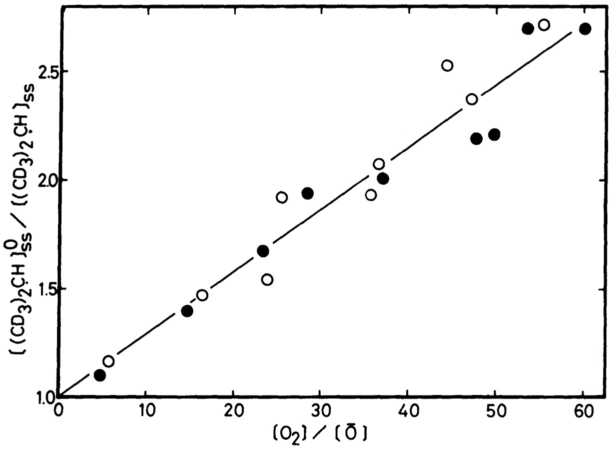

Fig. 6. Stern-Volmer plot for the competition between $O_2$ and $O(^3P)$ for the $(CD_3)_2CH$ radicals. Conditions for the open symbols: partial pressure (mTorr), $[O]_0$=3.32, $[\bar{O}]$=3.30, $[(CD_3)_2CH_2]$=1.31, $[O_2]_0$=19.44; total pressure 4.151 Torr; reaction time=4.46 ms. Conditions for the filled symbols: partial pressure (mTorr), $[O]_0$=2.99, $[\bar{O}]$=2.97, $[(CD_3)_2CH_2]$=1.003, $[O_2]_0$=15.43; total pressure=4.32 Torr; reaction time=4.51 ms. $[O_2]$ was calculated from $[O_2]_{added}+[O_2]_0-1/2[O]_0$.

the 95% confidence limits.

**C. Yields of $CD_2CHCD_3$ and $(CD_3)_2CO$.** The dependence of the $CD_2CHCD_3$ ($m/z$=47) and $(CD_3)_2CO$ ($m/z$=64) signals on the reaction time was measured by using a Kr lamp having a $CaF_2$ window and is shown in Fig. 7. The signal of $(CD_3)_2CO$ (open triangles) rises linearly with reaction time, while the signal of $CD_2CHCD_3$ (solid circles) increased but not linearly. The nonlinear increase of $CD_2CHCD_3$ with reaction time results from the consumption of $CD_2CHCD_3$ by Reaction 8.

$$CD_2CHCD_3 + O(^3P) \rightarrow \text{Products} \qquad (8)$$

If $CD_2CHCD_3$ is produced in Reaction 3 followed by Reaction 4a and consumed in Reaction 8, the concentration of $CD_2CHCD_3$ observed is given by Eq. 9, assuming that Reaction 4 is much faster than Reaction 3,

$$[CD_2CHCD_3] = \frac{k_3 f_{4a} [P]_0}{(k_8 - k_3)} (e^{-k_3[\bar{O}]t} - e^{-k_8[\bar{O}]t}) \qquad (9)$$

where $f_{4a}$, $[P]_0$, and $[\bar{O}]t$ represent the fraction of Reaction 4a in the total reaction of $(CD_3)_2\dot{C}H$+O, the original concentration of $(CD_3)_2CH_2$, and the product of the average oxygen-atom concentration and the reaction time,[36] respectively. In the present study, since the rate constant for Reaction 3 is very small, $7.91\times10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298K as will be described later, and the rate of Reaction 8, (3.3—4.50)$\times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [16,38] for $O+C_3H_6$, is 500 times faster than that of Reaction 3, the value of exp$(-k_3[\bar{O}]t)$ is nearly 1 and $k_8-k_3$ is nearly equal to $k_8$ under the present experimental conditions; $[\bar{O}]t < 1.5\times10^{12}$ molecules cm$^{-3}$. Thus Eq. 9 is simplified to Eq. 10.

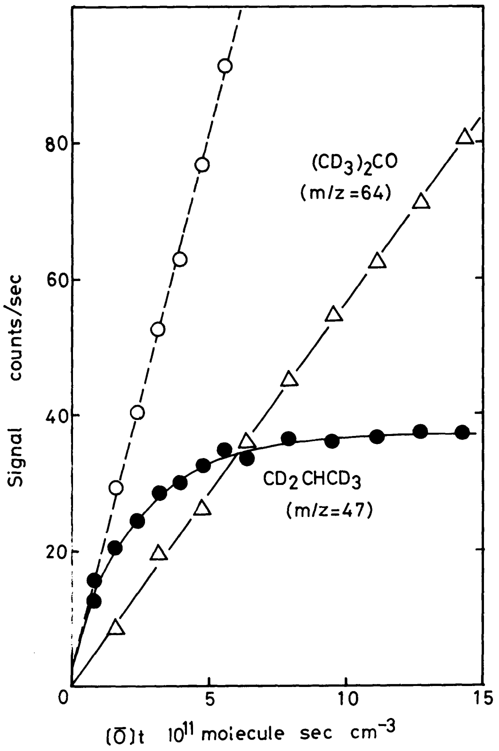

Fig. 7. Time dependence of $CD_2CHCD_3$ (solid circles) and $(CD_3)_2CO$ (open triangles) signals produced in the $O+(CD_3)_2CH_2$ reaction. A Kr lamp with a $CaF_2$ window (10.03 eV) was used for the photoionization. The conditions: partial pressure (mTorr), $[O]_0$=5.34, $[(CD_3)_2CH_2]$=0.95, $[O_2]_0$=24.60; total pressure=4.46 Torr. $[O_2]_0$ refers the amount of $O_2$ added to the $O_2$/He discharge. Reaction times used were 0.5—8.1 ms. Corrections for $[\bar{O}]$ were 1% or less. The $CD_2CHCD_3$ signals are corrected for the subsequent reaction to give $[CD_2CHCD_3]_T$ as indicated by open circles.

$$[CD_2CHCD_3] = \frac{f_{4a} k_3}{k_8} [P]_0 (1 - e^{-k_8[\bar{O}]t}) \qquad (10)$$

Equation 10 shows the $CD_2CHCD_3$ approaches a constant concentration at long reaction time. When the plots of $CD_2CHCD_3$ shown in Fig. 6 are fitted to Eq. 10, a value for $k_8$ of $(4.06\pm0.18)\times10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was calculated, which agrees well with the reported rate constants for $O+C_3H_6$.[16,38] The indicated errors due to the scattering of plots were calculated by the least square with the 95% confidence limits. The best fit line for Eq. 10 is shown as a solid line in Fig. 7. The total amount of $CD_2CHCD_3$ produced by Reaction 4a, $[CD_2CHCD_3]_T$, is given by Eq. 11,

$$[CD_2CHCD_3]_T = f_{4a} k_3 [P]_0 [\bar{O}]t \qquad (11)$$

Therefore, the total amount of $CD_2CHCD_3$ can be calculated by multiplying each observed $CD_2CHCD_3$ signal by $k_8[\bar{O}]t[1-\exp(-k_8[\bar{O}]t)]^{-1}$. These corrected points are shown as open circles in Fig. 7, and they are represented by the dashed straight line. The ratio of the slope of the dashed straight line to that for $(CD_3)_2CO$ is 2.8. The relative sensitivity of the photoi-

