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Oxidation of $(CD_3)_2\dot{C}X$ Radicals. III. Reaction of 2-Propanol and $(CD_3)_2\dot{C}(OH)$ Radicals with Atomic Oxygen

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The reaction of oxygen atoms with 2-propanol was studied in a fast flow system coupled with a photoionization mass spectrometer. Radicals formed in the primary attack of $O(^3P)$ atoms on 2-propanol were photoionized by the Xe lamp and identified as the $(CH_3)_2\dot{C}(OH)$ radical from $(CH_3)_2CH(OH)$ and $(CH_3)_2CD(OH)$ and the $(CD_3)_2\dot{C}(OH)$ radical from $(CD_3)_2CH(OH)$. The major primary product in the subsequent reaction of $O+(CD_3)_2\dot{C}(OH)$ was found to be acetone, $(CD_3)_2CO$, (62±4%). Formation of 1-propen-2-ol, $CD_3C(OH)=CD_2$, by deuterium abstraction and acetic acid, CD_3COOH, by oxygen addition were observed in the reaction of $O+(CD_3)_2\dot{C}(OH)$. In the reaction of $^{18}O+(CD_3)_2\dot{C}(OH)$, the acetone produced was mostly $(CD_3)_2CO$. This fact shows that acetone is produced predominantly by the hydrogen abstraction by $O(^3P)$ from the O-H in the $(CD_3)_2\dot{C}(OH)$ radical. A part of the acetone is produced also by the addition of $O(^3P)$ to the $(CD_3)_2\dot{C}(OH)$ radical; i.e., a small but significant signal of $(CD_3)_2C^{18}O$ was observed in the reaction of $^{18}O+(CD_3)_2\dot{C}(OH)$. The competition experiment between $O(^3P)$ and O_2 for the $(CD_3)_2\dot{C}(OH)$ radical shows that $(CD_3)_2\dot{C}(OH)$ react (0.16±0.02) times as fast with O_2 as with $O(^3P)$. This result suggests that the reaction of $(CD_3)_2\dot{C}(OH)$ with O_2 is very rapid. It is proposed that the rapid reaction is hydrogen abstraction by O_2 from the O-H in the $(CD_3)_2\dot{C}(OH)$ radical to form acetone and HO_2.

The study is extended[1] to reactions of oxygen atoms with 2-propanol and $(CD_3)_2\dot{C}(OH)$ radicals. There have been a few reports on the mechanism and the rate of the O+2-propanol reaction. Kato and Cvetanovic[2] studied the reaction of 2-propanol with oxygen atoms produced by the mercury photosensitized decomposition of dinitrogen monoxide. They suggested that abstraction of an α-hydrogen atom from 2-propanol to give $(CD_3)_2\dot{C}(OH)$ radicals takes place in the primary step, because they found the formation of pinacol, $[C(CH_3)_2OH]_2$, as a product. A large amount of acetone observed in the system was explained as a product of the radical-radical reaction. A kinetic investigation[3] reports that the rate constant for the reaction of $O(^3P)$ with 2-propanol is 1.3×10^{-14} cm^3 molecule^{-1} s^{-1} at 298K with an activation energy of 2.2 kcal mol^{-1}.

$$(CH_3)_2CH(OH)+O(^3P)\rightarrow(CD_3)_2\dot{C}(OH)+OH \quad (1)$$

In the present study, the reaction of oxygen atoms with 2-propanol was investigated in a fast-flow reactor coupled with a photoionization mass spectrometer in order to examine the following questions: (1) Can the $(CD_3)_2\dot{C}(OH)$ radical produced by the selective abstraction of an α-hydrogen suggested by Kato and Cvetanovic be detected by the photoionization mass spectrometry ?; (2) What products are produced by the radical-atom reaction ? Possible radical-atom reaction processes in both hydrogen abstraction and the oxygen atom addition are:
abstraction;

$$(CD_3)_2\dot{C}(OH)+O\rightarrow\begin{cases}(CH_3)_2CO\ (m/z=58)+OH & (2a)\\ CH_3C(OH)CH_2\ (m/z=58)+OH & (2b)\end{cases}$$

addition;

$$(CD_3)_2\dot{C}(OH)+O\rightarrow\begin{cases}(CH_3)_2CO\ (m/z=58)+OH & (2c)\\ CH_3COOH\ (m/z=60)+CH_3 & (2d)\end{cases}$$

subsequent to Reaction 1. In the previous study of the reaction of oxygen atoms with 1-hydroxyethyl radicals,[4] formation of acetaldehyde produced by hydrogen abstraction, a type of Reaction 2a, was observed as a major product (80%). Formation of vinyl alcohol, and formic and acetic acids, types of Reactions 2b and 2d, respectively, could not be observed.

Experimental

The experimental apparatus and procedures were the same as those mentioned before.[1] 2-Propanol (from Wako Pure Chemical Ind.), propan-2-*d*-2-ol, $(CH_3)_2CD(OH)$, and propan-1,1,1,3,3,3-d_6-2-ol, $(CD_3)_2CH(OH)$, (both from Merck Sharp & Dohm) were used without further purification except degassing. All measurements were done at room temperature, 298±3K, under the conditions [O]>2[2-propanol].[5]

Results

A. Reaction of 2-Propanol with $O(^3P)$. Radicals produced by the initial attack of $O(^3P)$ on three different 2-propanols such as $(CH_3)_2CH(OH)$, $(CH_3)CD(OH)$, and $(CD_3)_2CH(OH)$ were detected when a Xe resonance lamp having a sapphire window (8.44 eV) was used as a photoionization light source. Radical signals observed are shown in Fig. 1. Possible radicals produced by abstraction of an α-hydrogen (a) and a β-hydrogen (b) in each 2-propanol are as follows:

$$(CH_3)_2CH(OH)+O\rightarrow\begin{cases}(CD_3)_2\dot{C}(OH)\ (m/z=59)+OH & (1a)\\ \cdot CH_2CH(CH_3)(OH)\ (m/z=59)+OH & (1b)\end{cases}$$

$$(CH_3)_2CD(OH)+O \rightarrow (CD_3)_2\dot{C}(OH)\ (m/z=59)+OD \quad (3a)$$
$$\rightarrow \cdot CH_2CD(CH_3)(OH)\ (m/z=60)+OH \quad (3b)$$

$$(CH_3)_2CH(OH)+O \rightarrow (CD_3)_2\dot{C}(OH)\ (m/z=65)+OH \quad (4a)$$
$$\rightarrow CD_2CH(CD_3)(OH)\ (m/z=64)+OD \quad (4b)$$

Isotopic measurements shown in Fig. 1 demonstrate that the radicals observed are produced by selective abstraction of an α-hydrogen in 2-propanol as suggested by Kato and Cvetanovic.[2] Since no significant signals were observed at m/z=60 and 64 in Reactions 3 and 4 considering the natural abundance of ^{13}C (1.11%) and the background noise, it is concluded that more than 99% of the primary attack of $O(^3P)$ atoms on 2-propanol is abstraction of α-hydrogen (or deuterium).

