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Oxidation of $(CD_3)_2\dot{C}X$ Radicals. II. Reaction of $(CD_3)_2CHCl$ and $(CD_3)_2\dot{C}Cl$ Radicals with Atomic Oxygen

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The reaction of oxygen atoms with $(CD_3)_2CHCl$ in a fast flow system was studied with a photoionization mass spectrometer. The $(CD_3)_2\dot{C}Cl$ radical formed by the initial hydrogen abstraction at the 2-position was detected directly.

$$(CD_3)_2CHCl + O(^3P) \rightarrow (CD_3)_2\dot{C}Cl + OH \qquad (1)$$

The rate data for Reaction 1 were fitted by an Arrhenius expression: $k_1=(3.5^{+1.2}_{-0.9})\times10^{-11}\exp[(-4973\pm278\ \text{cal mol}^{-1})/RT]^{\dagger}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ (399—628 K). Among the products formed in the subsequent reaction of $(CD_3)_2\dot{C}Cl$ radicals with atomic oxygen, $CD_3CCl{=}CD_2$ (31%) produced by the deuterium abstraction and $(CD_3)_2CO$ (24%) by the oxygen addition were observed. Competition experiments show that $(CD_3)_2\dot{C}Cl$ radicals react (0.0079 ± 0.0010) times as fast with O_2 as with $O(^3P)$. In the presence of an excess of O_2, $CD_3CCl{=}CD_2$ was observed in decreased yield (3.5%) and $(CD_3)_2CO$ increased to 56%.

Since the formation of $(CD_3)_2\dot{C}H$ radicals was confirmed in the reaction of atomic oxygen with $(CD_3)_2CH_2$, the reaction of $(CD_3)_2CHCl$ with atomic oxygen is investigated in the present study as an analogy of the reaction. In the reaction of $O+(CD_3)_2CHCl$, it is supposed that the $(CD_3)_2\dot{C}Cl$ radical is produced by the initial attack of $O(^3P)$ on $(CD_3)_2CHCl$.

$$(CD_3)_2CHCl\ O(^3P)\rightarrow(CD_3)_2\dot{C}Cl+OH \qquad (1)$$

The subsequent reaction of the $(CD_3)_2\dot{C}Cl$ radicals with atomic oxygen can be considered as follows by the analogy of the O+propyl radical reaction:

$$(CD_3)_2\dot{C}Cl+O(^3P)\begin{cases}\rightarrow CD_3CCl=CD_2+OD & (2a)\\ \rightarrow (CD_3)_2CO+Cl & (2b)\\ \rightarrow CD_3CClO+CD_3 & (2c)\end{cases}$$

A question of interest is the change of the branching ratio of each process, 2a—c, due to a chlorine substitution for a hydrogen at 2-position of propane.

Experimental

The experimental setup and procedures were the same as those mentioned before.[1)] $(CD_3)_2CHCl$ was synthesized[2)] in this laboratory. All measurements were done at room temperature, 298±3 K, under the conditions $[O]\rangle0.5[(CD_3)_2CHCl]$.[3)]

Results and Discussion

A. Radicals and Molecules Detected in the $(CD_3)_2CHCl+O$ Reaction. Radicals produced in the reaction of $(CD_3)_2CHCl$ with atomic oxygen were detected at m/z=83 and 85 when a Xe lamp with a sapphire window (8.44 eV) was used as a photoionization light source. Mass spectra measured are shown in Fig. 1. Other products produced by subsequent reactions and the parent $(CD_3)_2CHCl$ were not photoionized by this lamp. Radicals observed at m/z=83 and 85 are $(CD_3)_2\dot{C}^{35}Cl$ and $(CD_3)_2\dot{C}^{37}Cl$, respectively. The ratio of the signal intensities at m/z=83 and 85 corresponds to the ratio of the natural abundance of ^{35}Cl (75.5%) and ^{37}Cl (24.5%). No observation of the signals at