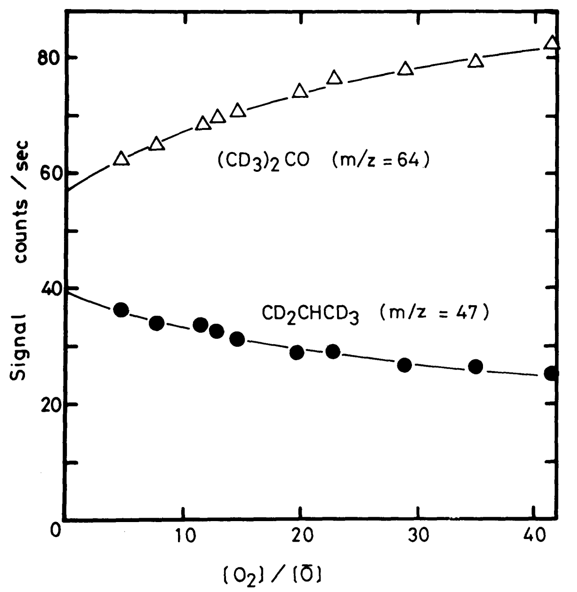

Fig. 8. Change of signals of $CD_2CHCD_3$ and $(CD_3)_2CO$ with the addition of $O_2$. Conditions: partial pressure (mTorr) $[O]_0=5.34$, $[\bar{O}]=5.32$, $[(CD_3)_2CH_2]=0.95$, $[O_2]_0=27.27$; reaction time= 6.30 ms; total pressure=4.46 Torr. $[O_2]$ was calculated from $[O_2]_{added}+[O_2]_0-1/2[O]_0$. The points shown on the left-hand side are obtained from just $[O_2]_0-1/2[O]_0$ (no $[O_2]_{added}$).

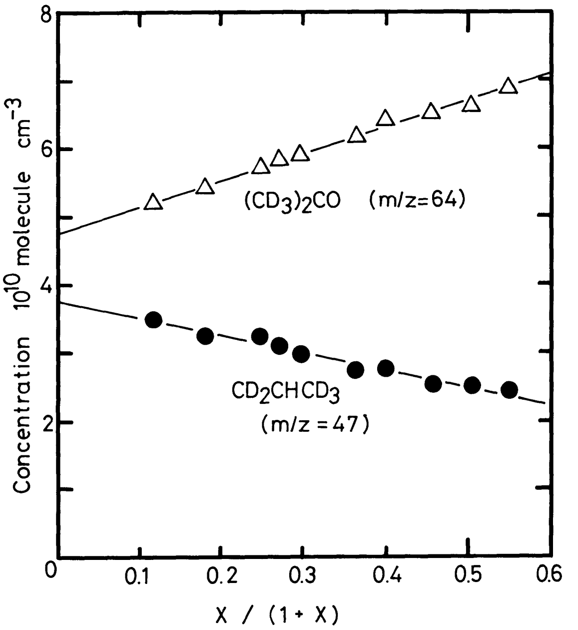

Fig. 9. The absolute concentrations of $CD_2CHCD_3$ and $(CD_3)_2CO$ are plotted against $X/(1+X)$ (see the text). Conditions are the same as in Fig. 8.

onization mass spectrometer for NO, $C_3H_8$, and $(CH_3)_2CO$ was mesured as 1 : 7.1 : 8.1 by using a Kr lamp ($CaF_2$). Assuming that the sensitivities of $CD_2CHCD_3$ and $(CD_3)_2CO$ are equal to those of $C_3H_8$ and $(CH_3)_2CO$, respectively, the ratio of the rate of formation of these two products was $CD_2CHCD_3$: $(CD_3)_2CO=3.2:1$ for the above conditions. Corrections for the consumption of acetone in the reactor is not important because the rate of the O+acetone reaction is very slow at room temperature[39] ($5-7\times10^{-16}$ $cm^3$ $molecule^{-1}$ $s^{-1}$).

The effect of the $O_2$ surviving from the $O_2$/He discharge on the yield of products might not be neglected. The $CD_2CHCD_3$ and $(CD_3)_2CO$ signals were measured when molecular oxygen was added to the system. The signal of $CD_2CHCD_3$ decreased and that of $(CD_3)_2CO$ increased when $O_2$ was added, as shown in Fig. 8. The two points on the left-hand side are obtained with only the $O_2$ surviving from the $O_2$/He discharge (no addition of $O_2$). In Fig. 8, $CD_2CHCD_3$ is in its steady-state concentration and $(CD_3)_2CO$ is not under these experimental conditions. If the fraction of $CD_2CHCD_3$ produced in Reaction 7 is represented by $s_{7a}$, the steady-state concentration of $CD_2CHCD_3$ is given by Eq. 12 when both $O(^3P)$ and $O_2$ are present, where $X$ is defined in Eq. 13.

$$[CD_2CHCD_3]_{ss} = \left\{f_{4a} + \frac{(s_{7a}-f_{4a})X}{1+X}\right\}\frac{k_3}{k_8}[P] \tag{12}$$

$$X = \frac{k_7}{k_4}\,\frac{[O_2]}{[\bar{O}]} \tag{13}$$

Similarly, the concentration of $(CD_3)_2CO$ at reaction time $t$ is represented by Eq. 14;

$$[(CD_3)_2CO] = \left\{f_{4b} + \frac{(s_{7b}-f_{4b})X}{1+X}\right\}k_3[P][\bar{O}]t \tag{14}$$

where $s_{7b}$ refers to the fraction of $(CD_3)_2CO$ produced in Reaction 7. Since the ratio of $k_7/k_4$ was determined previously, the concentrations of $CD_2CHCD_3$ and $(CD_3)_2CO$ can be plotted against $X/(1+X)$, as are shown in Fig. 9. The absolute concentrations of $CD_2CHCD_3$ and $(CD_3)_2CO$ were calculated using the instrumental sensitivities to propylene, $C_3H_6$ and acetone, $(CH_3)_2CO$, as measured by adding known partial pressures of both molecules to the reactor. Since the initial concentration of $(CD_3)_2CH_2$ and reaction time are known, values for $f_{4a}$ and $f_{4b}$ can be determined from the intercepts of the two lines and those for $s_{7a}$ and $s_{7b}$ are determined from the slopes. Here the value for $k_3$ of $7.91\times10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ was used, as will be discussed later, and the value for $k_8$ of $4.06\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ was used. Values obtained are ($0.61\pm0.07$), ($0.17\pm0.01$), ($0.20\pm0.02$), and ($0.31\pm0.02$), for $f_{4a}$, $f_{4b}$, $s_{7a}$, and $s_{7b}$, respectively. The indicated errors due to the scattering of plots were calculated by the least square with the 95% confidence limits.

