Laser-Induced Fluorescence of Methyl Substituted Vinoxy Radicals and Reactions of Oxygen Atoms with Olefins

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Received: May 15, 1998

Laser-induced fluorescence spectra in the 330−370 nm region are assigned to the five expected methyl substituted vinoxy radicals: 1-methylvinoxy, 2-methylvinoxy, 1,2-dimethylvinoxy, 2,2-dimethylvinoxy, and 1,2,2-trimethylvinoxy radicals. Substituted vinoxy radicals were produced by photolyses or by chlorine or fluorine atom reactions with ketones, aldehydes, or ethers. These radicals were also observed when reacting oxygen atoms with olefins such as propene, *cis*- and *trans*-2-butene, isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. These results extend our knowledge of the replacement mechanism in O + olefin reactions, i.e., a methyl radical or a hydrogen atom can be expelled directly from the triplet biradical formed by an O atom addition to an olefin. Methyl substituted vinoxy radicals can also be produced by the release of a methyl radical from the 2-position carbon of an energized singlet aldehyde or ketone formed by a 1,2-migration of a hydrogen atom in the triplet biradical.

Introduction

It has been shown[1−4] that the vinoxy radical (CH_2CHO) is produced in the reaction of ethylene with atomic oxygen, $O(^3P)$, reaction 1a. The vinoxy radical could be measured by the laser-induced fluorescence (LIF) method.[1,3] Also, there is a hydrogen migration process,[5−7] reaction 1b.

$$CH_2{=}CH_2 + O(^3P) \rightarrow CH_2CHO + H \qquad (1a)$$

$$\rightarrow CH_3 + CHO \qquad (1b)$$

Recently several new LIF spectra of halogenated vinoxy-type radicals were observed when reacting oxygen atoms with halogenated ethylenes.[8,9] These results show that many kinds of vinoxy-type radicals can be measured by LIF.

In the present paper, new LIF spectra observed when reacting oxygen atoms with olefins such as propene, *cis*- and *trans*-2-butene, isobutene, 2-methyl-2-butene, or 2,3-dimethyl-2-butene are reported. These new spectra appear to belong to the family of methyl substituted vinoxy-type radicals. Identification of these spectra are supported by using several sources of each radical.

Experimental Section

The apparatus used was similar to that described previously[8] and will only be reviewed briefly here. Methyl substituted vinoxy radicals were produced by reacting several olefins with atomic oxygen, which was generated by excimer laser photolysis of SO_2 at 193 nm[10−12] (Lambda Physik 120 icc).

$$SO_2 + h\nu \rightarrow SO + O(^3P) \qquad (2)$$

Typical pressures used were 0.5−6 mTorr of olefins, about 4 mTorr of SO_2, and 1.5 Torr of collider gas (He). Laser fluences were typically 3−6 mJ cm^{-2}. Fluorescence was induced by a frequency-doubled tunable dye laser (Lumonics HD-300) pumped by a Nd:YAG laser (Quanta-Ray DCR-11) for the range from 332 to 362 nm and a Lambda Physik FL-3002E tunable dye laser pumped by a Lambda Physik COMPex 110 excimer laser operating on the XeCl transition at 308 nm to cover the range from 343 to 375 nm. Fluorescence was collected at right angles relative to the collinear counterpropagating laser beams and was measured with a Hamamatsu R 268 photomultiplier tube using band-pass filters (L40 + B390, transmit 410−520 nm). The probe laser beam was perpendicular to the gas flow. The probe laser line width was 0.2 cm^{-1}. Fluorescence signals from the photomultiplier tube were averaged (every 10 laser shots) by a boxcar integrator (Stanford Research System SR250) and then transferred to a microcomputer for analysis and storage. Data were acquired with a delay time of about 150 μs between the photolysis and probe lasers.