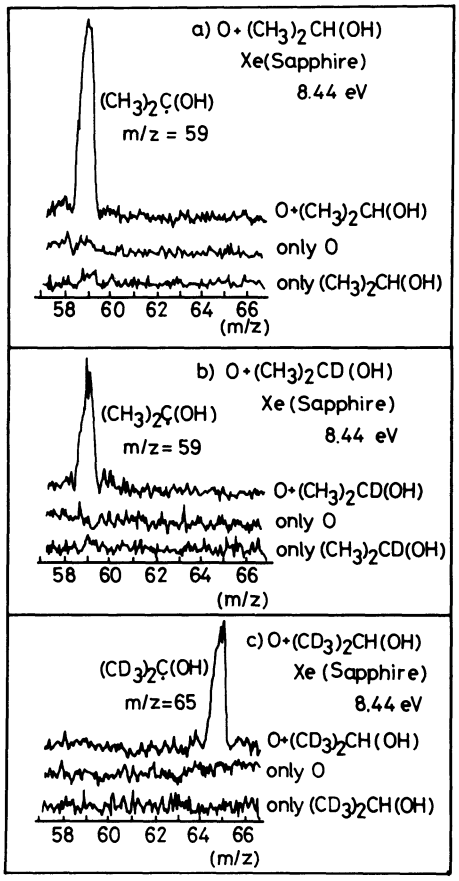

Fig. 1. Mass spectra of $(CH_3)_2C(OH)$ and $(CD_3)_2C(OH)$ radicals produced in O+2-propanol. A Xe lamp with a sapphire window (8.44 eV) was used for the ionization. a) O+$(CH_3)_2$CH(OH); b) O+$(CH_3)_2$CD(OH); c) O+$(CD_3)_2$CH(OH). The conditions: $[O]_0$=0.87 mTorr; $[2\text{-propanol}]_0$=0.41 mTorr; reaction time 4.4 ms; total pressure 3.8 Torr.

The pseudo-first-order decay rates of $(CD_3)_2CH(OH)$ were measured in the presence of a large excess of oxygen atoms. $(CD_3)_2CH(OH)$ was photoionized by the Ar lamp with a LiF window (11.83 and 11.62 eV) and measured at m/z=66 (M^+). Values for k_4 obtained are listed in Table 1. The 95% confidence limits were calculated form the least-squares line using 8 points for each run and 24 points for the average values. The value of $(4.3\pm0.4)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} for k_4 is 33 times larger than the rate for the reaction $(CD_3)_2$CH(OH)+O reported by Ayub and Roscoe.[3] The rate constant for the reaction O+$(CD_3)_2$CD(OH) was also measured and shown in Table 1. The rate for Reaction 3 was about 40% slower than that for Reaction 4 at 298K. The rate of reaction O+$(CH_3)_2$CH(OH) could not be measured[8] because signals for $(CD_3)_2$CH(OH) coincide with one of the signals of products formed in the reaction of O+$(CH_3)\dot{C}$(OH) as will be described later.

B. Radical-Atom Reactions. Products produced in the reaction of oxygen atoms with radicals produced in Reactions 1, 3, and 4 were measured by using a Kr lamp having a CaF_2 window (10.03 eV). Mass spectra observed in the reaction of $(CH_3)_2CH(OH)+O$ are shown in Fig. 2a. The signal observed at m/z=58 should be from acetone, $(CH_3)_2CO$, and/or 1-propen-2-ol, $CH_3C(OH)CH_2$, which are expected in Reaction 2. The signal at m/z=59 is the isotope (^{13}C) signal of the molecule at m/z=58. The same mass spectra were observed in the reaction of $(CD_3)_2CD(OH)+O$. A small signal at m/z=63 and a large signal at m/z=64 were observed when $(CD_3)_2CH(OH)$ reacted with oxygen atoms (Fig. 2b). Possible reaction processes of the reaction $(CD_3)_2\dot{C}(OH)+O$ in both hydrogen abstraction and the oxygen addition reaction are:
abstraction;

$$O+(CD_3)_2\dot{C}(OH) \rightarrow (CD_3)_2CO\ (m/z=64)+OH \quad (5a)$$
$$\rightarrow CD_3C(OH)CD_2\ (m/z=63)+OH \quad (5b)$$

addition;

Table 1. First-Order Decay Rate for the Reaction[a] of 2-Propanol with Atomic Oxygen at 298K

	Total pressure	Flow velocity	$[O]_0$	$[2\text{-propanol}]_0$	$k\times10^{13}$
	Torr	m s^{-1}	mTorr	mTorr	cm^3 molecule^{-1} s^{-1}
O+$(CD_3)_2$CH(OH)	4.593	22.3	6.192	0.101	4.1±0.6
	4.642	22.3	4.127	0.0837	4.5±0.4
	4.638	22.3	8.236	0.0842	4.2±0.5
					Av. 4.3±0.4
O+$(CH_3)_2$CD(OH)	4.602	22.3	6.827	0.0923	2.7±0.3

a) Reaction time used was 0.9—9 ms for each run.

$$O + (CD_3)_2\dot{C}(OH) \rightarrow (CD_3)_2CO\ (m/z=64) + OH \quad (5c)$$
$$\rightarrow CD_3COOH\ (m/z=63) + CD_3 \quad (5d)$$

subsequent to Reaction 4. Since the ionization potential of acetic acid has been reported[9] to be 10.4 eV, acetic acid cannot be ionized by the Kr lamp with the CaF_2 window (10.03 eV). This was confirmed by the test that no signal of CH_3COOH was observed by adding known partial pressures of CH_3COOH to the reactor. Therefore, the signal observed at m/z=63 in Fig. 2b should be from 1-propen-2-ol $CD_3C(OH)=CD_2$. Since the signal intensity of $CD_3C(OH)=CD_2$ is much weaker than that of $(CD_3)_2CO$, most of the signal at m/z=58 in Fig. 2a might be from $(CH_3)_2CO$.