**D. Yield of $CD_3CHO$.** The dependence of the signal at $m/z$=49 shown in Fig. 4 on the reaction time was measured by using a Kr lamp having a $MgF_2$ window and is shown in Fig. 10. The signal at $m/z$=66, $(CD_3)_2C^{18}O$, is also plotted as a reference. The signal at $m/z$=49 increased with reaction time but the increase was not linear. The nonlinear increase results from the consumption of $CD_3CH^{18}O$ by Reaction 15, and so the concentration of $CD_3CH^{18}O$ can be expressed by Eq. 16,

$$CD_3CHO + O(^3P) \rightarrow \text{Products} \qquad (15)$$

$$[CD_3CH^{18}O] = \frac{0.192\, f_{4c}k_3}{k_{15}}[P](1-e^{-k_{15}[\bar{O}]t}) \qquad (16)$$

where the value of 0.192 represents the fraction of $^{18}O(^3P)$ in the sum of $^{18}O(^3P)$ and $^{16}O(^3P)$. When the measured values of $CD_3CH^{18}O$ shown in Fig. 10 are fitted to Eq. 16, a value for $k_{15}$ of $(5.6\pm0.5)\times10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$ was calculated, which agrees well with the reported rate constants for $O+CH_3CHO$,[16,33,40] $(4.3-5)\times10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$. The indicated errors due to the scattering of plots were calculated by the least square with the 95% confidence limits. The best fit line for Eq. 16 is shown as a solid line in Fig. 10. The large intercept results from the signal due to $(CD_3)_2\dot{C}H$ radicals. As described before, the $(CD_3)_2\dot{C}H$ radicals should be in the steady-state concentration and the signals of $(CD_3)_2\dot{C}H$ are independent of the reaction time under the experimental conditions shown in Fig. 10. Each signal at $m/z=49$ minus the intercept is taken to be the signal of $CD_3CH^{18}O$. The total amount of $CD^3CH^{18}O$ produced in Reaction 4c, $[CD_3CH^{18}O]_T$, can be calculated by multiplying each observed $CD_3CH^{18}O$ signal by $k_{15}[\bar{O}]t[1-\exp(-k_{15}[\bar{O}]t)]^{-1}$. These corrected points are shown as open circles in Fig. 10, and they are represented by the dashed straight line. The ratio of the slope of the dashed line to that for $(CD_3)_2C^{18}O$ is 0.12. The relative sensitivity of the photoionization mass spectrometer for $CH_3CHO$, and $(CD_3)_2CO$ was measured as 1:9.87 by using a Kr lamp with a $MgF_2$ window. The ratio of the rate of formation of these two products was estimated to be $CD_3CH^{18}O$: $(CD_3)_2C^{18}O=1:0.86$ for the above conditions.

Signals at $m/z=49$ and 66 were measured when molecular oxygen containing 19.2% of $^{36}O_2$ in $O_2$ was added to the system. The results are listed in Table 3. The signal at $m/z=66$, $(CD_3)_2C^{18}O$, increased with addition of $O_2$ but the apparent signal at $m/z=49$ was nearly constant. As shown in Fig. 10, the signal at $m/z=49$ consists of $CD_3CH^{18}O$ and $(CD_3)_2\dot{C}H$. Between them, the signal of $(CD_3)_2\dot{C}H$ should decrease by the addition of $O_2$. This decrease is given by Eq. 6. Since the value for $k_7/k_4$ of 0.029 was determined previously and the signal intensity for the steady-state concentration of $(CD_3)_2\dot{C}H$ ($[2\text{-pr}]_{ss}=17.2$ counts $s^{-1}$) under the condition of $[O_2]/[\bar{O}]=3.66$ was determined from the intercept of the line in Fig. 10, the signal intensity for $[2\text{-pr}]^0_{ss}$ of 19.2 counts $s^{-1}$ was calculated by Eq. 6. Using this value of $[2\text{-pr}]^0_{ss}$, the signal intensity for $[2\text{-pr}]_{ss}$ was calculated for each $[O_2]/[\bar{O}]$ by Eq. 6 as is shown in Table 3. The signal for $CD_3CH^{18}O$ was obtained from the difference between the total signal at $m/z=49$ and the calculated signal of $[2\text{-pr}]_{ss}$.

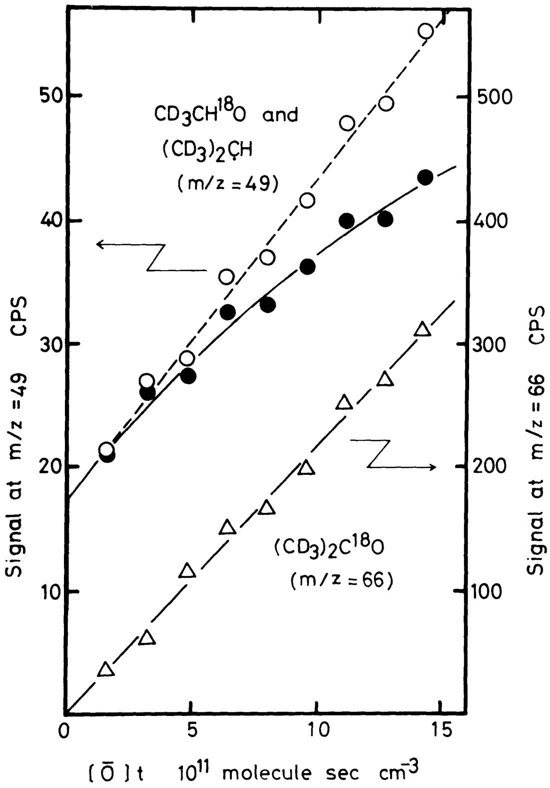

Fig. 10. Time dependence of $CD_3CH^{18}O$ (solid circles) and $(CD_3)_2C^{18}O$ (open triangles) signals produced in the $^{18}O+(CD_3)_2CH_2$ reaction. 19.2% of $^{36}O_2$ in $O_2$ was diluted in He and discharged. A Kr lamp with a $MgF_2$ window (10.64 and 10.03 eV) was used for the photoionization. The conditions: partial pressure (m Torr), $[O]_0=5.42$, $[(CD_3)_2CH_2]=2.37$, $[O_2]_0=22.28$; total pressure=4.48 Torr. $[O_2]_0$ refers to the amount of $O_2$ added to the $O_2$/He discharge. Reaction times used were 0.9—8.1 ms. Corrections for $[\bar{O}]$ were 1.5% or less. The $CD_3CH^{18}O$ signals are corrected for subsequent reaction to give $[CD_3CH^{18}O]_T$ as indicated by open circles. The large intercept for the signal at $m/z=49$ resulted from the signal of $(CD_3)_2CH$ radicals.

