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Mechanism of the Reactions of Butenes with O(^{3}P): The Yields of CH_3 and C_2H_5

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The mechanism of the reactions of O(^{3}P) with three isomeric butenes (*trans*-2-, iso- and 1-butene) was investigated observing the yields of CH_3 and C_2H_5 radicals by using a photoionization mass spectrometry at room temperature (298 ± 5 K) and pressure of 5 Torr (He buffer). The branching fractions for the CH_3 channel were determined as 0.52 ± 0.10, 0.24 ± 0.08, and 0.05 ± 0.01 for the reactions of O atoms with *trans*-2-butene, isobutene, and 1-butene, respectively. Also, the yield of the C_2H_5 for these reactions was estimated as 0.29 ± 0.05 for both *trans*-2-butene and 1-butene but was quite low for isobutene (<0.05). The possible mechanisms are discussed based on the present results as well as the previous studies.

Introduction

The reactions of oxygen atom with alkenes are important in understanding the combustion processes of hydrocarbons such as alkanes. The initial step of the reaction has been suggested to be the addition of atomic oxygen to the double bond, forming a biradical in the triplet state. The prototype reaction, that is, O(^{3}P) with C_2H_4, has been extensively investigated over the decades,[1−13] where the main concern has been focused on the competition between the direct hydrogen release channel

$$O(^3P) + C_2H_4 \rightarrow CH_2CHO + H \qquad (1a)$$

and the C−C bond cleavage channel following the hydrogen atom migration

$$O(^3P) + C_2H_4 \rightarrow CH_3 + CHO \qquad (1b)$$

Recently, the products of this reaction 1b has been measured by Yoshida et al. The branching fraction for reaction 1b was determined by the relative concentration of CH_3 as 0.53 ± 0.04 in the pressure range of 1−5 Torr.[14] The result was consistent with the direct analysis for the product yield ($\phi(CH_2CHO) = 0.46$) of the counterpart channel 1a.[15]

For the reactions of larger alkenes, the addition of O(^{3}P) has been known to occur mainly at the less alkyl-substituted end of the double bond. The commonly accepted interpretation is that the alkyl substitution at one end enhances the electron density on the other end and thus enhances the electrophillic attack by O(^{3}P). Such a site selectivity of O(^{3}P) reaction with alkenes has been extensively investigated by Cvetanović,[16] followed by many works mostly conducted by quantitative measurements of the final stable products.[17] Unfortunately, quantitative information of the direct product yields of these reactions has not been reported except for the reactions with propene and 1-butene.[15]

Washida et al. conducted a laser-induced fluorescence (LIF) study on some methyl-substituted vinoxy radicals for two isomeric butene (2- and iso-C_4H_8) reactions with O(^{3}P) and discussed relative importance of the competing channels qualitatively.[18] Bersohn and co-workers observed the H atom, CH_2CHO, CO, OH, and HCO as products from the reaction of O(^{3}P) with several alkenes by using a LIF method and a cavity ring-down spectroscopy.[19,20] However, due to the complexity for larger alkenes arising from the many possible product channels, this work supplied only qualitative information regarding the branching fractions of these products. Therefore, further (and more detailed) experimental evidence is desirable to get perspective view of the reaction mechanisms.

In the present work, reactions of O(^{3}P) with three butenes (*trans*-2-butene, isobutene, and 1-butene)

$$O(^3P) + CH_3CH{=}CHCH_3 \rightarrow \text{products} \qquad (2)$$

$$O(^3P) + (CH_3)_2C{=}CH_2 \rightarrow \text{products} \qquad (3)$$

$$O(^3P) + CH_3CH_2CH{=}CH_2 \rightarrow \text{products} \qquad (4)$$

were investigated by using a photoionization mass spectrometry.

Production rates of CH_3 and mass number 29 species (specified as C_2H_5, as shown in the text) were examined, and these products were confirmed to be the primary products from reactions 2−4, respectively. The yields of CH_3 as well as C_2H_5 in these reactions were measured and discussed on the basis of the site selectivity of the addition of oxygen atom to the substituted/unsubstituted carbon atoms in the double bond.

Experimental Section

Experiments were carried out by using photoionization mass spectrometry (PI-MS) coupled with pulsed laser photolysis in

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a quasistatic reactor, which is almost the same as that used in another report.[14] Reaction products with mass numbers of 15 (CH_3) and 29 (C_2H_5 and/or HCO) in the reactions of O + butenes were analyzed. A H lamp with an MgF_2 filter (10.2 eV) and a Cl lamp with a CaF_2 filter (9.1−8.9 eV) were used for detection of the CH_3 radical (ionization potential (IP) = 9.84 eV),[21] and for the C_2H_5/HCO radical (IP = 8.12 eV[22]/8.14 eV [23]), respectively. The $O(^3P)$ atom was generated by the photolysis of SO_2 with an ArF excimer laser (Lambda Physik COMPex 102)

$$SO_2 + h\nu\ (193\text{nm}) \rightarrow O(^3P) + SO \tag{5}$$

Gas flows were regulated using mass flow controllers and were premixed before entering the reactor. The flow speed in the reactor was kept fast enough to complete refreshment within the cycle of the photolytic laser pulse at 10 Hz. The total pressure in the reactor was measured using a capacitance manometer (MKS Baratron 122A). He (Nippon Sanso, >99.9999%), butenes (*trans*-2-, iso-, and 1-C_4H_8, Tokyo Kasei, >99%), C_2H_4 (Takachiho, >99.99%), SO_2 (Showa Denko, >99.9%), C_2H_6 (Nippon Sanso, >99.7%), and NO (Nippon Sanso, diluted in He at 5.14%) were used without further purification. CCl_4 (Kanto Chemical, >99.7%) was purified through trap−trap distillation. They were diluted in He and stored in a glass reservoir before use. All the experiments were conducted at room temperature (298 ± 5 K) and pressure of 5 Torr (1 Torr ≈ 133.322 Pa) using He as a buffer gas.