Signals obtained when the Ar lamp with the LiF window (11.83 and 11.62 eV) was used are shown in Fig. 3. Figures 3a′, 3b′, and 3c′ show mass spectra of three different isotopic 2-propanols. Parent ions of 2-propanols were observed in all cases. In addition to the parent ions, fragment ions produced by an α-hydrogen (deuterium) elimination from the 2-propanols are observed. In reactions of atomic oxygen with each 2-propanol, signals of acetic acid, CH_3COOH (m/z=60) for $(CH_3)_2CH(OH)$ and $(CH_3)_2CD(OH)$, and CD_3COOH (m/z=63) for $(CD_3)_2CH(OH)$, were observed in addition to the large signals of acetones. Since the instrumental sensitivities to acetone and acetic acid are 45 and 25 times higher than that for 2-propanol, respectively, the real concentrations of the products are much lower than they appear in Fig. 3.

In the reaction O+2-propanol, three products (acetone, acetic acid, and 1-propen-2-ol were observed as expected. Among them, acetone is the largest. Ace-

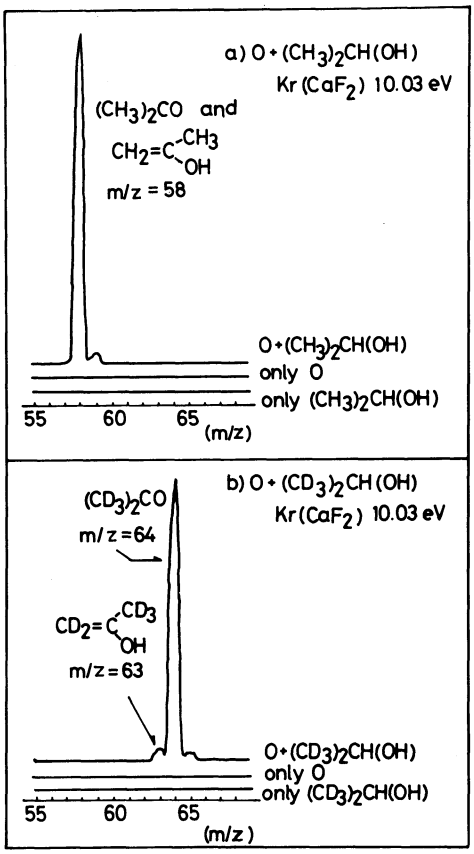

Fig. 2. Mass spectra of the reaction products produced in O+2-propanol. A Kr lamp having a CaF_2 window (10.03 eV) was used. a) O+$(CH_3)_2CH(OH)$; b) O+$(CD_3)_2CH(OH)$. The conditions: $[O]_0$=0.84 mTorr; $[2\text{-propanol}]_0$=0.27 mTorr; $[O_2]_0$=15 mTorr; reaction time 4.4 ms; total pressure 3.9 Torr.

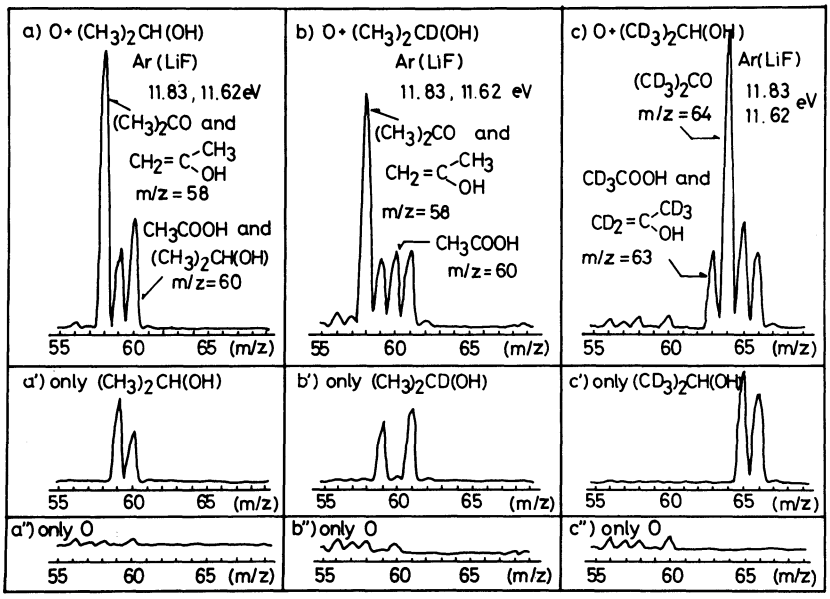

Fig. 3. Mass spectra of the reaction products produced in O+2-propanol. An Ar lamp with a LiF window (11.83 and 11.62 eV) was used. a) O+$(CH_3)_2CH(OH)$; b) O+$(CH_3)_2CD(OH)$; c) O+$(CD_3)_2CH(OH)$. The conditions: $[O]_0$=0.98 mTorr; $[2\text{-propanol}]_0$=0.28 mTorr; $[O_2]_0$=5.8 mTorr; reaction time 4.3 ms; total pressure 4.0 Torr.