The signal of $CD_3CH^{18}O$ increased with the addition of $O_2$ as shown in Table 3. The absolute concentrations of $CD_3CH^{18}O$ and $(CD_3)_2C^{18}O$ were determined using the measured instrumental sensitivities to $CH_3CHO$ and $(CD_3)_2CO$.

As shown in Table 3, the formation of both $CD_3CH^{18}O$ and $(CD_3)_2C^{18}O$ increased when molecular oxygen was added to the system. The concentrations of $CD_3CH^{18}O$ and $(CD_3)_2C^{18}O$ were plotted against $X/(1+X)$, where $X$ is given by Eq. 13. The plots are shown in Fig. 11. As described before, from the slopes and intercepts of these straight lines values for $f_{4b}$, $f_{4c}$, $s_{7b}$, and $s_{7c}$ can be determined,[41] where $s_{7c}$ refers to the fraction of $CD_3CHO$ produced in Reaction 7. In these calculations, the fraction of $^{18}O$ in O (19.2%) was used and the effect of the consumption of $CD_3CH^{18}O$ by Reaction 15 was taken into account.[41] The values calculated are (0.18±0.02), (0.21±0.03), (0.32±0.03), and (0.44±0.08), for $f_{4b}$, $f_{4c}$, $s_{7b}$, and $s_{7c}$, respectively.

Table 3. Observed Signals at $m/z$=49 and 66 and Absolute Concentrations of $CD_3CH^{18}O$ and $(CD_3)_2C^{18}O$ in the Reaction of $(CD_3)_2CH_2+^{18}O+^{18}O_2$[a)]

| $O_2$ added mTorr | $[O_2]/[\bar{O}]$[b)] | Signal at $m/z$=49 cps | $[2\text{-pr}]_{ss}$[c)] cps | $[CD_3CH^{18}O]$[d)] cps | $[CD_3CH^{18}O]$[e)] $10^{10}$molecule cm$^{-3}$ | Signal at $m/z$=66 cps | $[(CD_3)_2C^{18}O]$[e)] $10^{10}$molecule cm$^{-3}$ |
|---|---|---|---|---|---|---|---|
| 0 | 3.66 | 40.03 | 17.30 | 22.73 | 2.24 | 255.23 | 2.55 |
| 19.58 | 7.31 | 41.18 | 15.87 | 25.31 | 2.50 | 271.25 | 2.71 |
| 47.65 | 12.55 | 40.33 | 14.12 | 26.21 | 2.59 | 283.26 | 2.83 |
| 65.74 | 15.93 | 42.16 | 13.15 | 29.01 | 2.86 | 249.27 | 2.94 |
| 87.90 | 20.07 | 40.93 | 12.15 | 28.78 | 2.84 | 305.28 | 3.05 |
| 113.01 | 24.76 | 41.99 | 11.16 | 30.83 | 3.04 | 310.29 | 3.10 |
| 151.61 | 31.97 | 42.97 | 9.95 | 33.02 | 3.26 | 331.30 | 3.31 |
| 207.00 | 42.31 | 41.47 | 8.61 | 32.86 | 3.24 | 335.31 | 3.35 |

a) Experimental conditions are: $[^{18}O]/([^{18}O]+[^{16}O])=0.192$, $[^{36}O_2]/([^{36}O_2]+[^{32}O_2])=0.192$, $[O]_0=5.42$ mTorr, $[(CD_3)_2CH_2]=2.37$ mTorr, $[O_2]_0=22.28$ mTorr, reaction time=6.299 ms, $[\bar{O}]=5.36$ mTorr, and total pressure=4.48 Torr. b) $[O_2]$ was calculated by $[O_2]_s+[O_2]_{added}$, where $[O_2]_s=[O_2]_0-1/2[O]_0$ refers to the $O_2$ surviving from the $O_2$/He discharge. c) The value for $[2\text{-pr}]_{ss}$ were calculated form Eq. 6 as follows; each value for $[2\text{-pr}]^0_{ss}/[2\text{-pr}]_{ss}$ can be calculated by using the known values of $k_7/k_4$ and $[O_2]/[O]$. The absolute intensity for $[2\text{-pr}]^0_{ss}$ of 19.2 counts s$^{-1}$ was determined from the intercept of the line shown in Fig. 10, in which the values for $[O_2]/[\bar{O}]$ and $[2\text{-pr}]_{ss}$ were 3.66 and 17.2 counts s$^{-1}$,respectively. d) Signal intensity for $CD_3CH^{18}O$ was determined from (signal at $m/z$=49)−(signal for $[2\text{-pr}]_{ss}$). e) The absolute concentrations for $CD_3CH^{18}O$ and $(CD_3)_2C^{18}O$ were determined by the instrumental sensitivities to $CH_3CHO$ and $(CH_3)_2CO$ as measured by adding known partial pressures of both gases to the reactor.

These values for $f_{4b}$ and $s_{7b}$ are in good agreement with the values obtained from Fig. 9. Combining the results obtained from Figs. 9 and 11, the branching fractions in Reactions 4 and 7 are:

$$(CD_3)_2\dot{C}H+O \xrightarrow{(61\pm7)\%} CD_2CHCD_3$$
$$\xrightarrow{(18\pm2)\%} (CD_3)_2CO$$
$$\xrightarrow{(21\pm3)\%} CD_3CHO \qquad (4)$$

$$(CD_3)_2\dot{C}H+O_2 \xrightarrow{(20\pm2)\%} CD_2CHCD_3$$
$$\xrightarrow{(32\pm3)\%} (CD_3)_2CO$$
$$\xrightarrow{(44\pm8)\%} CD_3CHO \qquad (7)$$

The values for $f_{4b}$ and $s_{7b}$ are averaged for the two measurements.

**E. Rate Constant for $(CD_3)_2CH_2+O(^3P)$ Reaction.** As described before, the determination of the rate constant for Reaction 3 is necessary in order to determine the fractions in Reaction 4. Since the rate of Reaction 3 at room temperature is too slow to measure by the pseudo-first-order decay of $(CD_3)_2CH_2$ under the present experimental conditions, the pseudo-first-order decay of $(CD_3)_2CH_2$ was measured over a temperature range of 381—627K in a large excess of oxygen atoms $[O]\gg[(CD_3)_2CH_2]$ by changing the contact time of $(CD_3)_2CH_2$ with oxygen atoms. An Ar lamp having a LiF window (11.83 and 11.62 eV) was used to photoionize $(CD_3)_2CH_2$. Since there was no signal from reaction product at $m/z$=50 when $(CD_3)_2CH_2$ reacted with atomic oxygen (see Fig. 4), the bimolecular rate of Reaction 3 can be measured from the decay of the signal of $(CD_3)_2CH_2$ at $m/z$=50. The results are presented in Table 4. The 95% confidence limits were calculated from the least squares line using ten points (ten different reaction times) for each run.