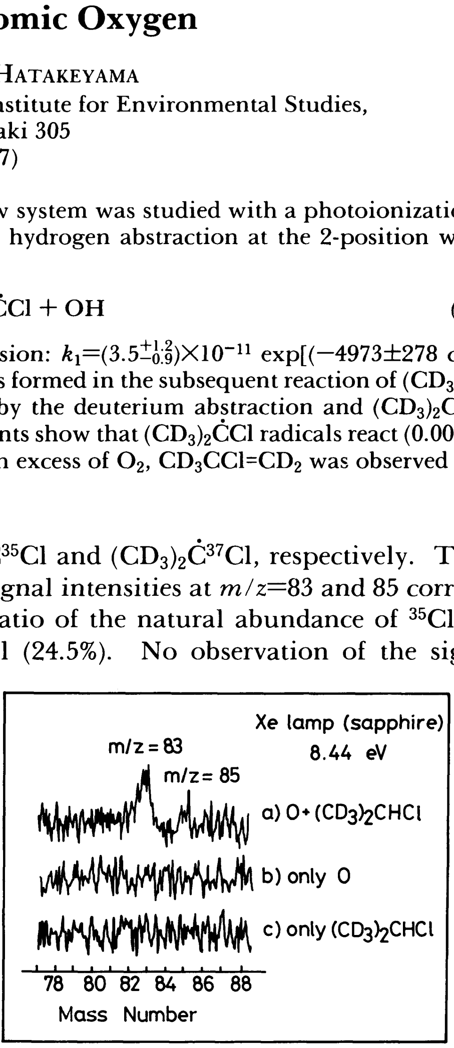

Fig. 1. Mass spectra of the $(CD_3)_2\dot{C}Cl$ radical produced in the $O+(CD_3)_2CHCl$ reaction. A Xe lamp having a sapphire window (8.44 eV) was used for the photoionization. The conditions: Partial pressure (mTorr), $[O]_0=3.5$, $[(CD_3)_2CHCl]=0.82$; reaction time=4.6 ms; total pressure=3.6 Torr.

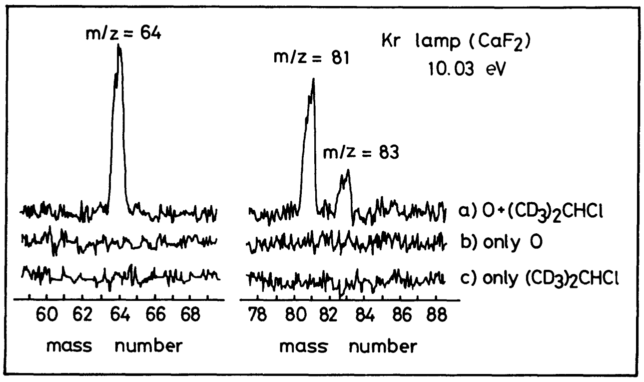

Fig. 2. Mass spectra of the reaction products produced in the $O+(CD_3)_2CHCl$ reaction. A Kr lamp having a CaF_2 window (10.03 eV) was used for the photoionization. The conditions: partial pressure (mTorr), $[O]_0=3.1$, $[(CD_3)_2CHCl]=0.63$; reaction time=4.6 ms; total pressure=3.6 Torr.

[†] 1 cal=4.184 J.

Table 1. Rate Data for $O(^3P)+(CD_3)_2CHCl$ at 399—628 K

T	$[P\text{-}Cl]_0$[a]	$[O]_0$	Total pressure	k_3
K	mTorr	mTorr	Torr	10^{-14} cm^3 molecule^{-1} s^{-1}
628	0.102	6.211	5.38	67.2±5.3
621	0.099	5.689	5.21	57.1±5.2
606	0.081	6.338	5.54	62.9±6.6
588	0.113	4.996	5.61	48.2±5.2
513	0.121	5.932	5.38	25.8±4.1
496	0.098	6.018	6.07	24.6±3.6
421	0.123	6.230	6.12	9.02±0.81
414	0.139	8.440	6.80	8.11±0.74
408	0.114	6.795	6.65	8.83±0.44
399	0.141	6.833	6.83	6.31±0.73

a) $[P\text{-}Cl]_0$ represents the original concentration of $(CD_3)_2CHCl$.

m/z=82 and 84 (deuterium abstraction by $O(^3P)$) shows that the initial attack of $O(^3P)$ on $(CD_3)_2CHCl$ occurs in selective abstraction of a hydrogen at 2-position of $(CD_3)_2CHCl$; Reaction 1.