tone can be produced by both hydrogen abstraction and oxygen addition reactions. In order to distinguish these two possibilities, 2-propanol was reacted with ^{18}O (19.2% of $^{36}O_2$ in $^{32}O_2$ was diluted in helium and discharged). When the $(CH_3)_2\dot{C}(OH)$ and $(CD_3)_2\dot{C}(OH)$ radicals react with the $^{18}O(^3P)$, the acetone produced by hydrogen abstraction and by oxygen addition should be different:

$$(CH_3)_2\dot{C}(OH)+{}^{18}O \begin{cases} \rightarrow (CH_3)_2CO(m/z=58)+{}^{18}OH & \text{abstraction} \quad (2a') \\ \rightarrow (CH_3)_2C^{18}O(m/z=60)+OH & \text{addition} \quad (2c') \end{cases}$$

$$(CD_3)_2\dot{C}(OH)+{}^{18}O \begin{cases} \rightarrow (CD_3)_2CO(m/z=64)+{}^{18}OH & \text{abstraction} \quad (5a') \\ \rightarrow (CD_3)_2C^{18}O(m/z=66)+OH & \text{addition} \quad (5c') \end{cases}$$

The mass spectra obtained are shown in Fig. 4. Weak signals at $m/z=60$ and 66 were observed in $^{18}O+(CH_3)_2\dot{C}(OH)$ and $^{18}O+(CD_3)_2\dot{C}(OH)$ reactions, respectively. Relative signal intensities at $m/z=58$ and 60 in the $(CH_3)_2\dot{C}(OH)+{}^{18}O$ reaction and at $m/z=64$ and 66 in the $(CD_3)_2\dot{C}(OH)+{}^{18}O$ reaction were observed to be 100 : 3.04±0.02 and 100 : 3.10±0.04, respectively. Since the 19.2% oxygen-18 was used in this study, acetone produced by the oxygen addition reaction is about 15% of the total acetone produced under these particular conditions and most of acetone is produced by the hydrogen abstraction from the OH of the radicals.

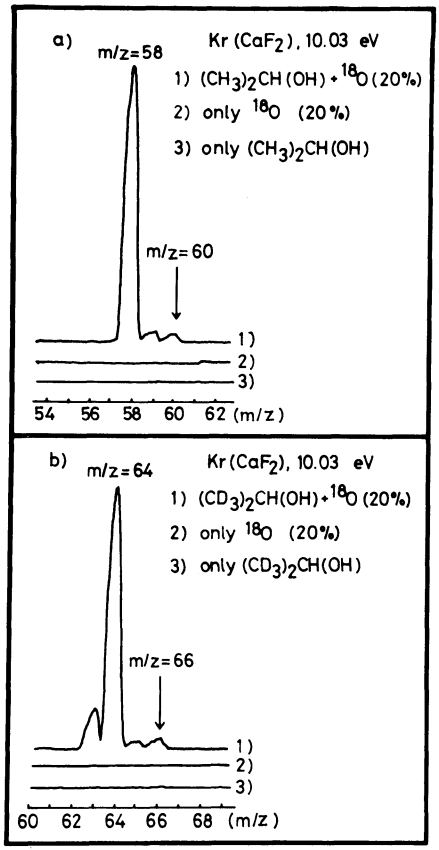

Fig. 4. Mass spectra of the reaction products produced in 2-propanol+^{18}O (19.2% of $^{36}O_2$ in $^{32}O_2$ was diluted in He and discharged). A Kr lamp with a CaF_2 window (10.03 eV) was used for the photoionization. a) $(CH_3)_2CH(OH)+{}^{18}O$; b) $(CD_3)_2CH(OH)+{}^{18}O$. The conditions: $[O]_0$= 0.61 mTorr; [2-propanol]$_0$=0.26 mTorr; $[O_2]_0$=3 mTorr; reaction time 4.4 ms; total pressure 3.9 Torr.

C. Competition between $O(^3P)$, O_2, and NO for $(CD_3)_2C(OH)$. The signal obtained by Reaction 4a increased linearly with $(CD_3)_2CH(OH)$ partial pressure up to a few mTorr. The $(CD_3)_2\dot{C}(OH)$ signal was almost independent both of reaction time (0.5—5 ms) and oxygen atom concentration (0.2—1 mTorr†). This means that $(CD_3)_2\dot{C}(OH)$ radicals are in their steady-state concentration due to the balance between Reactions 4 and 5. The steady-state concentration of $(CD_3)_2\dot{C}(OH)$ radicals decreased when molecular oxygen was added to the system. This decrease is caused by the competition between $O(^3P)$ and O_2 for the $(CD_3)_2\dot{C}(OH)$ radicals and the competition would result in a Stern-Volmer type of equation,

$$\frac{[(CD_3)_2\dot{C}(OH)]^0_{ss}}{[(CD_3)_2\dot{C}(OH)]_{ss}} = 1 + \frac{k_7[O_2]}{k_5[\overline{O}]} \qquad (6)$$

where the superscript zero indicates the conditions with no O_2 present and k_7 is the effective second-order rate constant for the reaction of $(CD_3)_2\dot{C}(OH)$ with O_2.

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

Results of O_2 addition experiment are presented in Fig. 5 by an open triangle and open circles. A value for $[(CD_3)_2\dot{C}(OH)]^0_{ss}$ was determined by plotting $([(CD_3)_2\dot{C}(OH)]_{ss})^{-1}$ against $[O_2]/[\overline{O}]$ and then determining $([(CD_3)_2\dot{C}(OH)]^0_{ss})^{-1}$ from the intercept of a least-square fit in order to remove the effect of O_2 surviving from the discharge. The average oxygen-atom concentration, $[\overline{O}]$, was calculated by the method mentioned before[1] using the value of $n=5$[10] (the correction was 4.6%). The amount of O_2 in the system was calculated from $[O_2]_{added}+[O_2]_0-1/2[O]_0$, where $[O_2]_0$ and $[O]_0$ represent the concentration of O_2 in the O_2-He mixture before discharge and the original concentration of oxygen atoms when the O_2-He mixture was discharged, respectively. The open triangle in Fig. 5 is the point which was obtained with no added O_2 (effect of O_2 just surviving from the discharge). The value for k_7/k_5 calculated from the slope of the plots (an open triangle and open circles) in Fig. 5 is (0.16±0.02). Error limits due to the scatter of plots were calculated by the least square with the 95% confidence limits. The value for k_7/k_5 suggests that the rate of the reaction of $(CD_3)_2\dot{C}(OH)+O_2$ is 6.4 times slower than that of the $(CD_3)_2\dot{C}(OH)+O(^3P)$ reaction.

When oxygen atoms were produced by NO titration of N atoms formed in a microwave discharge through

† 1 Torr=133.322 Pa.