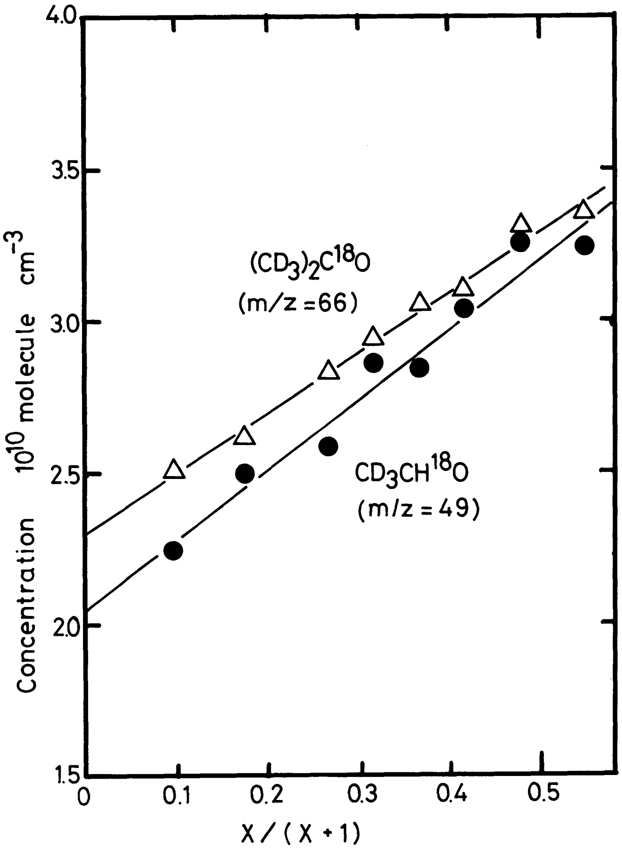

Fig. 11. The absolute concentrations of $CD_3CH^{18}O$ (solid circles) and $(CD_3)_2C^{18}O$ (open triangles) are plotted against $X/(1+X)$. Conditions are the same as those in Table 3.

The bimolecular rate constants of $k_3$ are plotted in

Table 4. Rate Data[a] for $O(^3P)+(CD_3)_2CH_2$ at 385—627 K

| $T$ | $[P]_0$[b] | $[O]_0$ | Total pressure | Flow rate | $k_3$ |
|---|---|---|---|---|---|
| K | mTorr | mTorr | Torr | $m\,s^{-1}$ | $10^{-14}\,cm^3\,molecule^{-1}\,s^{-1}$ |
| 627 | 0.052 | 1.681 | 5.68 | 43.4 | 198±22 |
| 605 | 0.073 | 3.837 | 5.26 | 40.9 | 113±18 |
| 573 | 0.101 | 4.129 | 5.83 | 41.2 | 93.8±9.6 |
| 561 | 0.103 | 6.836 | 5.73 | 41.0 | 80.2±6.5 |
| 491 | 0.114 | 5.801 | 5.62 | 36.2 | 34.6±4.2 |
| 485 | 0.102 | 7.026 | 5.31 | 36.1 | 36.4±5.3 |
| 426 | 0.098 | 8.381 | 6.18 | 31.7 | 15.1±1.3 |
| 421 | 0.182 | 10.79 | 6.07 | 31.9 | 14.0±1.6 |
| 385 | 0.146 | 12.52 | 6.68 | 28.3 | 6.71±0.73 |
| 381 | 0.102 | 13.32 | 6.65 | 28.1 | 7.46±0.66 |

a) The rate constant was calculated from the equation of $\ln [P]/[P]_0=-k_3[\bar{O}]t$, where $[P]$ and $[P]_0$ represent the signal of $(CD_3)_2CH_2$ in the presence and absence of oxygen atoms, respectively. b) $[P]_0$ represents the original concentration of $(CD_3)_2CH_2$.

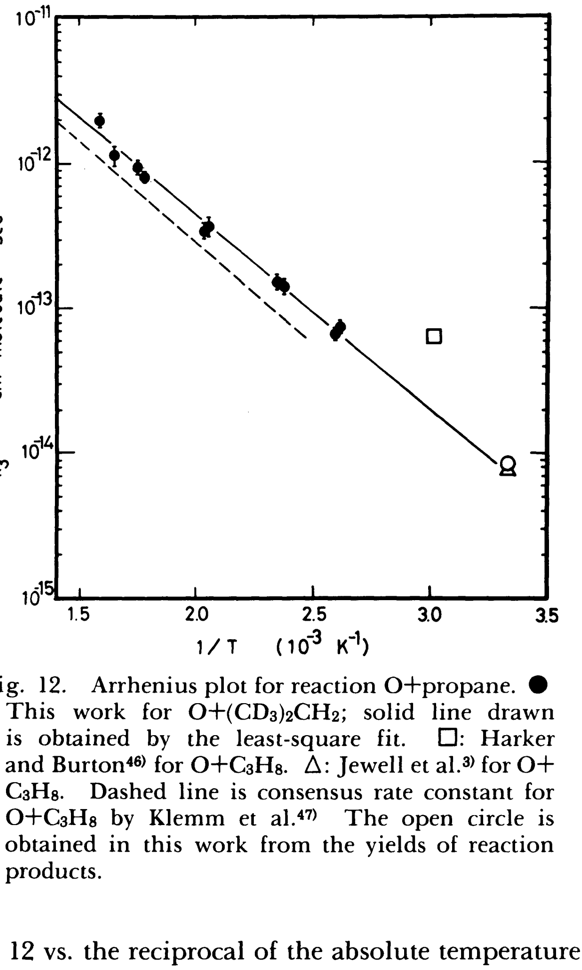

Fig. 12. Arrhenius plot for reaction O+propane. ● This work for $O+(CD_3)_2CH_2$; solid line drawn is obtained by the least-square fit. □: Harker and Burton[46] for $O+C_3H_8$. △: Jewell et al.[3] for $O+C_3H_8$. Dashed line is consensus rate constant for $O+C_3H_8$ by Klemm et al.[47] The open circle is obtained in this work from the yields of reaction products.