Reference LIF spectra of the methyl substituted vinoxy radicals were measured by photolysis and also by chlorine or fluorine atom reactions with appropriate precursor molecules. For the photolyses, 0.7−1.5 mTorr of precursor molecules (ketones or ethers) diluted by He (1.5 Torr) were photolyzed by the ArF excimer laser. Data were acquired with a delay time of 45 μs between the photolysis and probe lasers. In the case of chlorine atom reactions, radicals were produced by reacting 1−4 mTorr of precursor molecules (aldehydes or ketones) with atomic chlorine, which was generated by the photolysis of CCl_4 (30−100 mTorr) at 193 nm[13] with 1.5 Torr of carrier gas (He).

$$CCl_4 + h\nu \rightarrow Cl + CCl_3 \qquad (3a)$$

$$\rightarrow 2Cl + CCl_2 \qquad (3b)$$

The time delay between the photolysis and the probe lasers was 250−550 μs. In the case of the fluorine atom reactions, radicals were generated by reacting 0.2−2 mTorr of precursor molecules (ketones and aldehydes) with atomic fluorine, which was produced in a microwave discharge (2450 MHz) of 6 Torr of a fluorine−helium mixture (0.01−0.03% F_2).

S1089-5639(98)02258-0 CCC: $15.00

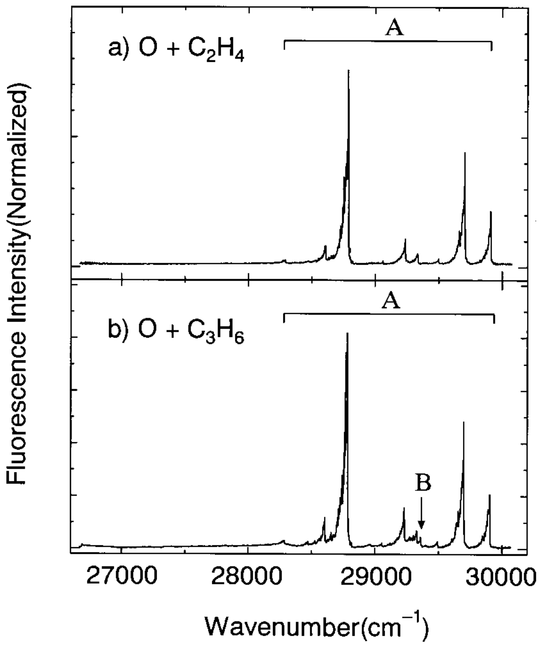


Figure 1. Laser-induced fluorescence excitation spectrum of radicals produced in (a) O(^{3}P) + C_2H_4 and (b) O(^{3}P) + C_3H_6 reactions. The fluorescence intensitiy is normalized for laser power. The spectral resolution is 0.2 cm^{-1}. Measurements are carried out at room temperature (296 ± 4 K). (a) The pressures of C_2H_4, SO_2, and He are 5.0 mTorr, 0.4 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 1.9 mJ cm^{-2}. The time delay between the photolysis and the probe is 540 μs. (b) The pressures of C_3H_6, SO_2, and He are 5.9 mTorr, 3.5 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 3 mJ cm^{-2}. The time delay between the photolysis and the probe is 150 μs.

All experiments were carried out at room temperature (296 ± 4 K). The gases and chemicals were purchased from the following suppliers and used without further purification: He (99.999%, Nippon Sanso), O_2 (99.9%, Nippon Sanso), F_2 (99%, Central Glass); C_2H_4 (99.5%), C_3H_6 (99%), *cis*- and *trans*-2-C_4H_8 (both 99%), and iso-C_4H_8 (99%) (all from Takachiho); $(CH_3)_2C{=}CHCH_3$ (>99%), $(CH_3)_2C{=}C(CH_3)_2$ (>99%), CH_3COCH_2Cl (95%), $CH_3CHClCOCH_3$ (99%), CH_3CH_2CHO (99%), and $(CH_3)_2CHCOCH_3$ (99%) (all from Tokyo Kasei); CCl_4 (99.8%), $CH_3CH_2COCH_3$ (99%), and $(CH_3)_2CHCHO$ (95%) (all from Wako Pure Chemicals); $(CH_3)_2CO$ (99%) and $CH_3COCH_2COCH_2$ (98%) (both from Dojindo); $CH_3COCH(CH_3)COCH_3$ (85%), $CH_2{=}C(CH_3)OCH_3$ (97%), and $CH_3CH{=}CHOC_2H_5$ (cis and trans mixture, 98%) (all from Aldrich).