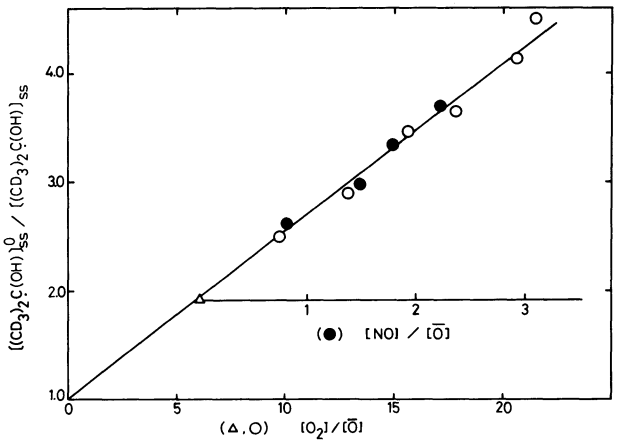

Fig. 5. Stern-Volmer plot for the competition between O_2 and $O(^3P)$ (open symbols), and NO and $O(^3P)$ (filled symbols) for $(CD_3)_2C(OH)$ radicals. A Xe lamp with a sapphire window (8.44 eV) was used to photoionize $(CD_3)_2C(OH)$. The conditions: $[O]_0$=0.632 mTorr; $[\bar{O}]$=0.588 mTorr; $[(CD_3)_2CH(OH)]$=0.288 mTorr; $[O_2]_0$=4.073 mTorr; reaction time=4.540 ms; total pressure= 3.909 Torr. $[O_2]$ was calculated from $[O_2]_{added}+[O_2]_0-1/2[O]_0$.

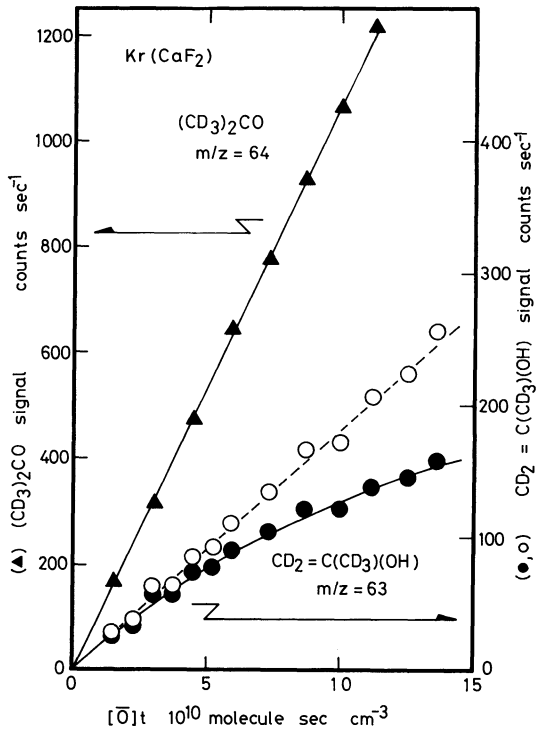

Fig. 6. Time dependence of $(CD_3)_2CO$ and $CD_3C(OH)=CD_2$ produced in the $O+(CD_3)_2CH(OH)$ reaction. A Kr lamp with a CaF_2 window (10.03 eV) was used for the photoionization. The conditions: $[O]_0$=0.517 mTorr; $[(CD_3)_2CH(OH)]_0$= 0.362 mTorr; $[O_2]_0$=1.667 mTorr; total pressure= 3.699 Torr. Reaction time used was 0.91—9.11 ms. Corrections for [O] were 12% or less. The $CD_3C(OH)=CD_2$ signals are corrected for the subsequent reaction to give $[CD_3C(OH)=CD_2]_T$ as indicated by open circles (see the text).

N_2-He mixture and were reacted with $(CD_3)_2CH(OH)$, signals of $(CD_3)_2\dot{C}(OH)$ radicals were quenched by the excess of NO. This means that the reaction of $(CD_3)_2\dot{C}(OH)+NO$ should be extremely fast. In order to measure the rate of the reaction $(CD_3)_2\dot{C}(OH)+NO$, small amount of NO were added to the system of $(CD_3)_2\dot{C}(OH)+O+O_2$. In these experiments, NO was added under the conditions shown by an open-triangle in Fig. 5 (the O_2 present in the reactor is just from the O_2 surviving from the discharge). The decrease of the steady-state concentrations of $(CD_3)_2\dot{C}(OH)$ radicals by the addition of the small amounts of NO are shown by the value of $[(CD_3)_2\dot{C}(OH)]^0_{ss}/[(CD_3)_2\dot{C}(OH)]_{ss}$ (solid circles in Fig. 5). From the slope of the plots of solid circles, the value for k_8/k_5 of (0.780±0.085) was obtained. Here, k_8 is the rate of the reaction $(CD_3)_2\dot{C}(OH)+NO$.

$$(CD_3)_2\dot{C}(OH)+NO \rightarrow (CD_3)_2CO+HNO \qquad (8)$$

The rate of the reaction of $(CD_3)_2\dot{C}(OH)+NO$ is extremely rapid. The rate is close to that of the $(CD_3)_2\dot{C}(OH)+O$ reaction. The large rate constant can be explained by a hydrogen atom abstraction by NO from the $(CD_3)_2\dot{C}(OH)$ radical. This was confirmed by measuring the signals of products. In the presence of NO, signals of acetic acid and 1-propen-2-ol disappeared and only the signal of acetone was observed.