Fig. 12 vs. the reciprocal of the absolute temperature. A linear least square treatment yields the Arrhenius expression:

$$k_3 = (2.0^{+1.0}_{-0.7}) \times 10^{-10} \exp\left(\frac{-6086 \pm 392\,\mathrm{cal\,mol^{-1}}}{RT}\right) \quad (17)$$

in units of $cm^3\,molecule^{-1}\,s^{-1}$. The indicated errors were calculated by the least-square with 95% confidence limits. The rate constant for Reaction 3 at 298K calculated from Eq. 17 is $6.94\times10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$.

The rate constant for Reaction 3 can also be calculated from the sum of the absolute yields of the three reaction products; $CD_2CHCD_3$, $(CD_3)CO$, and $CD_3CHO$. The value for $k_3$ of $7.9\times10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$ was calculated[42] from absolute concentrations of products produced initially by Reaction 4. The value is in reasonable agreement with that calculated from Eq. 17. Therefore, the value of $7.91\times10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$ was used for $k_3$ in all calculations in this study.

## Discussion

The observation of propyl radicals by photoionization using the Xe resonance lamp (8.44 eV) is reasonable because the ionization potentials for the propyl radicals are low (Table 1). The detection of propyl radicals using photoionization by the Xe lamp has been reported by Bayes et al.[43] Only the $(CD_3)_2\dot{C}H$ radical was formed in the reaction of $O+(CD_3)_2CH_2$. For comparison, the reaction of oxygen atoms with propane-2,2-$d_2$, $(CH_3)_2CD_2$, gave both $\cdot CH_2CD_2CH_3$ ($m/z$=45) and $(CH_3)_2\dot{C}D$ ($m/z$=44). The ratio of the signal at $m/z$=44 to 45 was about 3 : 2. Therefore, the abstraction of the 1- or 2-hydrogen from propane is very sensitive to the small difference in the bond dissociation energies of C-H and C-D. Jewell et al.[3] observed the formation of $(CH_3)_2CO$ and $C_2H_5CHO$ in the $O+C_3H_8$ system. This result also suggests that both $n$-propyl and isopropyl radicals are produced by the primary attack of O atoms on $C_3H_8$.[29]

$CD_2CHCD_3$, $(CD_3)_2CO$, and $CD_3CHO$ were observed as major products of the $O+(CD_3)_2\dot{C}H$ reaction. In addition, the signal of $CD_2CO$ was observed in this study. Since the signals for $CD_2CO$ were proportional to the square of $[\bar{O}]t$, $CD_2CO$ probably is produced by secondary reactions.[29] In the previous discharge-flow experiments involving $O+C_3H_8$,[3,4] the formation of $C_2H_5CHO$, $C_2H_6$, $C_2H_4$, $CH_2O$, $CH_4$, $CO_2$, $CO$, $H_2O$, and $H_2$ has been reported in addition to propene, acetone and acetaldehyde. These products, except for $C_2H_5CHO$, are probably produced in secondary reactions.

Propene, $CD_2CHCD_3$, was a major product of the $O+(CD_3)_2CH$ reaction. Propene can be produced by hydrogen abstraction, Reaction 4a. Similar hydrogen abstraction reactions were found for O+$t$-$C_4H_9$[1] and O+*cyclo*-$C_6H_{11}$.[2] These results disagree with the findings by Hoyerman and Sievert,[7] who observed no formation of olefins in the reactions of O+alkyl radicals.

As shown in Table 2 and Fig. 5, the products $CD_3CDO$ ($m/z$=48) and $CD_3CD^{18}O$ ($m/z$=50) were observed in the $^{16}O$ and $^{18}O+(CD_3)_2CH_2$ systems. These products might be produced by secondary reactions following $O+CD_2CHCD_3$. According to the previous studies on $O+C_3H_6$,[37,44,45] Reaction 8 proceeds as follows:

$$\begin{array}{llr} & \nearrow (\mathrm{CD_3CHDCDO})^* \rightarrow & \\ & \qquad\qquad \mathrm{CD_3CHD + CDO} & (8a) \\ \mathrm{CD_2CHCD_3 + O} & & \\ & \searrow (\mathrm{CD_3(CO)CHD_2})^* & \\ & \quad \rightarrow \mathrm{CD_3 + CHD_2CO} & (8b) \\ & \quad \rightarrow \mathrm{CHD_2 + CD_3CO} & (8c) \end{array}$$

Since no signals at $m/z$=63 were observed as shown in Fig. 4, the vibrationally hot $CD_3CHDCDO$ and $CD_3COCHD_2$ were not stabilized for the present experimental conditions. $CD_3CHD$ produced in Reaction 8a reacts with oxygen atoms and can produce $CD_3CHO$ and $CD_3CDO$.

$$\begin{array}{llr} & \nearrow \mathrm{CD_3CDO + H}\ (m/z=48) & (18a) \\ \mathrm{CD_3CHD + O} & & \\ & \searrow \mathrm{CD_3CHO + D}\ (m/z=47) & (18b) \end{array}$$

$CD_3CDO$ shown in Table 2 and Fig. 5 might be produced in Reaction 18a. As described before, yields of acetaldehyde were determined from the signals of $CD_3CH^{18}O$ ($m/z$=49). If Reaction 18b occurred, the yield of $CD_3CH^{18}O$ was overestimated. The fraction of Reaction 18b should be less than 18a because of the difference of the bond energy of C-H and C-D. Therefore, the signal of $CD_3CH^{18}O$ from Reaction 18b should be smaller than that of $CD_3CD^{18}O$ ($m/z$=50). From the measurement of the signal intensities at $m/z$=49 and 50 in the $^{18}O+(CD_3)_2CH_2$ reaction, it was determined that the effect of Reaction 18b on the total signal of $CD_3CH^{18}O$ was less than 20%. Thus the lower error limit of the yield of acetaldehyde should be increased in 20%; $f_{4c}=0.21^{+0.03}_{-0.07}$.

The value for $k_7/k_4$ of 0.029±0.004 was obtained from the competition experiment between O and $O_2$ for the $(CD_3)_2\dot{C}H$ radical. The rate constant for the reaction of isopropyl radicals, $i$-$C_3H_7$, with molecular oxygen has been reported[43], to be $(14.1\pm2.4)\times10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298K. Assuming that the rates of reactions of $(CD_3)_2CH+O_2$ and $i$-$C_3H_7+O_2$ are equal, the value for $k_4$ can be calculated as $4.9\times10^{-10}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. The rate of Reaction 4 is very rapid, but slower than the rate of reaction of $t$-butyl radical+O,[1] $8.7\times10^{-10}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

Propene, $CD_2CHCD_3$, was produced by deuterium abstraction. The excess energy of Reaction 4a is about 63 $\mathrm{kcal\,mol^{-1}}$. The yield of propene was 61% of the total $O+(CD_3)_2CH$ reaction. Yields of olefins from other O+alkyl radical reactions were 80% (isobutene) from O+$t$-$C_4H_9$,[1] and 52% (cyclohexene) from O+*cyclo*-$C_6H_{11}$.[2] These yields appear to correlate with the number of hydrogen atoms which can be abstracted; nine equivalent hydrogen atoms in the $t$-butyl radical to produce isobutene, six in the isopropyl radical to produce propene, and four in the cyclohexyl radical to produce cyclohexene.