Experimental Results

All the experiments were carried out in an excess of C_4H_8 against the initial O atom. The main concern in this study is to measure the product yields of CH_3 in the reactions 2−4

$$O(^3P) + CH_3CH{=}CHCH_3 \rightarrow C_3H_5O + CH_3 \tag{2a}$$

$$\rightarrow \text{other products} \tag{2b}$$

$$O(^3P) + (CH_3)_2C{=}CH_2 \rightarrow C_3H_5O + CH_3 \tag{3a}$$

$$\rightarrow \text{other products} \tag{3b}$$

and

$$O(^3P) + CH_3CH_2CH{=}CH_2 \rightarrow C_3H_5O + CH_3 \tag{4a}$$

$$\rightarrow \text{other products} \tag{4b}$$

The signal intensity for CH_3 was calibrated by comparison with that produced in the reference reaction, in which the branching fraction for CH_3 has been well established

$$O(^3P) + C_2H_4 \rightarrow CH_3 + CHO \quad (\phi(CH_3) = 0.53 \pm 0.04)^{14} \tag{1b}$$

For calibration of C_2H_5, which is one of the probable products of *m*/*z* = 29, the following reactions were used; i.e., Cl atom was generated by the ArF laser photolysis of CCl_4 in a mixture of CCl_4 and C_2H_6 highly diluted with He, then C_2H_5 was produced by the reaction

$$Cl + C_2H_6 \rightarrow C_2H_5 + HCl \tag{5}$$

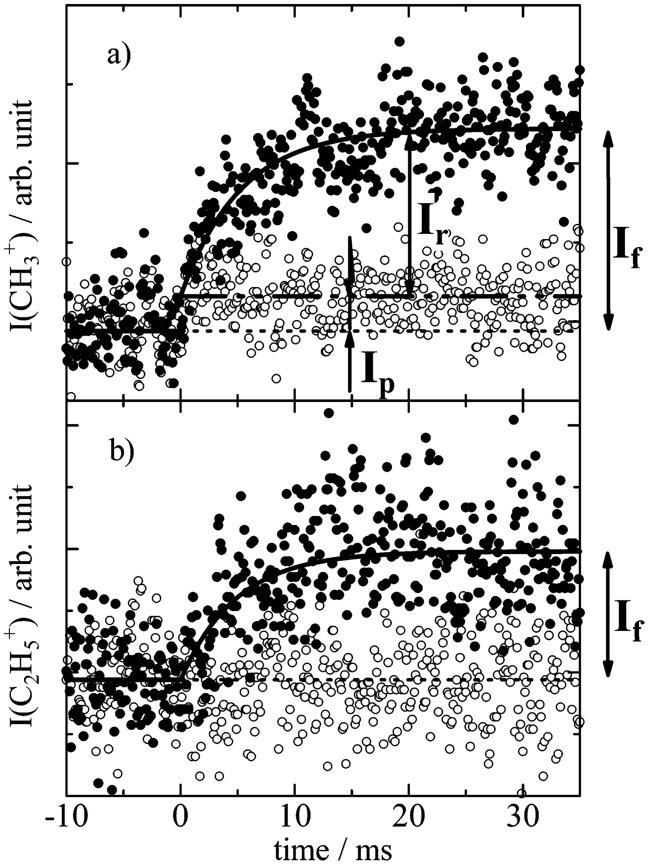

Figure 1. Typical time profiles for (a) CH_3 (*m*/*z* = 15, H lamp) and (b) C_2H_5 (*m*/*z* = 29, Cl lamp). Experimental conditions: [*trans*-2-C_4H_8] = 4.8 × 10^{12} molecules cm^{-3}; [SO_2] = 1.3 × 10^{13} molecules cm^{-3}. Solid curves (—) and dotted lines (···) denote results of single-exponential fitting and background signals, respectively. I_f and I_p represent the product fraction with and without coexistence of O atom, respectively, and $I_r = I_f - I_p$ (net fraction in the O + *trans*-C_4H_8 reaction).

Here, the initial O and Cl atom concentrations were kept low (typically, ≤5.4 × 10^{11} atoms cm^{-3} except for the worst case of O + 1-butene measurements of CH_3 yield as [O] ~1.6 × 10^{12} atoms cm^{-3}) enough to reduce the effect of subsequent radical−radical or radical−atom reactions. Also, pseudo-first-order conditions were established for all measurements, respectively (for example, $[O]_0$ = 1.5−3.8 × 10^{11} atoms cm^{-3} for rate measurements, which was 17 times lower than [C_4H_8] in the worst case).

Typical time evolutions of the signal intensity for *m*/*z* = 15 and 29 are shown in parts a and b of Figure 1, respectively. After the 193-nm photolysis in the *trans*-2-butene/SO_2/He mixture, CH_3^+ (*m*/*z* = 15) signal intensity increased immediately and then asymptotically increased with a time constant of few milliseconds toward the final level (denoted by I_f).

The initial fast rise is due to the CH_3 radical produced in the photolysis by the 193-nm radiation by reason of the large absorption cross sections (σ(193 nm) = 1−10 × 10^{-18} cm^2 $molecule^{-1}$)[24] for butenes because the signal is kept nearly constant at the initial level when there is no O atom coexistent (shown by open circles (○) and dot−dashed lines labeled by I_p in Figure 1a). It is also reasonable to conclude that the subsequent gradual increase of CH_3^+ signal (denoted by I_r) originates only from the CH_3 radical and not from fragmentation in the ionization of some other reaction intermediates. The energy of the H lamp used here (slightly above the ionization threshold energy of CH_3) is insufficient to cause successive fragmentation and ionization of the most probable parent vinoxy-type radicals such as CH_2COCH_3 or CH_3CHCHO.