D. Yields of the Products. Two products, $(CD_3)_2CO$ and $(CD_3)_2C(OH)CD_2$, were observed during the $O+(CD_3)_2CH(OH)$ reaction when the Kr lamp with the CaF_2 window was used. The time dependences of these products are shown in Fig. 6. On the time scale shown, $(CD_3)_2CO$ rises linearly with reaction time, while $CD_3C(OH)=CD_2$ increases not linearly. The time dependence of the $CD_3C(OH)=CD_2$ can be understood as the result that the $CD_3C(OH)=CD_2$ can react further with oxygen atoms.

$$CD_3C(OH)=CD_2+O \rightarrow \text{Products} \qquad (9)$$

The concentration of $CD_3C(OH)=CD_2$ is expressed by Eq. 10.

$$[CD_3C(OH)=CD_2] = \frac{f_{5b}k_4[(CD_3)_2CH(OH)]}{k_9 - k_4} \times (e^{-k_4[\bar{O}]t} - e^{-k_9[\bar{O}]t}) \qquad (10)$$

Here f_{5b} represents the fraction of Reaction 5b in the total reaction of $(CD_3)_2C(OH)+O$. Since the value for k_4 of 4.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} was determined, the plots of $CD_3C(OH)=CD_2$ shown in Fig. 6 can be fitted to Eq. 10. The best fit line is shown by a solid line in Fig. 6, and a value for k_9 of $(7.1\pm0.5)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} was calculated. The indicated errors due to the scattering of plots were calculated by the least square with the 95% confidence limits. The rate for Reaction 9 is 1.7 times faster than the rate for the reac-

tion O+ propene. It is possible to correct the observed $CD_3C(OH)=CD_2$ signals for subsequent reactions by multiplying each observed value by $k_9[\bar{O}]t[1-\exp(-k_9[\bar{O}]t)]^{-1}$ in order to give the total amount of $CD_3C(OH)=CD_2$ formed, $[CD_3C(OH)=CD_2]_T$. These corrected points are shown as open circles in Fig. 6, and they are well represented by the dashed straight line.

Signals for $(CD_3)_2CO$ at $m/z=64$ and CD_3COOH+ $CD_3C(OH)=CD_2$ at $m/z=63$ observed by using the Ar lamp with a LiF window are shown in Fig.7. Since the rate for the reaction of acetic acid with atomic oxygen is expected to be very slow, the signal only from CD_3COOH should rise linearly with reaction time. This was confirmed in the reaction $O+(CH_3)_2\dot{C}D(OH)$, in which the signal of CH_3COOH can be observed without overlapping of other signals (see Fig. 3b).

The effect of O_2 on the yield of products was measured by adding O_2 to the system. The results are shown in Fig. 8. The signal of $(CD_3)_2CO$ increased while signals of $CD_3C(OH)=CD_2$ and CD_3COOH decreased[11] when O_2 was added. The two points on the left-hand side in each Figs. 8a and 8b are the points obtained from the O_2 just surviving from the O_2/He discharge (no addition of O_2). Since the standard sample gas of 1-propen-2-ol is not available, the absolute concentration of $CD_3C(OH)=CD_2$ cannot be determined. The absolute concentration of $(CD_3)_2CO$ was determined from the sensitivity of acetone to the instrument. The concentration of $(CD_3)_2CO$ is represented by Eqs. 11 and 12 when both $O(^3P)$ and O_2 are present in the system.

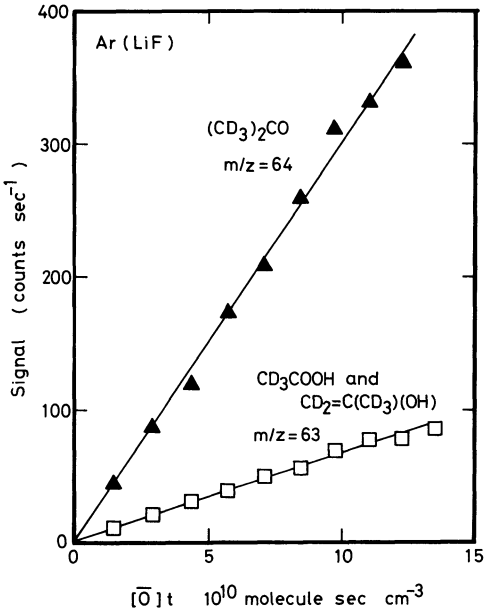

Fig. 7. Time dependence of signals at $m/z=63$ and 64 in the $O+(CD_3)_2CH(OH)$ reaction. An Ar lamp with a LiF window (11.83 and 11.62 eV) was used. The conditions: $[O]_0=0.496$ mTorr; $[(CD_3)_2CH(OH)]_0=0.289$ mTorr; $[O_2]_0=1.748$ mTorr; total pressure=3.791 Torr. Reaction time used was 0.91—9.11 ms. Corrections for $[\bar{O}]$ were 5% or less.

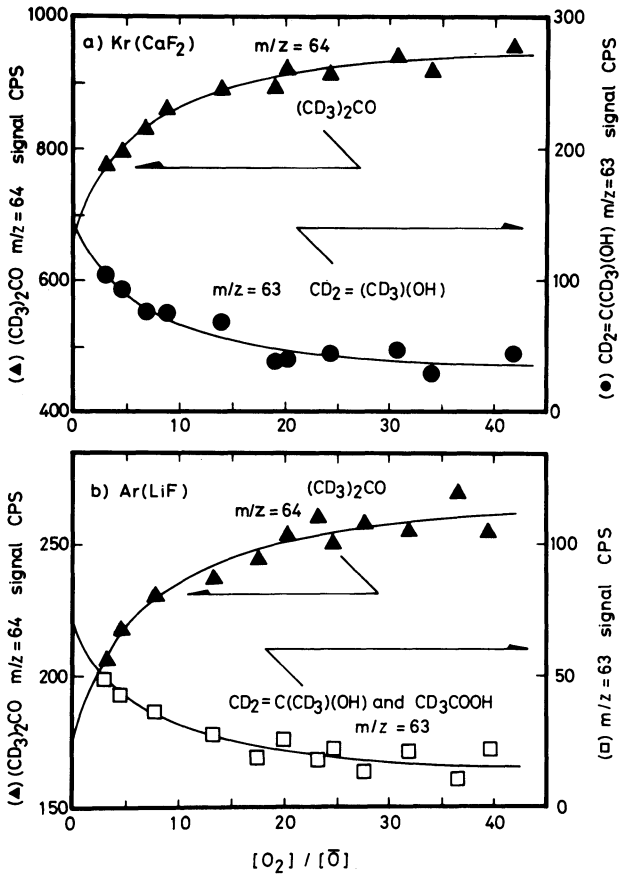

Fig. 8. Change of signals at $m/z=63$ and 64 with the addition of O_2. A Kr lamp with a CaF_2 window (a) and an Ar lamp with a LiF window (b) were used for the photoionization. The conditions for (a): $[O]_0=0.517$ mTorr; $[\bar{O}]=0.487$ mTorr; $[(CD_3)_2CH(OH)]_0=0.362$ mTorr; $[O_2]_0=1.667$ mTorr; reaction time=4.556 ms; total pressure=3.699 Torr. The conditions for (b): $[O]_0=0.496$ mTorr; $[O]_0=0.473$ mTorr; $[(CD_3)_2CH(OH)]_0=0.289$ mTorr; $[O_2]_0=1.748$ mTorr; reaction time=4.556 ms; total pressure=3.791 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 $[O_2]_{added}$).