Results and Discussion

LIF Spectra Observed in O(^{3}P) + Olefin Reactions. Figures 1−3 show LIF spectra observed in the region of 332−375 nm when ethylene, propene, *trans*-2-butene, isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene react with atomic oxygen. Figure 1a gives the known spectrum of the $\tilde{B}\leftrightarrow\tilde{X}$ transition of vinoxy radicals (marked by A) which was measured anew in the present study. Since other new LIF spectra (marked by B−F) are observed when reacting oxygen atoms with higher olefins and are in a similar wavelength region, we expect them to be the $\tilde{B}\leftrightarrow\tilde{X}$ transitions of methyl substituted vinoxy-type radicals.

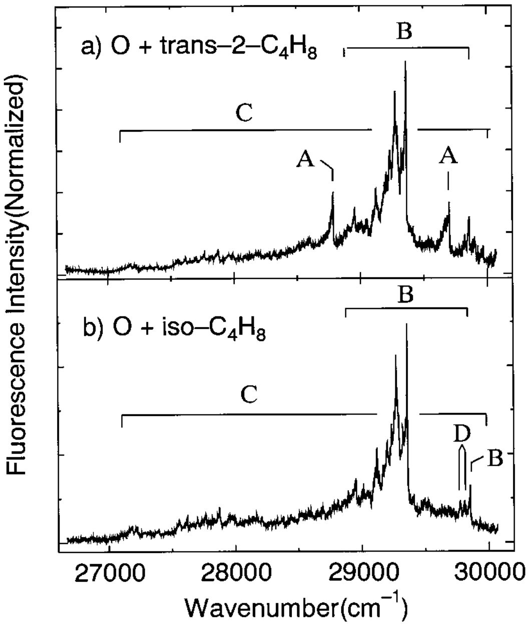


Figure 2. LIF excitation spectrum of radicals produced in (a) O + *trans*-2-butene and (b) O + isobutene reactions at room temperature (296 ± 4 K). The fluorescence intensity is normalized for laser power. The spectral resolution is 0.2 cm^{-1}. (a) The pressures of *trans*-2-butene, SO_2, and He are 0.5 mTorr, 3.6 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 6.1 mJ cm^{-2}. The time delay between the photolysis and the probe is 145 μs. (b) The pressure of isobutene, SO_2, and He are 0.8 mTorr, 3.6 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 3.4 mJ cm^{-2}. The time delay between the photolysis and the probe is 145 μs.

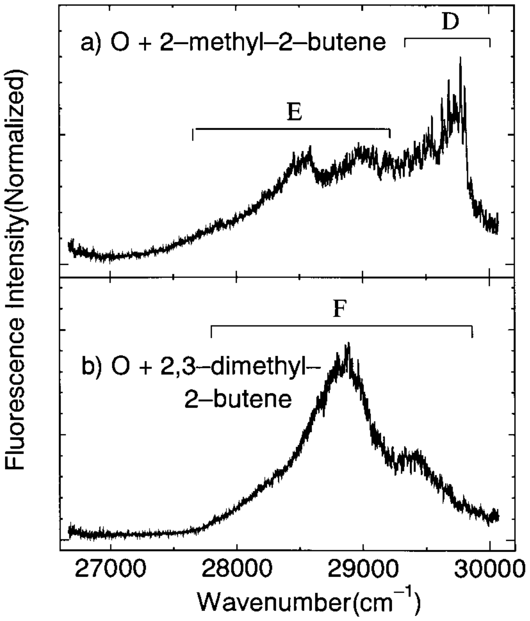


Figure 3. LIF excitation spectrum of radicals produced in (a) O + 2-methyl-2-butene and (b) O + 2,3-dimethyl-2-butene at 296 ± 4 K. The fluorescence intensity is normalized for laser power. The spectral resolution is 0.2 cm^{-1}. (a) The pressures of 2-methyl-2-butene, SO_2, and He are 1.8 mTorr, 3.8 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 4.5 mJ cm^{-2}. The time delay between the photolysis and the probe is 145 μs. (b) The pressures of 2,3-dimethyl-2-butene, SO_2, and He are 1.4 mTorr, 4.2 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 4.3 mJ cm^{-2}. The time delay between the photolysis and the probe is 145 μs.