To reduce the effects of the initial photolytic products in the measurements of $O(^3P)$ + alkenes reactions, the laser fluence

TABLE 1: Observed Rise Rate Constants of O + Butenes (in cm^3 molecule^{-1} s^{-1})[a]

reaction	k (CH$_3$)	k (C$_2$H$_5$)	k	ref
O + *trans*-2-C_4H_8	$(2.24 \pm 0.37) \times 10^{-11}$	$(2.07 \pm 0.43) \times 10^{-11}$	2.18×10^{-11}	25
O + iso-C_4H_8	$(2.02 \pm 0.70) \times 10^{-11}$	N/A	1.78×10^{-11}	25
O + 1-C_4H_8	$(4.08 \pm 0.51) \times 10^{-12}$	$(4.15 \pm 0.43) \times 10^{-12}$	4.18×10^{-12}	26

[a] k and refs denote the reported reaction rate constants (the error limits are two standard deviations of linear regressions).

(1−3 mJ cm^{-3}) as well as the concentrations of C_4H_8 ($\leq 4 \times 10^{13}$ molecule cm^{-3}) was kept as low as possible. Accordingly, initial concentrations of the photolytic products were kept below 6×10^{10} molecules cm^{-3}, even though the initial instant rise could not be completely eliminated. As the signal observed in the absence of O atoms (the photolytically produced CH_3) was nearly constant (ascribed by I_p in Figure 1a), the amount of CH_3 produced in the reactions 2a, 3a, or 4a (shown by I_r in Figure 1a) was simply evaluated by subtracting the initial photolytic fraction, denoted as I_p, from the total signal I_f.

This gradual rise I_r seems to attribute to CH_3 radical produced directly in the reaction of O(^{3}P) + *trans*-2-butene

$$O(^3P) + CH_3CH{=}CHCH_3 \rightarrow C_3H_5O + CH_3 \qquad (2a)$$

because the derived rate constant (k_2) from the pseudo-first-order analysis agrees very well with the reported reaction rate constants,[25] as compared in Table 1. The pseudo-first-order analysis is applied as follows. If CH_3 is formed in reaction 2a and other channels (2b) and the heterogeneous loss of O atom from the system

$$O(^3P) \rightarrow \text{loss} \qquad (w)$$

are also considered, the solution for the kinetics of O atom under the pseudo-first-order condition gives the single-exponential equation

$$[O] = [O]_0 \exp(-k't) \qquad (i)$$

where $k' = k_2[C_4H_8] + k_w$, $k_2 = k_{2a} + k_{2b}$. Thus, the CH_3^+ signal (shown by the solid curve deduced from the plot of I_r) should follow

$$I_r(CH_3^+) \propto 1 - \exp(-k't) \qquad (ii)$$

therefore, the linear relationship of the observed rise rate (k') for CH_3^+ signal vs initial concentration of *trans*-2-butene (shown in Figure 2a) and the intercept give a rate constant (k_2) and k_w, respectively.

Similarly, the gradual rise of CH_3 in the O + isobutene as well as the 1-butene reactions observed in this study was concluded to represent CH_3 directly produced in the reactions

$$O(^3P) + (CH_3)_2C{=}CH_2 \rightarrow C_3H_5O + CH_3 \qquad (3a)$$

and

$$O(^3P) + C_2H_5CH{=}CH_2 \rightarrow C_3H_5O + CH_3 \qquad (4a)$$

The rate constants obtained by the pseudo-first-order analysis of the observed rise rate (k') for CH_3^+ signals vs initial concentration of isobutene and 1-butene are also summarized in Table 1 compared with the previous data.[25,26] The present results of the CH_3 formation rate for all three butenes are confirmed to agree well with the reported rate constants. Therefore, CH_3 was confirmed to be the primary product from the reactions 2−4, respectively. It should be noted that the primary reaction intermediates (O-butene adducts) must be very short-lived ($\ll 1$ μs) so that the lifetimes could not be measured by using millisecond observation in this study. Thus, CH_3 production rate is limited by reaction of O atoms with the butenes.

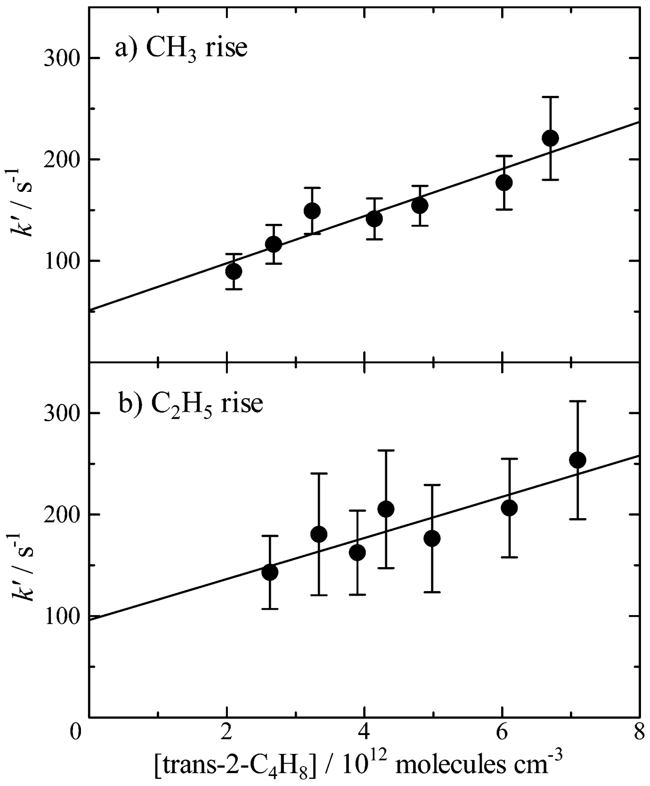

Figure 2. Plots of first-order rise rate constant (k') for the O + *trans*-2-butene as a function of the initial concentration for *trans*-2-butene: (a) CH_3 rise; and (b) C_2H_5 rise.