Acetone, $(CD_3)_2CO$, and acetaldehyde, $CD_3CHO$, were formed by the oxygen atom addition. The isopropoxyl radical, $(CD_3)_2CH\text{-}O\cdot$, formed in Reaction 4 would have approximately 90 $\mathrm{kcal\,mol^{-1}}$ excess energy and should rapidly decompose to $(CD_3)_2CO+H$ and $CD_3CHO+CD_3$. Excess energies for Reactions 4b and 4c are 77.1 and 82.9 $\mathrm{kcal\,mol^{-1}}$, respectively. Yields of acetone (18%) and acetaldehyde (21%) are similar, reflecting the similar exothermicities. The ratio of deuterium abstraction to oxygen atom addition was 1.6 : 1.

In the presence of an excess of $O_2$ the same products were observed but in different proportions; propene decreased to 20% and acetone and acetaldehyde increased to 32 and 44%, respectively. This trend is very similar to the case of the $t$-butyl radical.[11] It is proposed that the formation of these products occurs by the reaction of propylperoxyl radicals with atomic oxygen.

$$\mathrm{(CD_3)_2\dot{C}H + O_2} \xrightarrow{+M} \mathrm{(CD_3)_2C(H)OO} \qquad (7')$$

$$\begin{array}{llr} & \nearrow \mathrm{CD_2CHCD_3 + OD + O_2} & (19a) \\ \mathrm{(CD_3)_2C(H)OO + O} & \longrightarrow \mathrm{(CD_3)_2CO + H + O_2} & (19b) \\ & \searrow \mathrm{CD_3CHO + CD_3 + O_2} & (19c) \end{array}$$

Here Reaction 19a is a deuterium abstraction reaction from the peroxyl radical by $O(^3P)$; after abstraction, $O_2$ departs from the peroxy biradical ($\cdot CD_2CH(CD_3)OO\cdot$) and propene is produced. In Reactions 19b and 19c oxygen atoms attack the radical oxygen ($\text{-O-O}\cdot$). The resulting hot propoxyl radical decomposes to the fragements $(CD_3)_2CO+H$ and $CD_3CHO+CD_3$. Reactions 19a and 19c are 49 and 55 $\mathrm{kcal\,mol^{-1}}$ exothermic, respectively.

Various studies of the rate of the $O+C_3H_8$ reaction are summarized in Fig. 12. Harker and Burton[46] measured the OH radical produced by Reaction 1 by molecular modultion spectroscopy. They obtained a value for $k_1$ of $6.5\times10^{-14}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 329K. Jewell et al.[3] measured the decay of O-atoms and also propane in the $O+C_3H_8$ discharge-flow system and proposed a value for $k_1$ of $7.8\times10^{-15}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 306K. In a recent article, Klemm et al.[47] reported the measurement of the rate of the $O+C_3H_8$ reaction by both flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence techniques over a temperature range of 411—1018K; they proposed the Arrhenius expression: $k_1=(1.66\pm0.16)\times10^{-10}\ \exp[(-6290\pm120\ \mathrm{cal\,mol^{-1}})/RT]$ in unit of $\mathrm{cm^3\ molecule^{-1}}$

$s^{-1}$. Rate constants for O+$(CD_3)_2CH_2$ obtained in this study agree well with the value by Klemm et al. in both activation energy and frequency factor considering the error of the measurements. The rate constant extrapolated to room temperature, $6.94\times10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, using Eq. 17 differs by 1.6 factor with the value of $k_3$ calculated from the absolute yields of products, $7.81\times10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Both values of $k_3$ at room temperature agree well with the rate constant for O+$C_3H_8$ at 306K reported by Jewell et al.

## Conclusion

(1) Isopropyl-$d_6$ radicals, $(CD_3)_2CH$, produced in the reaction of propane-1,1,1,3,3,3-$d_6$, $(CD_3)_2CH_2$, with atomic oxygen were detected directly by the photoionization mass spectrometer.

(2) The reaction of $(CD_3)_2\dot{C}H$ radicals with atomic oxygen proceeds by deuterium abstraction (61%) and by an oxygen atom addition reaction (39%).

(3) The product in the deuterium abstraction was propene-1,1,3,3,3-$d_5$, $CD_2CHCD_3$. Acetone-$d_6$, $(CD_3)_2CO$ and acetaldehyde-2,2,2-$d_3$, $CD_3CHO$ were produced by the oxygen atom addition reaction with yields of 18 and 21%, respectively.

(4) The reaction of $(CD_3)_2\dot{C}H$ radicals with molecular oxygen was $0.029\pm0.004$ times as fast as that with atomic oxygen. From the rate constant for the $O_2$+$C_3H_7$ reaction reported, the rate constant for the reaction of O+isopropyl radicals was estimated to be $4.9\times10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$.

(5) In the reaction of isopropylperoxyl radicals with molecular oxygen, the yield of $CD_2CHCD_3$ decreased to 20% and the yields of $(CD_3)_2CO$ and $CD_3CHO$ increased to 32 and 44%, respectively.

(6) The rate data for the reaction of O+$(CD_3)_2CH_2$ were fitted by an Arrhenius expression; $k_3=(2.01^{+1.0}_{-0.7})\times 10^{-10}\exp[(-6086\pm392\ \mathrm{cal\ mol^{-1}})/RT]$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (381—627 K). The rate constant obtained from the yields of products was $7.9\times10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298K.

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14) Reaction of propane with atomic oxygen starts by the hydrogen abstraction reaction

$$C_3H_8+O\rightarrow C_3H_7+OH \qquad \text{(A)}$$

OH radicals can also be produced by the subsequent radical-atom reactions. OH radicals can react with $C_3H_8$ faster than Reaction A

$$C_3H_8+OH\rightarrow C_3H_7+H_2O \qquad \text{(B)}$$

The rate constants for Reactions A and B at 298K have been reported to be $(8—15)\times10^{-15}$ (Refs. 3, 15, 16) and $(0.8—2)\times10^{-12}$ $cm^3$ $molecules^{-1}$ $s^{-1}$ (Refs. 17—23), respectively. OH radicals are destroyed by the following two reactions:

$$OH+O\rightarrow H+O_2 \qquad \text{(C)}$$

$$OH+\text{wall}\rightarrow \text{removal of OH} \qquad \text{(D)}$$

Therefore, in order to avoid an effect of the OH radicals on the formation of $C_3H_7$ radicals, the ratio of $k_B[C_3H_8]/k_C[O]$ must be less than 0.1. The rate constant of Reaction C has been reported to be $(3—4)\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Refs. 24—27) at 298K. The above requirement means that the kinetic experiments should be done under the condition that the concentration of oxygen atoms must be at least twice as large as the concentration of propane.