For all of the measurements shown in Figures 1−3, oxygen atoms were generated by pulsed laser photolysis of SO_2. In preliminary experiments, oxygen atoms were generated in a microwave discharge of an oxygen−helium mixture. This resulted in very strong fluorescence from formaldehyde around 28 250 and 29 450 cm^{-1}, and these bands obscured the spectra shown in Figures 2 and 3. Formaldehyde is probably produced by a secondary reaction such as reaction 4.[14]

$$CH_3 + O \rightarrow CH_2O + H \qquad (4)$$

C_3H_6 + O Reaction. As shown in Figure 1b, strong fluorescence of vinoxy radicals (marked by A) is observed when reacting oxygen atoms with propene, reaction 5a.

$$(CH_3)HC{=}CH_2 + O \rightarrow CH_2CHO + CH_3 \qquad (5a)$$

$$\rightarrow CH_2C(CH_3)O + H \qquad (5b)$$

$$\rightarrow CH_3CHCHO + H \qquad (5c)$$

Observation of vinoxy radicals produced in the reaction of propene with O has been reported previously[2,15,16]

An additional weak fluorescence appeared at 29 363 cm^{-1} (spectrum B, shown by an arrow in Figure 1b) and is thought to belong to the cis/trans mixture of the 2-methylvinoxy radical, CH_3CHCHO, produced by reaction 5c. No fluorescence of 1-methylvinoxy radicals, $CH_2C(CH_3)O$ (reaction 5b), is observed. Reference spectra of 1- and 2-methylvinoxy radicals will be shown in the next section.

***cis-* and *trans*-2-C_4H_8 + O Reaction.** Figure 2a shows a LIF spectrum observed when reacting oxygen atoms with *trans*-2-butene. The same spectrum is observed during the reaction of *cis*-2-butene with atomic oxygen. The fluorescing molecules are assigned to the cis/trans mixture of 2-methylvinoxy (spectrum B) and 1-methylvinoxy (spectrum C) radicals because the spectral profiles and wavelengths of both spectra are quite similar to the jet-cooled LIF spectra of the $\tilde{B} \leftrightarrow \tilde{X}$ electronic transitions of 1-methylvinoxy and of a cis/trans mixture of 2-methylvinoxy radicals,[17] which have been produced in the photolysis of methyl isopropenyl ether and ethyl-1-propenyl ether at 193 nm, respectively. The 1- and 2-methylvinoxy radicals probably are produced by reactions 6b and 6a, respectively.

$$(CH_3)CH{=}CH(CH_3) + O \rightarrow CH_3CHCHO + CH_3 \qquad (6a)$$

$$\rightarrow CH_2C(CH_3)O + CH_3 \qquad (6b)$$

$$\rightarrow CH_3CHC(CH_3)O + H \qquad (6c)$$

The formation of the 1-methylvinoxy radical by reaction 6b is interesting because it requires the migration of a hydrogen atom from one carbon atom to the other. A similar migration has been reported previously with formation of the CHClCHO radical in the CH_2CCl_2 + O reaction.[9] No fluorescence of 1,2-dimethylvinoxy radicals, reaction 6c, was observed.

The weak fluorescence of unsubstituted vinoxy radicals shown in Figure 2a (marked by A) probably was produced by reaction of oxygen atoms with the 0.7% 1-butene impurity contained in the *cis*- and *trans*-2-butene.

$$(C_2H_5)CH{=}CH_2 + O \rightarrow CH_2CHO + C_2H_5 \qquad (7)$$

Formation of vinoxy radicals in the reaction of 1-butene + O has been reported.[2,15,16]

Additional experiments were conducted to confirm the sources of the two spectra (B and C). The LIF spectrum shown in Figure 4a is observed following the photolysis of ethyl-1-propenyl ether, at 193 nm.