In Figure 3, the dependences of the CH_3 signal at the final plateau (I_f) against initial concentrations of O atoms are plotted for the reactions of O atoms with three butenes, compared with those for the reference reaction of O(^{3}P) + ethylene (reaction 1). Here, the initial concentration of O atom is evaluated by using the input laser fluence and the absorption cross section of SO_2 at 193 nm (σ(193 nm) = $6.8 \pm 1.5 \times 10^{-18}$ cm^2 molecule^{-1}).[27,28] It should be noted that the concentration of the O atom was varied by controlling the concentration of SO_2, whereas the input laser fluence was kept constant so as to keep the amount of CH_3 produced by the photolysis of butenes constant.

The slope of the linear dependence of CH_3 signal represents the relative reaction product yield, i.e.

$$I_f(CH_3^+) = \alpha[O(^3P)] + I_p \qquad (iii)$$

where α is the slope of linear dependence and I_p corresponds to the photolytically produced CH_3 signal as shown in Figure 1. The slope α includes the instrumental coefficient of signal intensity (expressed as $F(CH_3^+)$) and branching fraction of CH_3 ($\phi(CH_3)$), i.e.

$$\alpha = F(CH_3^+)\phi(CH_3) \qquad (iv)$$

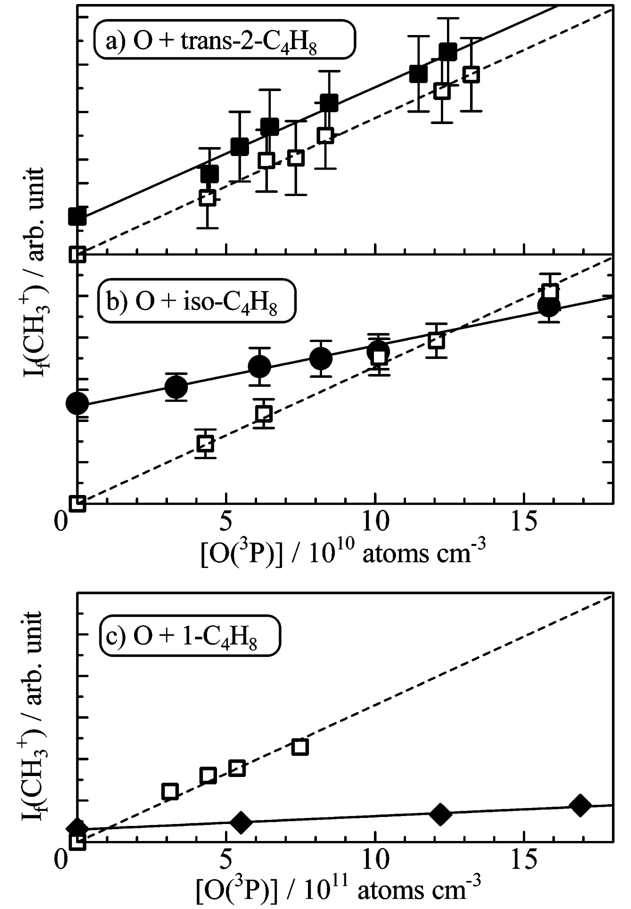

Figure 3. The product signal intensities of CH_3 from the reactions of $O(^3P)$ with butenes against the initial concentrations of O atoms: (a) O + *trans*-2-C_4H_8; (b) O + iso-C_4H_8; (c) O + 1-C_4H_8. Experimental conditions: $[C_2H_4] = 1.3 \times 10^{14}$ molecules cm^{-3}; [*trans*-2-C_4H_8] = 4.8×10^{12} molecules cm^{-3}; [1-C_4H_8] = 1.9×10^{13} molecules cm^{-3}. Filled circles fitted by solid lines indicate the intensities (I_f) obtained from O + C_4H_8 respectively, and open squares fitted by dotted lines indicate those from O + C_2H_4.

So, the ratio of the two slopes directly corresponds to the ratio of product yields of objective and reference reaction (O + C_4H_8/O + C_2H_4), i.e.

$$\alpha_{O+C_4H_8}/\alpha_{O+C_2H_4} = (F(CH_3^{+})\phi_{O+C_4H_8}(CH_3))/(F(CH_3^{+})\phi_{O+C_2H_4}(CH_3)) = \phi_{O+C_4H_8}(CH_3)/\phi_{O+C_2H_4}(CH_3) \qquad (v)$$

Therefore, magnitudes of the branching fraction for CH_3 production can be evaluated if that for the reference reaction 1b is given as $\phi_{O+C_2H_4}(CH_3) = 0.53$,[14] i.e.

$$\phi_{O+C_4H_8}(CH_3) = 0.53\,(\alpha_{O+C_4H_8}/\alpha_{O+C_2H_4}) \qquad (vi)$$

Even if the estimated concentrations of O atom are not accurate, the relative CH_3 yields are not seriously affected by this uncertainty. The product yields of the CH_3 are determined from the comparison of the magnitudes of the slopes in Figure 3 as 0.52 ± 0.10, 0.24 ± 0.08, and 0.05 ± 0.01 for the reactions with *trans*-2-butene (reaction 2a), isobutene (reaction 3a), and 1-butene (reaction 4a), respectively. Error limits include two standard deviations of linear fitting above and the propagation of error from reference branching fraction of O + C_2H_4. It should be noted that this estimate is affected by experimental uncertainty such as the loss of reactants. However, the systematic errors of those experimental conditions are approximately less than 10%, therefore, these errors are not included for the final results.