Products produced in the reaction of oxygen atoms with $(CD_3)_2\dot{C}Cl$ radicals were measured by using a Kr lamp having a CaF_2 window (10.03 eV). Mass spectra obtained are shown in Fig. 2. Signals for $(CD_3)_2CO$ (m/z=64), $CD_3C^{35}Cl{=}CD_2$ (m/z=81), and $CD_3C^{37}ClCD_2$ (m/z=83) were observed as expected in Reaction 2.

Since ionization potential for acetyl chloride, CH_3COCl, has been reported4) to be 11.02 eV, CD_3COCl formed by Reaction 2c cannot be ionized by the Kr resonance line but should be ionized by the Ar resonance lines (11.83 and 11.62 eV). Detection of CD_3COCl was investigated by using an Ar lamp with a LiF window. Since mass numbers of CD_3COCl and $CD_3CCl{=}CD_2$ are identical in the present case, $(CD_3)_2CHCl$ was reacted with ^{18}O (19.2% of $^{36}O_2$ in $^{32}O_2$ was diluted in helium and discharged by microwave) and the measurement of the signals for $CD_3C^{18}O^{37}Cl$ at m/z=85 was investigated. However, no significant signal at m/z=85 was observed except the isotope (^{13}C) signal of the parent $(CD_3)_2CH^{35}Cl$ molecule. In order to determine whether CD_3COCl is produced in Reaction 2 or not, the sensitivity measurement of acetyl chloride to the instrument when the Ar lamp was used as a photoionization light source was carried out by adding known partial pressures of CH_3COCl to the reactor. Surprisingly, no signal was observed even when up to 1 mTorr[††] of CH_3COCl was added to the reactor. Since about 5×10^4 counts s^{-1} signals were obtained for 1 mTorr of NO in the reactor, we have to conclude that acetyl chloride cannot be ionized by the Ar resonance lines, and it cannot be determined whether Reaction 2c occurs or not.

B. Rate Constant for the $(CD_3)_2CHCl$ Reaction. The pseudo-first-order decay rates of $(CD_3)_2CHCl$ by Reaction 1 were measured over a temperature range of 399—628 K in a large excess of oxygen atoms by changing the contact time of $(CD_3)_2CHCl$ with oxygen atoms. An Ar lamp with a LiF window was used to photoionize $(CD_3)_2CHCl$ and the bimolecular rates of Reaction 1 were measured from the decay of the signal of $(CD_3)_2CH^{37}Cl$ at m/z=86. Values for k_1 obtained are listed in Table 1. The 95% confidence limits were calculated from the least squares line using ten points for each run. The concentration of oxygen atoms was corrected using a stoichiometric factor of n=6 as described in the preceeding paper.1) The correction for oxygen atom consumption was 5% or less.

The linear least square treatment for the values of k_1 shown in Table 1 yields the Arrhenius expression of $k=A\exp(-E_a/RT)$.

$$k_1=(3.5^{+1.2}_{-0.9})\times10^{-11}\ \exp\left(\frac{-4973\pm278\ \text{cal mol}^{-1}}{RT}\right); \quad (3)$$

in unit 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 1 at 298K calculated by Eq. 3 is 7.8×10^{-15} cm^3 molecule^{-1} s^{-1}.

The rate constants for the reaction of atomic oxygen with 2-chloropropane, $(CH_3)_2CHCl$, have been measured over a temperature range of 336—622K by Herron and Huie.5) The Arrhenius expression obtained from their data was $k=(4.3^{+0.9}_{-0.6})\times10^{11}\ \exp[(-5206\pm139)/RT]$ cm^3 molecule^{-1} s^{-1} with a value at 298K of $k=6.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1}. Values of Arrhenius activation energy, frequency factor, and the rate at 298K obtained in the present study for the $O+(CD_3)_2CHCl$ reaction are in good agreement with those measured in the $O+(CH_3)_2CHCl$ reaction by Herron and Huie.