$$(CH_3)CH{=}CHOC_2H_5 + h\nu \rightarrow CH_3CHCHO + C_2H_5 \qquad (8)$$

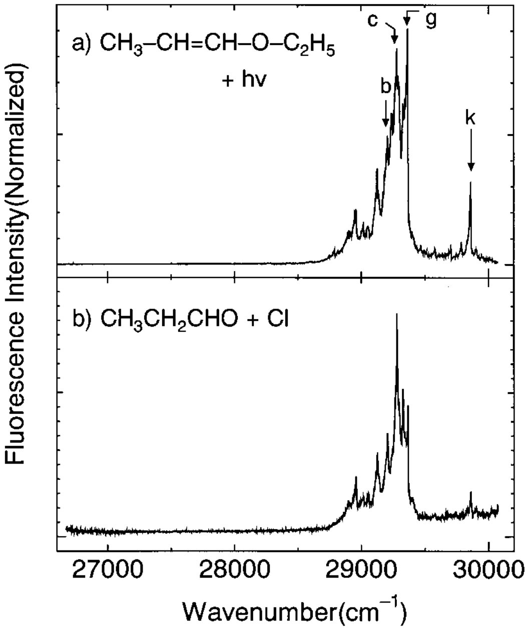


Figure 4. LIF excitation spectra of the cis/trans mixture of 2-methylvinoxy radical, CH_3CHCHO, produced in (a) photolysis of ethyl-1-propenyl ether at 193 nm and (b) propionaldehyde + Cl reaction at 296 ± 4 K. (a) The pressures of ethyl-1-propenyl ether and He are 0.8 mTorr and 1.5 Torr, respectively. The laser fluence (193 nm) is 2.9 mJ cm^{-2}. The time delay between the photolysis and the probe is 45 μs. (b) The pressures of C_2H_5CHO, CCl_4, and He are 2.0 mTorr, 62 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 2.4 mJ cm^{-2}. The time delay between the photolysis and the probe is 245 μs. For marking by b, c, g, and k, see the text.

The jet-cooled LIF spectrum of the 2-methylvinoxy radical was observed[17] previously in this photolysis system. The peaks marked by b, c, g, and k in Figure 4a appear identical to the peaks in the jet-cooled spectrum (marked B, C, G, and K in their paper[17]). Figure 4b shows a LIF spectrum observed when propionaldehyde reacts with atomic chlorine.

$$CH_3CH_2CHO + Cl \rightarrow CH_3CHCHO + HCl \qquad (9)$$

The spectra shown in Figure 4a,b and the spectrum B shown in Figure 2 have identical bandhead positions but somewhat different intensity distributions due to the different energetics involved. Thus spectrum B is assigned to the cis/trans mixture of 2-methylvinoxy radical formed in reaction 6a.

Figure 5a shows a LIF spectrum observed when reacting chlorine atoms with acetone, reaction 10.

$$(CH_3)_2CO + Cl \rightarrow CH_2C(CH_3)O + HCl \qquad (10)$$

Figure 5b gives a LIF spectrum observed following the photolysis of 2,4-pentanedione at 193 nm, reaction 11.

$$CH_3COCH_2COCH_3 + h\nu \rightarrow CH_2C(CH_3)O + CH_3CO \qquad (11)$$

Since the formation of the acetyl radical has been reported in the photolysis of 2,4-pentanedione,[18] the counterradical, 1-methylvinoxy, should also be formed. Both spectra shown in Figure 5a,b are similar to the jet-cooled LIF spectrum observed in the photolysis of 2-methoxypropene[17] at 193 nm. The peaks shown by arrows (a−p) in Figure 5a are identical to those reported in the jet-cooled spectrum. In addition to the spectra shown in Figure 5a,b, the same spectra were observed in many reaction systems such as photolysis of 2-methoxypropene,

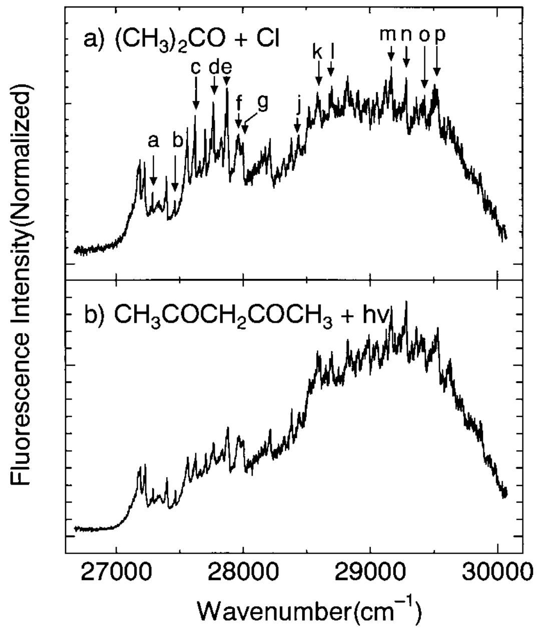


Figure 5. LIF excitation spectrum of the 1-methylvinoxy radical, $CH_2C(CH_3)O$, produced in (a) acetone + Cl reaction and (b) photolysis of 2,4-pentanedione at 193 nm at 296 ± 4 K. (a) The pressures of acetone, CCl_4, and He are 4.4 mTorr, 26 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 2.4 mJ cm^{-2}. The time delay between the photolysis and the probe is 245 μs. (b) The pressures of 2,4-pentanedione and He are 1.5 mTorr and 1.5 Torr, respectively. The laser fluence (193 nm) is 1.9 mJ cm^{-2}. The time delay between the photolysis and the probe is 45 μs. For marking by a−p, see the text.