$$[(CD_3)_2CO] = \left\{(f_{5a}+f_{5c})+\frac{(s_{7a}-f_{5a}-f_{5c})X}{1+X}\right\}\times k_4[(CD_3)_2CH(OH)][\bar{O}]t \quad (11)$$

$$X=\frac{k_7}{k_5}\frac{[O_2]}{[\bar{O}]} \quad (12)$$

Here s_{7a} is the fraction of $(CD_3)_2CO$ produced in Reaction 7. Using the value for k_7/k_4 determined before, the absolute concentrations of $(CD_3)_2CO$ are plotted against $X/(1+X)$ and are shown in Fig. 9. Under each experimental condition, values for $(f_{5a}+f_{5c})$ determined from the intercepts of lines in Figs. 9a and 9b are (0.64±0.05) and (0.60±0.06), respectively. From the

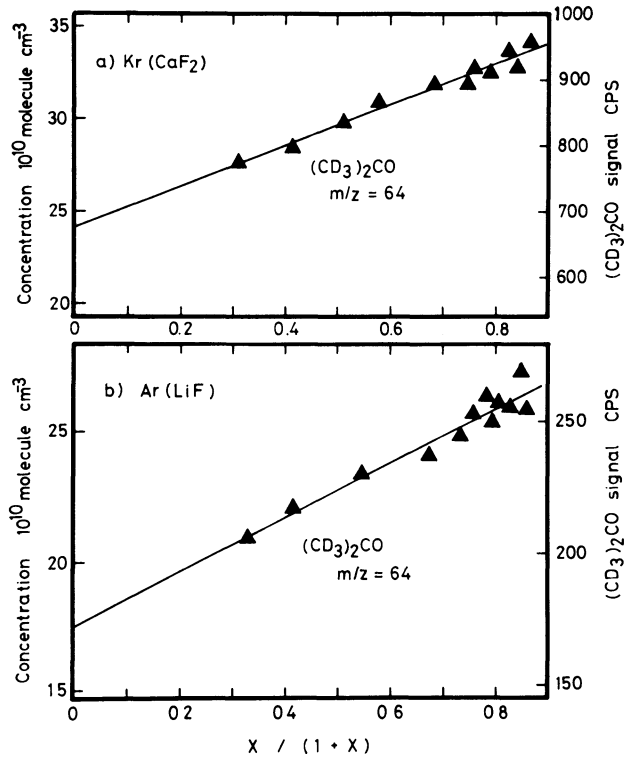

Fig. 9. The absolute concentrations of $(CD_3)_2CO$ are plotted against $X/(1+X)$. The conditions for (a) and (b) are the same as the cases of (a) and (b) in Fig.8, respectively.

slopes of straight lines shown in Figs. 9a and 9b, values for s_{7a} of (0.94±0.07) and (0.96±0.14) were calculated, respectively. The indicated errors due to the scattering of plots were calculated by the least square with the 95% confidence limits.

$$(CD_3)_2C(OH)+O \xrightarrow{(62\pm4)\%} (CD_3)_2CO \qquad \text{(5a) and (5c)}$$

$$(CD_3)_2C(OH)+O_2 \xrightarrow{(95\pm8)\%} (CD_3)_2CO \qquad \text{(7a)}$$

Signals at m/z=63 observed by the use of the Ar lamp consist of the signals of $CD_3C(OH)=CD_2$ and CD_3COOH. From the mass spectra shown in Figs. 3a, b, and c, however, it is probable that the greater part of the signal at m/z=63 is from CD_3COOH. Supposing that all the signals at m/z=63 is from acetic acid, the absolute concentrations of CD_3COOH were determined from the instrumental sensitivity of acetic acid. From the slope and intercept of the plots of $X/(1+X)$ vs. absolute concentrations of CD_3COOH, values for f_{5d} and s_{7d} can be calculated to be (0.28±0.04) and (0.02±0.06), respectively. Therefore, tentatively;

$$(CD_3)_2\dot{C}(OH)+O \xrightarrow{(28\pm4)\%} CD_3COOH \qquad \text{(5d)}$$

$$(CD_3)_2\dot{C}(OH)+O_2 \xrightarrow{(2\pm6)\%} CD_3COOH \qquad \text{(7d)}$$

Discussion

The selective abstraction of an α-hydrogen (deuterium) in the primary attack of $O(^3P)$ atoms on 2-propanol agreed well with the suggestion of Kato and Cvetanovic.[2] The result of the α-hydrogen abstraction agreed also with the case of O+ethanol reaction.[4] The rate constant for the reaction $O+(CD_3)_2CH(OH)$ at 298K, $(4.3\pm0.4)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, was 33 times larger than the rate constant for $O+(CH_3)_2CH(OH)$ reaction reported by Ayub and Roscoe.[3] In the present study, the rate measurements were carried out under the conditions of $[O]_0/[2\text{-propanol}]_0 \geqslant 50$. Under these conditions, the consumption of oxygen atoms in the reactor (reaction time was 0.9—10 ms) was less than 5% of the original oxygen atom concentration on the basis of a stoichiometric factor of n=5.[10] On the other hand, the rate measurements by Ayub and Roscoe were done by observing the decay of oxygen atoms under a large excess of 2-propanol. Probably, many subsequent reactions are possible under their experimental conditions and their estimation of the stoichiometric factor for the decay of oxygen atoms is not correct.