The estimated initial concentration of CH_3 is kept sufficiently low ($[CH_3] = 1-5 \times 10^{10}$ molecules cm^{-3}); therefore, the effect of side reactions such as CH_3-CH_3 self-reaction can be neglected in obtaining the reaction product yields. Also, the effect of the reactions of the O atom with the initially produced CH_3 and other possible photolytic products are regarded as minor in the present evaluation.

Typical time profiles for the ion signals ($m/z = 29$) as a reaction product of $O(^3P)$ + *trans*-2-butene is also shown in Figure 1b. In contrast to the CH_3 signal shown in Figure 1a, initial rapid rise (photolytic product) for $m/z = 29$ was almost negligible. The signal intensity gradually increased with a simple exponential-association time dependence toward a final plateau I_f. The similar evolution of the signal intensity for $m/z = 29$ was observed for $O(^3P)$ + 1-butene, but the signal was too weak to evaluate accurately the magnitude of the branching fraction for O + isobutene. Increment of the signal intensity at $m/z = 29$ was not observed when SO_2 was absent for all butenes. The pseudo-first-order analysis of the gradual increase for the $m/z = 29$ signal intensity vs initial concentration of butenes (shown in Figure 2b for the case of *trans*-2-butene) gives rate constants in excellent agreement with those obtained by CH_3. The results of those analyses are also shown in Table 1. It is therefore reasonable to conclude that these signals result from the reaction of O atoms with butenes. The signals cannot be simply concluded as $C_2H_5^+$ ions although they represent direct products of these reactions since another possible product HCO radical has the same mass number. Unfortunately, the ionization energies are so close to each other that they cannot be easily separated.

Recently, Quandt et al. reported that production of the HCO radical was very minor in the reactions of the O atom with all butenes studied here.[19] Taking account of their result, it is assumed in this study that the signal of $m/z = 29$ is mainly from C_2H_5, then the yields were evaluated by comparing the signal intensity with that observed in a reference reaction Cl + C_2H_6 (reaction 5) initiated by the photolysis of CCl_4. Concentrations for the Cl atom were estimated by the absorption cross section for CCl_4 ($\sigma(193\text{ nm}) = 8.4 \times 10^{-19}$ cm^2 molecule^{-1}, $\phi(Cl) = 1.5$).[29]

In order to estimate the yield of C_2H_5 for *trans*-2-butene and 1-butene, the $m/z = 29$ signal intensity (C_2H_5 radical) was measured as a function of initial concentrations of O atom and was compared with that from reaction 5 as shown in Figure 4, where abscissa was set common for the O and Cl atom concentrations. The plots show linear dependence on the [O] or [Cl], and the product branching fraction for C_2H_5 was determined from the ratio of the slopes. As a result, the C_2H_5 product yields were estimated to be 0.29 ± 0.05 for both *trans*-2- and 1-butenes. Error limits include two standard deviations of linear regression and propagation of error from reported absorption cross sections of SO_2, although it should be noted again that this estimate is affected to some extent by experimental uncertainty such as the difference of the loss of O and Cl atoms. The results of the yields for CH_3 and C_2H_5 in the reactions $O(^3P)$ + butenes obtained in this study are summarized in Table 2.

A further trial was also made to resolve the source of the signal at $m/z = 29$, though it was assigned to be C_2H_5 based on the results by Quandt et al.[19] Since the rate of reaction for C_2H_5

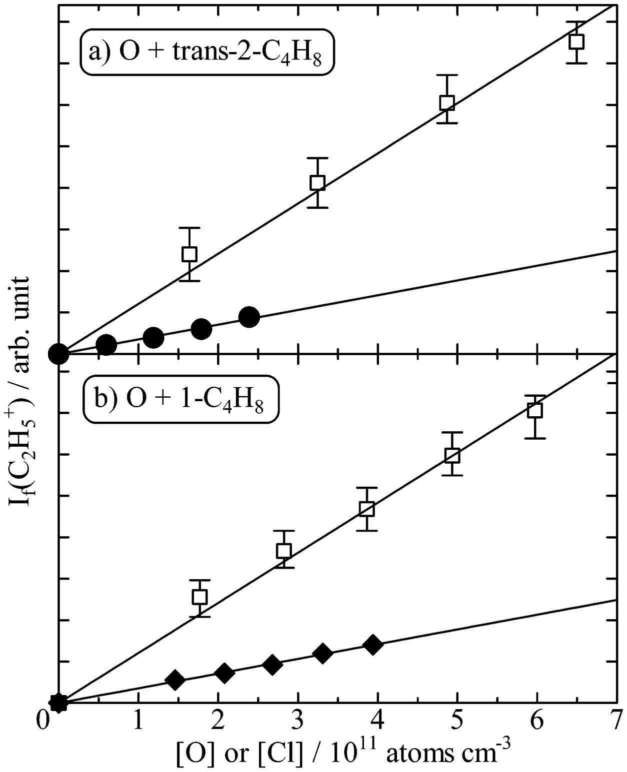

Figure 4. The product signal intensities of mass number 29 (C_2H_5 and/or HCO) from the reactions of O(^{3}P) with butenes against the initial concentrations of O atoms: (a) O + *trans*-2-C_4H_8; (b) O + 1-C_4H_8. Experimental conditions: [*trans*-2-C_4H_8] = 4.8 × 10^{12} molecules cm^{-3}, [iso-C_4H_8] = 5.9 × 10^{12} molecules cm^{-3}, [1-C_4H_8] = 1.9 × 10^{13} molecules cm^{-3}. Filled circles and diamonds fitted by solid lines indicate the intensities (I_f) obtained from O + *trans*-2-C_4H_8 and 1-C_4H_8, respectively, and open squares fitted by dotted lines indicate those from Cl + C_2H_6.