C. Competition between $O(^3P)$ and O_2 for $(CD_3)_2\dot{C}Cl$. The steady-state concentrations of $(CD_3)_2\dot{C}Cl$ radicals were evidenced by no change of signals by changing the contact time of the reaction of $(CD_3)_2CHCl$ with oxygen atoms. The competition between $O(^3P)$ and O_2 for the $(CD_3)_2\dot{C}Cl$ radicals was measured by adding molecular oxygen to the system. The steady-state concentration of $(CD_3)_2\dot{C}Cl$ was decreased by the addition of O_2 and the competition results in a Stern-Volmer-type of equation,

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[††] 1 Torr=133.322 Pa.

$$\frac{[\text{pr-Cl}]^0_{ss}}{[\text{pr-Cl}]_{ss}} = 1 + \frac{k_5[O_2]}{k_2[O]} \tag{4}$$

where $[\text{pr-Cl}]_{ss}$ represents the steady-state concentration of $(CD_3)_2\dot{C}Cl$ radicals, the superscript zero refers to the condition in the absence of O_2 and k_5 is the effective second-order rate constant for the reaction of $(CD_3)_2\dot{C}Cl$ radicals with molecular oxygen.

$$(CD_3)_2\dot{C}Cl + O_2 \rightarrow \text{Products} \tag{5}$$

Figure 3 shows the result of an O_2 addition experiment. The concentration of $(CD_3)_2\dot{C}Cl$ radical was monitored by the signal at m/z=83, $(CD_3)_2\dot{C}^{35}Cl$. A value for $[(CD_3)_2\dot{C}Cl]^0_{ss}$ was determined by the method mentioned before.[5] The concentration of oxygen atoms, $[\bar{O}]$, was corrected using a stoichiometric factor of n=6 (the correction was 0.4%). The value for k_5/k_2 calculated from the slope is 0.0079±0.0010. Error limits due to the scatter of plots were calculated by the least square with the 95% confidence limits.

The value for k_5/k_2 suggests that the rate of the reaction of $(CD_3)_2\dot{C}Cl+O_2$ is 127 times slower than that of the $(CD_3)_2\dot{C}Cl+O$ reaction. This competition ratio of 127 is larger than that in the case of $(CD_3)_2\dot{C}H$ radicals where the ratio was 35. This result suggests that the rate of the reaction of $(CD_3)_2\dot{C}Cl+O_2$ is much slower than that of $(CD_3)_2\dot{C}H+O_2$ if the rate of the reaction of $(CD_3)\dot{C}$ Cl+O(^{3}P) and that of $(CD_3)_2\dot{C}H+O$ are close.

D. Time Dependence of Products. The dependence of the $(CD_3)_2CO$ and $CD_3CCl{=}CD_2$ signals on the reaction time was measured. Solid circles in Fig. 4 show the $CD_3C^{35}Cl{=}CD_2$ signal at m/z=81 in the O+$(CD_3)_2CHCl$ reaction. $CD_3CCl{=}CD_2$ approaches a constant concentration at long reaction time. This results from the fast reaction of O+$CD_3CCl{=}CD_2$, Reaction 6,

$$CD_3CCl{=}CD_2 + O \rightarrow \text{Products} \tag{6}$$

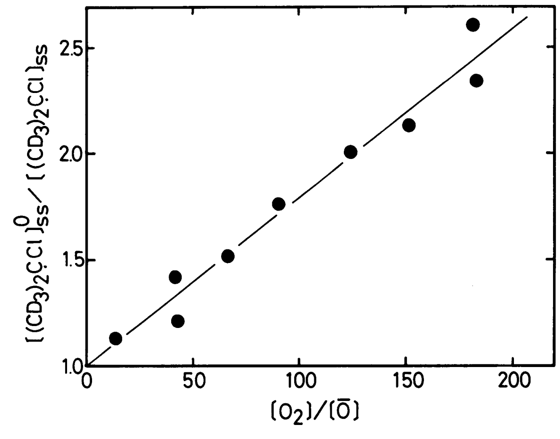

Fig. 3. Stern-Volmer plot for the competition between O_2 and O(^{3}P) for the $(CD_3)_2\dot{C}Cl$ radicals. Conditions: Partial pressure (mTorr), $[O]_0$=2.03, $[\bar{O}]$=2.02, $[(CD_3)_2CHCl]_0$=0.71; $[O_2]_0$=29.65; total pressure=3.58 Torr; reaction time=4.59 ms. $[O_2]$ was calculated from $[O_2]_{\text{added}}+[O_2]_0-1/2[O]_0$.