The major primary product in the subsequent reaction of $(CD_3)_2\dot{C}(OH)$ radicals with atomic oxygen was found to be acetone (62±4%). Formation of 1-propen-2-ol and acetic acid was observed in addition to $(CD_3)_2CO$. In the previous work of the O+ethanol reaction system[4] acetaldehyde (79±8%), which is equivalent to acetone in the present reaction system, was found to be major primary product in the reaction of 1-hydroxyethyl radical with atomic oxygen. No formation of vinyl alcohol, formic and acetic acids were observed. In the present study, however, it was demonstrated that the yield of products was largely affected by the amount of O_2 surviving from the discharge; i.e., the yield of acetone (acetaldehyde for O+ethanol) increased and yields of 1-propen-2-ol (vinyl alcohol for O+ethanol) and acetic acid (formic or acetic acids for O+ethanol) decreased in the presence of O_2. Therefore, in the previous O+ethanol system, vinyl alcohol and formic or acetic acids probably could be observed if the measurements were carried out carefully taking notice of the effect of O_2.

The isotope (^{18}O) experiments showed that acetone was produced predominantly by the hydrogen abstraction by $O(^3P)$ from the O-H in the $(CD_3)_2\dot{C}(OH)$ radical, Reaction 5a′. The result is consistent with that obtained in the O+ethanol system. In the present study, however, it was found that acetone can also be produced by the addition of $O(^3P)$ to the $(CD_3)_2\dot{C}(OH)$ radical, Reaction 5c′, in small but significant yield.

The reaction of $(CD_3)_2\dot{C}(OH)$ radicals with molecular oxygen was very rapid. The rate of the reaction of $(CD_3)_2\dot{C}(OH)+O_2$ was just 6.4 times slower than that of the $(CD_3)_2\dot{C}(OH)+O(^3P)$ reaction. This competition ratio is quite similar to the case of the 1-hydroxyethyl radical.[4] The rate of the reaction of $(CD_3)_2\dot{C}(OH)$+NO was found to be much faster. The reaction proceeds as fast as with atomic oxygen. These rapid reactions can be explained by the two body reactions to form acetone and HO_2 (HNO), Reactions 7a

and 8.

$$(CD_3)_2\dot{C}(OH) + O_2 \rightarrow (CD_3)_2CO + HO_2 \qquad (7a)$$

Reaction 7a was proved by the isotope (^{18}O) experiment; that is, in the experiment shown in Fig. 4b, the signal at m/z=66, $(CD_3)_2C^{18}O$, disappeared by adding the $^{18}O_2$ (20%)/$^{16}O_2$ mixture gas. The formation of acetone by Reaction 7a is consistent with the results obtained from the photooxidation of 2-propanol in air.[12]

Conclusion

(1) $(CD_3)_2\dot{C}(OH)$ and $(CD_3)_2\dot{C}(OH)$ radicals produced by a selective abstraction of an α-hydrogen in the primary attack of $O(^3P)$ atoms on 2-propanol were detected directly by the photoionization mass spectrometer. The results of the present and earlier study[4] show that $O(^3P)$ atoms react with simple alcohols by abstracting the most weakly bonded hydrogen atoms in the alcohol molecules.

(2) The major primary product in the reaction of $(CD_3)_2\dot{C}(OH)$ radicals with atomic oxygen is acetone, $(CD_3)_2CO$, (62%). Formation of 1-propen-2-ol and acetic acid was also observed.

(3) Acetone is produce predominantly by the hydrogen abstraction by $O(^3P)$ from the O-H in the $(CD_3)_2\dot{C}(OH)$ radical. A part of acetone is produced also by the addition of $O(^3P)$ to the $(CD_3)_2\dot{C}(OH)$ radical.

(4) The rate of the reaction of $(CD_3)_2\dot{C}(OH)$ radicals with molecular oxygen is 6.4 times slower than the reaction with atomic oxygen. This rapid reaction is explained by the hydrogen abstraction by O_2 from the O-H in the $(CD_3)_2\dot{C}(OH)$ radical.

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5) The reaction of 2-propanol with atomic oxygen is initiated by hydrogen abstraction, Reaction 1. The OH radicals produced react with 2-propanol faster than atomic oxygen. The rate constant of the 2-propanol+OH reaction has been reported[6,7] to be $(5—7)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. OH radicals are destroyed by the reaction OH+O→H+O_2 with a rate constant of $(3—4)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. Therefore, in order to make the effect of OH radicals on the formation of $(CD_3)_2\dot{C}(OH)$ radicals less than 10%, the concentration of oxygen atoms must be at least twice as large as the 2-propanol concentration.

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8) Signals at m/z=59 ($M-1^+$) and 60 (M^+) were observed when $(CH_3)_2CH(OH)$ was photoionized by the Ar lamp with the LiF window (11.83 and 11.62 eV). As will be demonstrated later in Fig. 3, signals for $(CH_3)_2CO$ and CH_3COOH were observed at m/z=58 and 60, respectively when $(CH_3)_2CH(OH)$ was reacted with oxygen atoms. Further, the isotope (^{13}C) signal of $(CD_3)_2CO$ appeared at m/z=59. Since the sensitivities of the instrument to $(CH_3)_2CO$ and CH_3COOH were 45 and 25 times higher than that to $(CH_3)_2CH(OH)$, respectively, when the Ar lamp was used, the effect of the signals of both products on the $(CD_3)_2CH(OH)$ signals at m/z=59 and 60 can not be neglected. In the rate measurements of the reaction $(CH_3)_2CD(OH)$+O, signals for $(CH_3)_2CD(OH)$ were measured at m/z=61. The signal at m/z=61 coincides with the isotope (^{13}C) signal of CH_3COOH. In this case, however, since the signal of CH_3COOH was not so strong as $(CH_3)_2CO$, the effect of the isotope signal of CH_3COOH on the $(CH_3)_2CD(OH)$ signal at m/z=61 was less than 6% even when the 50% of $(CH_3)_2CD(OH)$ ws consumed in the reactor.

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10) A stoichiometric factor of n=5 was used in the present study, because, as will be described later, the yield of acetone in the O+2-propanol reaction is much higher than that in the O+propane reaction, and acetone produced does not react further under the present experimental conditions.

11) The decrease of acetic acid by the addition of O_2 was confirmed also in the reaction of O+$(CH_3)_2CD(OH)$, in which the signal of CH_3COOH can be observed without the overlapping of the 1-propen-2-ol signal.

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