TABLE 2: Product Yields for O + Butenes

products/ reaction with	CH_3	C_2H_5	ref
trans-2-C_4H_8	0.52 ± 0.10	0.29 ± 0.05	This work
iso-C_4H_8	0.24 ± 0.08	N/A	This work
1-C_4H_8	0.05 ± 0.01	0.29 ± 0.05	This work
C_2H_4	0.53 ± 0.04	N/A	14

+ NO → products (reaction 6)[30] is much smaller than that for HCO + NO → products (reaction 7),[31] the rate of reaction of $m/z = 29$ product with NO was measured. The rate constant for C_2H_5 + NO (k_6) was also reinvestigated in this study, and it is found to be nearly equal to those of ($m/z = 29$) + NO produced in reactions 2 and 4 ($k_6 = (5.6 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$) but not in agreement with the reported k_7 (1.2 × 10^{-11} cm^3 $molecule^{-1}$).[30,31] It is therefore reasonable to conclude that the origin of $m/z = 29$ mainly comes from C_2H_5.

Discussion on the Reaction Mechanism. According to the pioneering works by Cvetanović[16,17] as well as the recent studies by Washida et al.[18] and Quandt et al.,[19] the main features of the reaction kinetics for O + alkenes (>C_2) can be summarized as follows.

1) The initial oxygen-atom attack is preferred to occur at the least alkyl-substituted end of the double bond, which explains that the electron-donating alkyl substitution promotes electron density on the other end, where the electrophilic oxygen atom prefers to attack.

2) The reaction proceeds via either the decomposition of initially formed triplet ketocarbenes or the subsequent decomposition following the intersystem crossing and the internal H-atom migration to the opposite carbon. In contrast to the reaction of O + C_2H_4, the direct release of the H atom is a minor channel partly because the bond dissociation energy is smaller for a C−C bond than a C−H bond. As the size of the substituted alkyl increases, the yield for the H atom decreases, especially for the alkenes in which both ends of the double bond are substituted by alkyl groups (RHC═CHR′). Even for alkenes of a type RR′C═CH_2, H atom (and its counterpart products) formation was highly depressed. This is probably caused by the fact that faster energy randomization (due to higher density of states) following O atom addition prohibits the preference of dissociation of the locally energized C−H bond.

3) Despite preference of the O-atom attack toward the unsubstituted carbon, it is also observed that direct formation of alkyl-substituted vinoxy radicals that can be accounted only from the unfavorable site was confirmed via the LIF measurements.[18] This may be caused by migration of the O atom from an unsubstituted carbon to the substituted one.

Since this is the first direct studies to evaluate the yield of CH_3 and C_2H_5 radicals produced in the reactions of O + alkyl substituted ethenes, the consistency of the product yields is examined by comparing the discussions given in the above works where the products of the counterpart of this study were discussed only semiquantitatively and/or qualitatively.

O + *trans*-2-Butene. Similar to the O + C_2H_4 reaction, since both ends of the double bond are equivalent, examination of two competing reaction pathways (i.e., direct-release channel vs subsequent dissociation following H-atom migration associated with intersystem crossing) is the main concern for this reaction

$$O(^3P) + CH_3CH{=}CHCH_3 \rightarrow {}^{\bullet}CH(CH_3){-}CH(O^{\bullet})CH_3$$

$$\rightarrow \mathbf{CH_3CHCHO} + CH_3 \quad \Delta H_{298K} = -122\ \mathrm{kJ\ mol^{-1}} \quad (2a\text{-}1)$$

$$\rightarrow CH_3CHC(O)CH_3 + H \quad \Delta H_{298K} = -97\ \mathrm{kJ\ mol^{-1}} \quad (2b\text{-}1)$$

$$\rightarrow \text{Intersystem crossing,} \quad \text{H-shift}$$

$$\rightarrow C_2H_5CO + CH_3 \quad \Delta H_{298K} = -125\ \mathrm{kJ\ mol^{-1}} \quad (2a\text{-}2)$$

$$\rightarrow \mathbf{CH_2C(O)CH_3} + CH_3 \quad \Delta H_{298K} = -127\ \mathrm{kJ\ mol^{-1}} \quad (2a\text{-}3)$$

$$\rightarrow CH_3CO + C_2H_5 \quad \Delta H_{298K} = -129\ \mathrm{kJ\ mol^{-1}} \quad (2b\text{-}2)$$

Heats of reactions are evaluated from reported [32] or estimated [33] standard enthalpies of formation. The main products observed in the previous work by Washida et al.[18] are underlined in the above scheme, although magnitudes of product branching fractions are uncertain. According to Washida et al.[18] and Quandt et al.,[19] reaction 2b-1 is minor since neither of the products, the H atom nor $CH_3CHC(O)CH_3$, were observed.

The present branching fraction for CH_3, 0.52 ± 0.10, is consistent with Washida et al. as CH_3 is a counterpart product for CH_3CHCHO (2a-1) and $CH_2C(O)CH_3$ (2a-3). The relatively high yield for C_2H_5, 0.29 ± 0.05, estimated in this study seems reasonable since reaction 2b-2 is the most exothermic channel among the dissociation channels from $C_2H_5C(O)CH_3$ formed via the intersystem crossing. Thermochemically, the reactions 2a-2 and 2a-3 are supposed to be less dominant than reaction 2b-1. This implies that a major part of CH_3 is formed by reaction 2a-1. The remaining product channels (~0.19) are not identified, though it may be reasonable that stabilization of the intermediate ($C_2H_5C(O)CH_3$) occurs even in the condition of low pressure