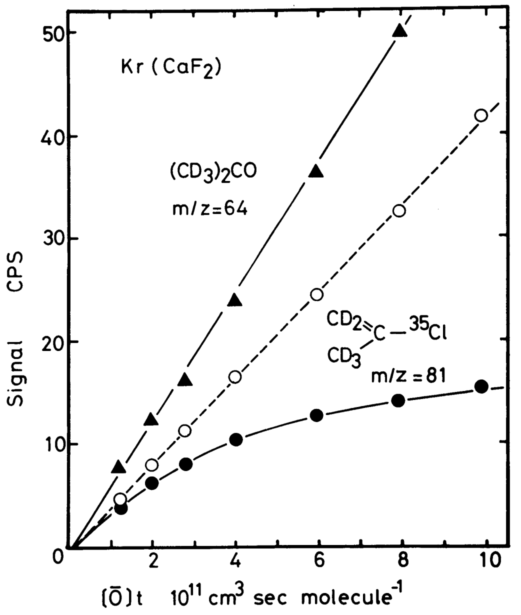

Fig. 4. Time dependence of $CD_3CCl{=}CD_2$ (solid circles) and $(CD_3)_2CO$ (solid triangles) signals produced in the O+$(CD_3)_2CHCl$ reaction. A Kr lamp with a CaF_2 window (10.03 eV) was used for the photoionization. The conditions: partial pressure (mTorr), $[O]_0$=2.62, $[(CD_3)_2CHCl]_0$=0.75, $[O_2]_0$=26,53; total pressure=3.55 Torr. Reaction times used were 1.4—11.5 ms. Correction for $[\bar{O}]$ were 0.7% or less. The $CD_3CCl{=}CD_2$ signals are corrected for the subsequent reaction to give $[CD_3CCl{=}CD_2]_T$ as indicated by open circles.

This approach to the steady-state concentration is given by Eq. 7, assuming that Reaction 2 is much faster than Reactions 1 and 6.

$$[CD_3CCl{=}CD_2] = \frac{f_{2a}k_1}{k_6}[\text{P-Cl}][1-\exp(-k_6[\bar{O}]t)] \tag{7}$$

Here f_{2a} and [P-Cl] represent the fraction of Reaction 2a in the total reaction of $(CD_3)_2\dot{C}Cl$ radicals with atomic oxygen, Reaction 2, and the original concentration of $(CD_3)_2CHCl$. The values of $[\bar{O}]t$, which is a product of the average oxygen atom concentration and the reaction time, were calculated by using a stoichiometric factor n=6 as described before. The correction for oxygen atom consumption was less than 0.7%. When the plots shown by solid circles are fitted to Eq. 7, a value for k_6 of $(2.5\pm0.1)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} is calculated. The best fit line for Eq. 7 is shown as a solid line in Fig. 4. The total amount of $CD_3CCl{=}CD_2$ produced by Reaction 2a, $[CD_3CCl{=}CD_2]_T$, is given by Eq. 8.

$$[CD_3CCl{=}CD_2]_T = f_{2a}k_1[\text{P-Cl}][\bar{O}]t \tag{8}$$

Therefore, the total amount of $CD_3CCl{=}CD_2$ can be calculated by multiplying each observed $CD_3CCl{=}CD_2$ value by $k_6[\bar{O}]t[1-\exp(-k_6[\bar{O}]t)]^{-1}$. These corrected points are shown as open circles in Fig. 4, and they are represented by the dashed straight line.

The time dependence of the $(CD_3)_2CO$ signal at m/z=64 produced in the O+$(CD_3)_2CHCl$ reaction is shown as triangles in Fig. 4. Since the reaction of O+$(CD_3)_2CO$ is slow on the time scale shown, $(CD_3)_2CO$ rises linearly.