chloroacetone, and acetone at 193 nm and also reaction of F + acetone, reactions 12−15.

$$CH_2{=}C(CH_3)OCH_3 + h\nu \rightarrow CH_2C(CH_3)O + CH_3 \tag{12}$$

$$ClCH_2COCH_3 + h\nu \rightarrow CH_2C(CH_3)O + Cl \tag{13}$$

$$CH_3COCH_3 + h\nu \rightarrow CH_2C(CH_3)O + H \tag{14}$$

$$CH_3COCH_3 + F \rightarrow CH_2C(CH_3)O + HF \tag{15}$$

It is concluded that the fluorescing radical responsible for the spectra shown in Figure 5a,b and the spectrum C in Figure 2a is the 1-methylvinoxy radical, $CH_2C(CH_3)O$.

Iso-C_4H_8 + O Reaction. Figure 2b gives a LIF spectrum observed when reacting oxygen atoms with isobutene. Spectra of the 1-methylvinoxy (spectrum C) and the cis/trans mixture of 2-methylvinoxy (spectrum B) radical appear strongly. Quandt et al.[16] reported recently that the LIF spectrum of the 2-methylvinoxy radical was observed in reactions of isobutene or 1-methyl-1-ethylethylene with atomic oxygen, but no unsubstituted vinoxy radical was found by LIF. The spectrum of the 2-methylvinoxy radical reported by Quandt et al. is quite similar to that of spectrum B. The very weak spectrum marked by D is thought to be the fluorescence of the 2,2-dimethylvinoxy radical formed in reaction 16c.

$$(CH_3)_2C{=}CH_2 + O \rightarrow CH_2C(CH_3)O + CH_3 \tag{16a}$$

$$\rightarrow CH_3CHCHO + CH_3 \tag{16b}$$

$$\rightarrow (CH_3)_2CCHO + H \tag{16c}$$

The reference spectrum of the 2,2-dimethylvinoxy radical will be shown in the next section.

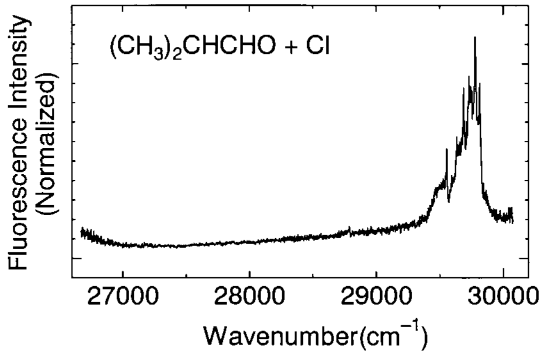


Figure 6. The LIF excitation spectrum of the 2,2-dimethylvinoxy radical, $(CH_3)_2CCHO$, produced in the isobutylaldehyde + Cl reaction at 296 ± 4 K. The pressures of isobutylaldehyde, CCl_4, and He are 1.1 mTorr, 62 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 2.3 mJ cm^{-2}. The time delay between the photolysis and the probe is 245 μs.

Since the signal of the 2-methylvinoxy radical (spectrum B in Figure 2b) is very strong, it is unlikely that this radical is formed by reaction of an impurity. Therefore, formation of the 2-methylvinoxy radical in this system appears to be another example of migration of a hydrogen atom from one carbon to the other (reaction 16b).