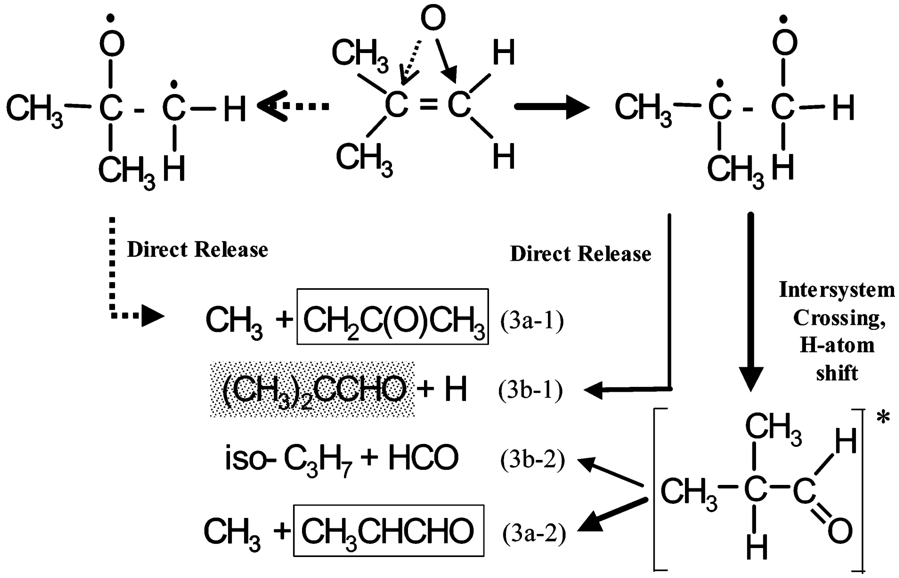

Figure 5. A schematic of the reaction mechanism for the $O(^3P) + iso\text{-}C_4H_8$.

~5 Torr. Stabilization channels will be discussed further at the end of this section.

O + Isobutene. The proposed reaction mechanism is

$$O(^3P) + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2C(O^\bullet){-}CH_2^\bullet \rightarrow \mathbf{CH_2C(O)CH_3} + CH_3 \quad \Delta H_{298K} = -120\ \mathrm{kJ\ mol^{-1}}\ (3a\text{-}1) \qquad (3a\text{-}1)$$

$$\rightarrow (CH_3)_2C(^\bullet){-}C(O^\bullet)H_2 \rightarrow (CH_3)_2CCHO + H \quad \Delta H_{298K} = -85\ \mathrm{kJ\ mol^{-1}} \qquad (3b\text{-}1)$$

$$\rightarrow \text{Intersystem crossing,}\quad \text{H-shift}$$

$$\rightarrow \mathbf{CH_3CHCHO} + CH_3 \quad \Delta H_{298K} = -115\ \mathrm{kJ\ mol^{-1}} \qquad (3a\text{-}2)$$

$$\rightarrow iso\text{-}C_3H_7 + HCO \quad \Delta H_{298K} = -98\ \mathrm{kJ\ mol^{-1}} \qquad (3b\text{-}2)$$

and also illustrated in Figure 5. Boldface products are those observed by Washida et al.[18] Reaction 3b-1 should be minor because the yield of either product, the H atom or $(CH_3)_2CCHO$, is small.[18,19]

The CH_3 yield, that is, the sum of the branching fractions for (3a-1) and (3a-2), was evaluated as 0.24 ± 0.08, which seems to be consistent with the observation by Washida et al.[18] Present study indicates only 0.24 for CH_3 as a product yield (and no C_2H_5), so that other residual product channels (~0.76) are still unidentified. Failure to observe a signal at $m/z = 29$ ($C_2H_5^+$ or HCO^+) in the present study, and the result by Min et al., who reported that no HCO was observed,[20] suggest that the branching fraction for HCO channel (3b-2) (including successive CO formation)[19] should be very small.

O + 1-Butene. The proposed reaction mechanism is complicated to account for the present result

$$O(^3P) + C_2H_5CH = CH_2 \rightarrow C_2H_5C(^\bullet)H{-}C(O^\bullet)H_2 \rightarrow C_2H_5CHCHO + H \quad \Delta H_{298K} = -82\ \mathrm{kJ\ mol^{-1}} \qquad (4b\text{-}1)$$

$$\rightarrow C_2H_5CH(O^\bullet){-}CH_2^\bullet \rightarrow CH_2C(O)C_2H_5 + H \quad \Delta H_{298K} = -85\ \mathrm{kJ\ mol^{-1}} \qquad (4b\text{-}2)$$

$$\rightarrow \mathbf{CH_2CHO} + C_2H_5 \quad \Delta H_{298K} = -120\ \mathrm{kJ\ mol^{-1}} \qquad (4b\text{-}3)$$

$$\rightarrow \text{Intersystem crossing,}\quad \text{H-shift A} \quad (\text{from } C_2H_5C(^\bullet)H{-}C(O^\bullet)H_2)$$

$$C_3H_7CHO^* \rightarrow n\text{-}C_3H_7 + HCO \quad \Delta H_{298K} = -105\ \mathrm{kJ\ mol^{-1}} \qquad (4b\text{-}4)$$

$$\rightarrow \mathbf{CH_2CHO} + C_2H_5 \quad \Delta H_{298K} = -120\ \mathrm{kJ\ mol^{-1}} \qquad (4b\text{-}5)$$

$$\rightarrow \text{Intersystem crossing,}\quad \text{H-shift B} \quad (\text{from } C_2H_5CH(O^\bullet){-}CH_2^\bullet)$$

$$C_2H_5COCH_3^* \rightarrow C_2H_5CO + CH_3 \quad \Delta H_{298K} = -135\ \mathrm{kJ\ mol^{-1}} \qquad (4a\text{-}1)$$

$$\rightarrow CH_2C(O)CH_3 + CH_3 \quad \Delta H_{298K} = -138\ \mathrm{kJ\ mol^{-1}} \qquad (4a\text{-}2)$$

$$\rightarrow CH_3CO + C_2H_5 \quad \Delta H_{298K} = -140\ \mathrm{kJ\ mol^{-1}} \qquad (4b\text{-}6)$$

and also illustrated in Figure 6. Although the yield of CH_3 is small (0.05 ± 0.01), reaction pathways from $C_2H_5CH(O^\bullet)\text{-}CH_2^\bullet$ (intersystem crossing B) should be included since no other feasible reaction channels seems to account for CH_3 production. It is energetically impossible that the ion signal at $m/z = 15$ comes from fragments produced in the photoionization of some larger radical species. Even if 2-butene as the manufacturing impurity was included in 1-butene, the upper limit of the contribution for the yield is only 0.01. The small yield of the products from intersystem crossing B corresponds to the observation for the minor products of $C_2H_5C(O)CH_3$ reported by Cvetanović,[16,17] which suggests that the substituted side attack by O atom still occurs and the site selectivity is not completely exclusive.