The rate constant for the O+$CD_3CCl=CD_2$ reaction was determined to be $(2.5\pm0.1)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. There is no previous determination of the rate constant for the reaction of O+2-chloropropene, $CH_3CCl=CH_2$, with which the value of k_6 can be compared. Since the standard sample of 2-chloropropene was not available, the pseudo-first-order decays were measured for the reaction of oxygen atoms with 1-chloro-1-propene, $CH_3CH=CHCl$ (cis- and trans-mixture from Tokyo Kasei), and 3-chloro-1-propene, $CH_2ClCHCH_2$ (from Tokyo Kasei). Results are listed in Table 2 with the value of the rate constants for O+$CD_3CCl=CD_2$ and $CD_3CH=CD_2$ reactions obtained by the steady-state approach method. In the measurements, since $CH_3CH=CHCl$ can be ionized by a Kr lamp with a CaF_2 window (10.03 eV) but $CH_2ClCH=CH_2$ cannot, an Ar lamp with a LiF window (11.83 and 11.62 eV) was used to ionize $CH_2ClCH=CH_2$. The rate for the O+$CD_3CCl=CD_2$ reaction is faster than that for the O+$CH_2ClCH=CH_2$, slower than that for the O+$CD_3CH=CD_2$, and close to that for the O+$CH_3CH=CHCl$ reaction. The rate constants for the reactions of 2-fluoro-1-propene and 3-fluoro-1-propene with oxygen atoms have been reported.[6,7] These values are close to those of chloropropenes and are also listed in Table 2.

It has been noted[8-10] for olefins that there is a good correlation between the rate constant with atomic oxygen and ionization potential. In the present case, since the rate constant for the O+$CH_3CH=CHCl$ reaction is close to that for O+$CD_3CCl=CD_2$, tentatively $CH_3CH=CHCl$ can be used as a standard sample to estimate the absolute concentration of $CD_3CCl=CD_2$. Supposing that the ionization cross sections of $CH_3CH=CHCl$ and $CD_3CCl=CD_2$ for the Kr resonance line of 10.03 eV are equal, the absolute concentrations of $CD_3CCl=CD_2$ were calculated using the instrumental sensitivity of $CH_3CH=CHCl$. The ratio of the slope of the dashed straight line to that for $(CD_3)_2CO$ is 0.67. The relative sensitivity of the instrument for $CH_3CHCH^{35}Cl$ and acetone was measured as 1 : 1.8 by using a Kr lamp (CaF_2). Thus the ratio of the rate of formation of these two products was tentatively $CD_3CCl=CD_2$:$(CD_3)_2CO$=1.2 : 1 considering the natural abundance of ^{35}Cl and ^{37}Cl.

E. Yields of the Products. The effect of the O_2 on the products was measured by adding O_2 to the system. The signal of $CD_3CCl=CD_2$ decreased and that of $(CD_3)_2CO$ increased when O_2 was added. Results are shown in Fig. 5. The two points on the left-hand side

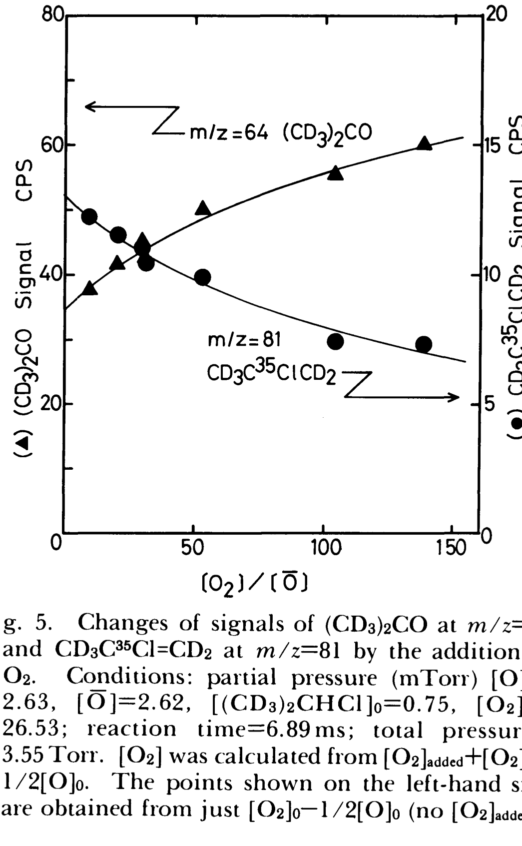

Fig. 5. Changes of signals of $(CD_3)_2CO$ at m/z=64 and $CD_3C^{35}Cl=CD_2$ at m/z=81 by the addition of O_2. Conditions: partial pressure (mTorr) $[O]_0$=2.63, $[\bar{O}]$=2.62, $[(CD_3)_2CHCl]_0$=0.75, $[O_2]_0$=26.53; reaction time=6.89 ms; total pressure=3.55 Torr. $[O_2]$ was calculated from $[O_2]_{added}+[O_2]_0-1/2[O]_0$. The points shown on the left-hand side are obtained from just $[O_2]_0-1/2[O]_0$ (no $[O_2]_{added}$).