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29) The reaction of $O+C_3H_8$ might proceed as follows:

$$\mathrm{O}+\mathrm{C_3H_8}\begin{array}{ll}\nearrow n\text{-}\mathrm{C_3H_7}+\mathrm{OH} & \text{(E)}\\ \searrow i\text{-}\mathrm{C_3H_7}+\mathrm{OH} & \text{(F)}\end{array}$$

$$n\text{-}\mathrm{C_3H_7}+\mathrm{O}\begin{array}{ll}\nearrow \mathrm{C_3H_6}+\mathrm{OH} & \text{(G)}\\ \rightarrow \mathrm{C_2H_5CHO}+\mathrm{H} & \text{(H)}\\ \searrow \mathrm{CH_2O}+\mathrm{C_2H_5} & \text{(I)}\end{array}$$

$$i\text{-}\mathrm{C_3H_7}+\mathrm{O}\begin{array}{ll}\nearrow \mathrm{C_3H_6}+\mathrm{OH} & \text{(J)}\\ \rightarrow \mathrm{(CH_3)_2CO}+\mathrm{H} & \text{(K)}\\ \searrow \mathrm{CH_3CHO}+\mathrm{CH_3} & \text{(L)}\end{array}$$

Ketene, $CH_2CO$ (see Ref. 30), can be produced by a secondary reaction (Ref. 31) such as;

$$\mathrm{CH_3CHO}+\mathrm{O}\rightarrow\mathrm{CH_3CO}+\mathrm{OH} \qquad \text{(M)}$$
$$\mathrm{CH_3CO}+\mathrm{O}\rightarrow\mathrm{CH_2CO}+\mathrm{OH} \qquad \text{(N)}$$

30) Since the photoionization mass spectrometer is very sensitive to ketene (5—20 times more sensitive than other organic compounds), its absolute concentration is much smaller than is suggested by the signal intensity.

31) N. Washida and K.D. Bayes, unpublished data.

32) $CH_3CO+O\rightarrow CH_3+CO_2$ (Refs. 31 and 33) subsequent to Reaction M in Ref. 29.

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36) The consumption of oxygen atoms in the reactor was corrected as follows: Oxygen atoms are destroyed by Reactions 3, 4, O, and P.

$$\mathrm{OD}+\mathrm{O}\rightarrow\mathrm{O_2}+\mathrm{D} \qquad \text{(O)}$$
$$(\text{or } \mathrm{OH}+\mathrm{O}\rightarrow\mathrm{O_2}+\mathrm{H})$$
$$\mathrm{CD_3}+\mathrm{O}\rightarrow\mathrm{CD_2O}+\mathrm{D} \qquad \text{(P)}$$

Further, a major part of the $CD_2CHCD_3$ produced in Reaction 4a and a small part of the $CD_3CHO$ produced in Reaction 4c react with atomic oxygen. According to the results by Kanofsky et al. (Ref. 37), the major routes of the $O+C_3H_6$ reaction are:

$$\mathrm{O}+\mathrm{C_3H_6}\begin{array}{ll}\nearrow \mathrm{CHO}+\mathrm{C_2H_5} & \text{(Qa)}\\ \searrow \mathrm{CH_3}+\mathrm{CH_3CO} & \text{(Qb)}\end{array}$$

Therefore, the stoichiometric factor, $n$, for the number of oxygen atoms consumed per $(CD_3)_2CH_2$ reacted varies from 2.5 to 8 depending on the reaction time. A value $n=6$ was used for all experiments in the present study. The value of $[\bar{O}]t$, which is a product of the average oxygen-atom concentration and the reaction time, were calculated by Eq. R.

$$[\bar{\mathrm{O}}]t=[\mathrm{O}]_0\int_0^t \exp(-nk_3[\mathrm{P}]t)\mathrm{d}t \qquad \text{(R)}$$

where, $[O]_0$, $k_3$, and $[P]$ are the original oxygen-atom concentration, the rate constant for Reaction 3, and the concentration of $(CD_3)_2CH_2$, respecrively. The value for $k_3$ of $7.91\times10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was used for this calculations as will be discussed later.

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41) For $(CD_3)_2C^{18}O$, since $^{18}O$ used is 19.2% in O, $f_{4b}$ and $s_{7b}$ were determined by Eq. S.

$$[(\mathrm{CD_3})_2\mathrm{C^{18}O}]=\left\{f_{4b}+\frac{(s_{7b}-f_{4b})X}{1+X}\right\}0.192k_3[\mathrm{P}][\bar{\mathrm{O}}]t \qquad \text{(S)}$$

For $CD_3CH^{18}O$, $f_{4c}$ and $s_{7c}$ were calculated by Eq. T since a correction of the consumption of $CD_3CH^{18}O$ by Reaction 15 is necessary.

$$[(\mathrm{CD_3})_2\mathrm{C^{18}O}]$$
$$=\left\{f_{4c}+\frac{(s_{7c}-f_{4c})X}{1+X}\right\}0.192k_3[\mathrm{P}][\bar{\mathrm{O}}]t\ \frac{1-\mathrm{e}^{-k_{15}[\bar{\mathrm{O}}]t}}{k_{15}[\bar{\mathrm{O}}]t} \qquad (T)$$

42) The amount of $(CD_3)_2CO$ produced when $[O_2]$ is zero was calculated to be $4.76\times10^{10}$ molecule cm$^{-3}$ in the case of Fig. 9. In the case of Fig. 11, the total amount of actone produced when $[O_2]$ is zero was $12.36\times10^{10}$ molecule cm$^{-3}$ (the amount of $(CD_3)_2C^{18}O$ was $2.37\times10^{10}$ molecule cm$^{-3}$). The ratio of the yield of three reaction products produced initially by Reaction 4, $f_{4a}:f_{4b}:f_{4c}$, was 3.56 : 1 : 1.16. Therefore, the sums of the amounts of three products are 27.24 and $69.36\times10^{10}$ molecule cm$^{-3}$ in cases of Figs. 9 and 11, respectively. Since the values for $[O]t$ were 11.06 and $11.14\times10^{11}$ molecule s cm$^{-3}$ for Figs. 9 and 11, respectively, values for $k_3$ calculated from $k_3[O][(CD_3)_2CH_2]t$=[total products] are 7.86 and $7.96\times10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for Figs. 9 and 11, respectively. The average value of $7.91\times10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was used for all subsequent calculations.

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