The present study indicates that the branching fraction of C_2H_5 for O + 1-butene is 0.29 ± 0.05. This is consistent with that found by Quandt et al., who monitored counterparts of C_2H_5 in the product channels (4b-3) and (4b-5) and reported that the CH_2CHO product yield is 0.17−0.37.[3,15,19] Although no experimental result is investigated to discern the relative importance of the two main channels (4b-3 and 4b-5), the preference on the initial attack of O atom suggests that the 4b-5 channel accounts for major part of the yield.

The residual branching fraction is still large (~0.66), therefore other production channels should be considered. Quandt et al.

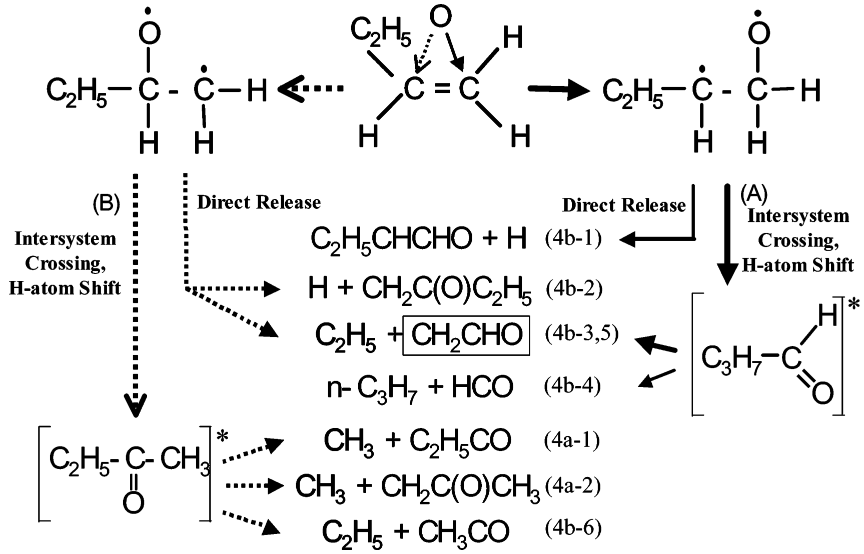

Figure 6. A schematic of the reaction mechanism for the O(^{3}P) + 1-C_4H_8.

reported that H atom yield is very low, as is in the case of isobutene;[19] therefore, reaction (4b-1) and (4b-2) should be minor. Koda et al. identified HCO as a reaction product, and they reported that the product yield was 0.26.[15] In contrast, Min et al. reported that the product branching fraction should be low because they could not observe HCO.[20] Therefore, channel (4b-4) may not be identified as one of the other missing major product channels.

Stabilization Channels in the O + Butene Reactions. For all three butenes, branching fractions for the unidentified product channels account for a large part of product channels as discussed above. Nonradical product channels such as adducts that are not detected by the present experiment may be such candidates. One of the possible nonradical products may be produced in the stabilization of the initial O adduct. For the O + ethylene reaction, which is in the case of the smallest alkene, the stabilization channel is negligible in a low-pressure region.[14] However, substitution by a larger alkyl group in an alkene increases density of states, which makes the energized intermediate more stable and stabilization channel will increase even in low pressure.[17]

In contrast, the dissociation channel is still dominant in the case of *trans*-2-butene despite the same molecular size of other butenes. One of the possible explanations is that *trans*-2-butene has extra C−C bonds at the double-bonded carbon atom so methyl is released in preference to the H atom because of the smaller bond dissociation energy.[19] The direct-release channel of the methyl group is still competitive for stabilization channel via intersystem crossing and H-shift so that the total of dissociation channels occupies a major part of the reaction mechanism. Another possible reason is that three dissociation channels via intersystem crossing (reactions 2a-2, 2a-3, and 2b-2) have nearly isothermal heats of reactions. The reaction intermediate ($C_2H_5COCH_3$) has a larger excess energy (477 kJ mol^{-1} [31]) than those for other two butenes (447−453 kJ mol^{-1} [31]), so that energized intermediate can dissociate more easily to successive radical + radical channels.

Product channels going to the radical + radical products are surely important in the combustion process of alkenes because the adducts must be decomposed more easily at high temperature. Alkyl-type and vinoxy-type radicals produced in such successive decomposition should be adequately included in the hydrocarbon combustion scheme.

Conclusion

The product yields of CH_3 and C_2H_5 for the reactions of oxygen atoms with butenes have been measured for the first time at room temperature and pressure of 5 Torr (He buffer). The branching fractions of the CH_3 product channel were determined as 0.52 ± 0.10, 0.24 ± 0.08, and 0.05 ± 0.01 for the reactions of O atom with *trans*-2-butene, isobutene, and 1-butene, respectively. Also, the yields of C_2H_5 for these reactions were evaluated as 0.29 ± 0.05 for both *trans*-2-butene and 1-butene and <0.05 for isobutene.

The product yields for CH_3 and C_2H_5 given in this study are consistent with those of the previous qualitative measurements for the counterparts in these reactions.

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