Table 2. Rate Constants for the Reaction of O(^{3}P)+Chloro- and Fluoro-Propene at 298 K

Reaction	Rare constant at 298K 10^{12} cm^3 molecule^{-1} s^{-1}	Method	Reference
O+$CH_3CH=CHCl$ (Cis- and trans-mixture)	(2.1±0.2)	Pseudo-first-order decay[a]	This work
O+$CH_2ClCH=CH_2$	(0.77±0.05)	Pseudo-first-order decay[b]	This work
O+$CD_3CCl=CD_2$	(2.5±0.1)	Steady-state approach	This work
O+$CD_3CH=CD_2$	(4.1±0.2)	Steady-state approach	Ref. 1
O+$CH_2FCH=CH_2$	0.73	Hg photosens. decomp of N_2O	Refs. 6, 7
O+$CH_3CF=CH_2$	1.7	Hg photosens. decomp of N_2O	Refs. 6, 7

a) The pseudo-first-order decay of $CH_3CH=CHCl$ was measured under the conditions: $[CH_3CH=CHCl]_0$=0.023 Torr, $[O]_0$=1.24 mTorr, total pressure=4.5 Torr and reaction time 0.9—7.3 ms. A Kr lamp with a CaF_2 window (10.03 eV) was used to photoionize $CH_3CH=CHCl$. The decay of the signal was measured at m/z=76. b) The pseudo-first-order decay of $CH_2ClCH=CH_2$ was measured under the conditions: $[CH_2ClCH=CH_2]_0$=0.022 Torr, $[O]_0$=2.14 mTorr, total pressure=4.5 Torr and reaction time 0.9—7.3 ms. An Ar lamp with a LiF window (11.83 eV and 11.62 eV) was used to photoionize $CH_2ClCH=CH_2$. The decay of the signal was measured at m/z=76.

are the points obtained by the O_2 just surviving from the O_2/He discharge (no addition of O_2). If the fraction of $CD_3CCl{=}CD_2$ produced in Reaction 5 is represented by s_{5a}, the concentration of $CD_3CCl{=}CD_2$ at reaction time t is given by Eqs. 9 and 10 when both $O(^3P)$ and O_2 are present.

$$[CD_3CCl{=}CD_2] = f_{2a} + \left\{\frac{(s_{5a}-f_{2a})X}{1+X}\right\}\frac{k_1}{k_6}[\text{P-Cl}]\times [1-\exp(-k_6[\bar{O}]t)] \tag{9}$$

$$X = \frac{k_5}{k_2}\frac{[O_2]}{[\bar{O}]} \tag{10}$$

Similarly, the concentration of $(CD_3)_2CO$ at reaction time t is represented by Eq. 11;

$$[(CD_3)_2CO)] = f_{2b} + \left\{\frac{(s_{5b}-f_{2b})X}{1+X}\right\}k_1[\bar{O}][\text{P-Cl}]\,t \tag{11}$$

where s_{5b} refers to the fraction of $(CD_3)_2CO$ produced in Reaction 5 and [P-Cl] represents the concentration of $(CD_3)_2CHCl$. Since the value for k_5/k_2 was determined before, the concentrations of $CD_3CCl{=}CD_2$ and $(CD_3)_2CO$ can be plotted against $X/(1+X)$, as shown in Fig. 6. Using the values for k_1 and k_6 determined before and known initial concentration of $(CD_3)_2CHCl$ and the reaction time, values for f_{2a} and f_{2b} can be determined from the intercepts of the two lines. The values for s_{5a} and s_{5b} can be calculated from the slopes of the two straight lines in Fig. 6. Here, the instrumental sensitivity of $CH_3CH{=}CHCl$ was used in order to estimate the absolute concentrations of $CD_3CCl{=}CD_2$ ($^{35}Cl+^{37}Cl$). Values obtained are 0.31 ± 0.03 for f_{2a}, 0.24 ± 0.03 for f_{2b}, 0.035 ± 0.003 for s_{5a}, and 0.56 ± 0.05 for s_{5b}.

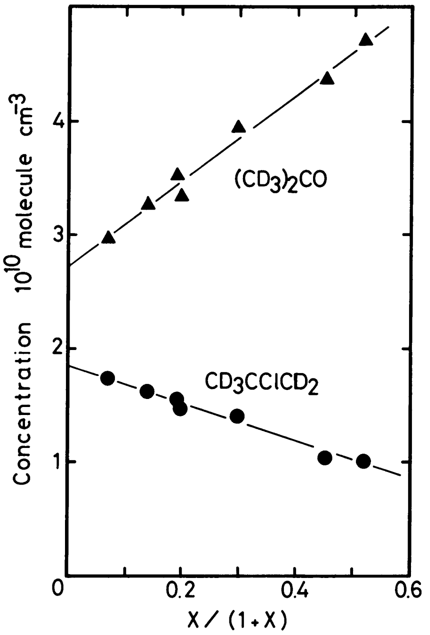

Fig. 6. The absolute concentrations of $(CD_3)_2CO$ and $CD_3CCl{=}CD_2$ ($^{35}Cl+^{37}Cl$) are plotted against $X/(1+X)$. Conditions are the same as the case of Fig. 5.

Table 3. Sum of the Heat of Formation of the Products of Reaction of $(CH_3)_2\dot{C}H$+O and $(CH_3)_2\dot{C}Cl$+O

Reaction	ΔH/kcal mol^{-1} [a]
C_3H_6+OH	14.2
$(CH_3)_2CO+H$	−0.9
$CH_3CHO+CH_3$	−5.7
$CH_3CCl{=}CH_2$ [b]+OH	3.3
$(CH_3)_2CO+Cl$	−22.9
$CH_3COCl+CH_3$	−24.2

a) Values of H^0_{298} are from Ref. 4. b) Calculated by the group additivity rule, Ref. 11.

$$\begin{array}{lll} (CD_3)_2\dot{C}Cl + O & \xrightarrow{31\pm3\%} & CD_3CCl{=}CD_2 \\ & \xrightarrow{24\pm3\%} & (CD_3)_2CO \end{array} \tag{2}$$

$$\begin{array}{lll} (CD_3)_2\dot{C}Cl + O_2 & \xrightarrow{3.5\pm0.3\%} & CD_3CCl{=}CD_2 \\ & \xrightarrow{56\pm5\%} & (CD_3)_2CO \end{array} \tag{5}$$

The yield of $CD_3CCl{=}CD_2$ from the oxygen atom reaction was 31%. This yield is smaller than the corresponding formation of $CD_3CH{=}CD_2$ (61%) in the reaction of $O+(CD_3)_2\dot{C}H$. On the other hand the yield of $(CD_3)_2CO$ (24%) is larger than that obtained in the $O+(CD_3)_2\dot{C}H$ reaction (18%). The results suggest that the probability of the deuterium abstraction from the radicals is decreased by the chlorine substitution for a hydrogen at 2-position of the isopropyl radical. The results might be explained from the exothermicity of the product channels shown in Table 3. The exothermicity of the addition routes was relatively raised by the chlorine substitution. Although the formation of CD_3COCl could not be observed, the most probable product corresponding to the residual 45% is CD_3COCl.

The channel of the deuterium abstraction (the $CD_3CCl{=}CD_2$ formation) decreased by the addition of O_2 and that of the oxygen atom addition (the $(CD_3)_2CO$ formation) increased as the case of the $(CD_3)_2\dot{C}H$ radical. These products are probably produced by the reaction of oxygen atoms with $(CD_3)_2CCl(O_2\cdot)$ radicals as described in the case of the $(CD_3)_2\dot{C}H$ radical.

$$(CD_3)_2\dot{C}Cl + O_2 \xrightarrow{+M} (CD_3)_2CCl(O_2\cdot) \tag{5}$$

$$(CD_3)_2CCl(O_2\cdot) + O \begin{array}{lll} \nearrow & CD_3CCl{=}CD_2 + OD + O_2\ (3.5\%) & \text{(12a)} \\ \rightarrow & (CD_3)_2CO + Cl + O_2\ (56\%) & \text{(12b)} \\ \searrow & CD_3COCl + CD_3 + O_2\ (40\%) & \text{(12c)} \end{array}$$

In the case of Reaction 12, product channels are affected more directly by the exothermicity.

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