2-Methyl-2-butene + O Reaction. The LIF spectrum observed when reacting oxygen atoms with 2-methyl-2-butene is shown in Figure 3a. Two new spectra (D and E in Figure 3a) are observed. The fluorescing molecules are expected to be 2,2-dimethylvinoxy and the cis/trans mixture of 1,2-dimethylvinoxy radicals via reactions 17a and 17b, respectively, because methyl scissions were significant in reactions 5, 6, and 16.

$$(CH_3)_2C{=}CH(CH_3) + O \rightarrow (CH_3)_2CCHO + CH_3 \tag{17a}$$

$$\rightarrow CH_3CHC(CH_3)O + CH_3 \tag{17b}$$

$$\rightarrow (CH_3)_2CC(CH_3)O + H \tag{17c}$$

A reference LIF spectrum of the 2,2-dimethylvinoxy radical was obtained by the reaction of isobutylaldehyde with chlorine atoms and is shown in Figure 6.

$$(CH_3)_2CHCHO + Cl \rightarrow (CH_3)_2CCHO + HCl \tag{18}$$

The same spectrum was observed when reacting fluorine atoms with isobutylaldehyde. The spectrum shown in Figure 6 and the spectrum D in Figure 3a are identical, and so the fluorescing molecule should be the 2,2-dimethylvinoxy radical.

The reference spectrum of the cis/trans mixture of 1,2-dimethylvinoxy radical was measured in the photolysis of 3-chloro-2-butanone at 193 nm.

$$CH_3CHClCOCH_3 + h\nu \rightarrow CH_3CHC(CH_3)O + Cl \tag{19}$$

The spectrum measured is shown in Figure 7 and is in good agreement with the spectrum E in Figure 3a. This same spectrum was obtained when reacting chlorine atoms with 2-butanone.

$$CH_3CH_2COCH_3 + Cl \rightarrow CH_3CHC(CH_3)O + HCl \tag{20}$$

Therefore, it is concluded that spectrum E in Figure 3a should be assigned to the cis/trans mixture of the 1,2-dimethylvinoxy radical. The LIF spectrum of 1,2,2-trimethylvinoxy radical,

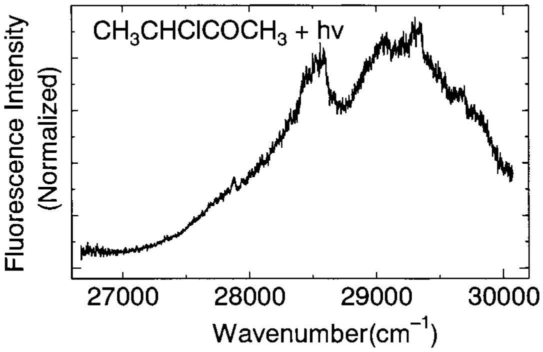


Figure 7. The LIF excitation spectrum of the cis/trans mixture of 1,2-dimethylvinoxy radical, $CH_3CHC(CH_3)O$, produced in the photolysis of 3-chloro-2-butanone (1.5 mTorr diluted in 1.5 Torr of He) at 193 nm (2.0 mJ cm^{-2}) at 296 ± 4 K. The time delay between the photolysis and the probe is 45 μs.

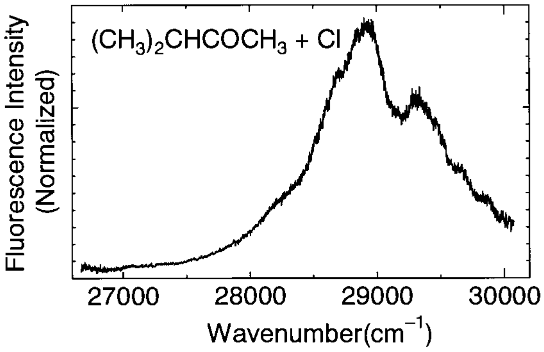


Figure 8. The LIF excitation spectrum of the 1,2,2-trimethylvinoxy radical, $(CH_3)_2CC(CH_3)O$, produced in the 3-methyl-2-butanone + Cl reaction at 296 ± 4 K. The pressures of 3-methyl-2-butanone, CCl_4, and He are 2.3 mTorr, 54 mTorr, and 1.5 Torr, respectively. The laser fluence (193 nm) is 1.9 mJ cm^{-1}. The time delay between the photolysis and the probe is 540 μs.

which might be formed in reaction 17c, could not be observed (see the reference spectrum shown in the next section).

2,3-Dimethyl-2-butene + O Reaction. Figure 3b shows a new LIF spectrum observed when reacting oxygen atoms with 2,3-dimethyl-2-butene. The only radical expected is the 1,2,2-trimethylvinoxy radical, produced by methyl scission.

$$(CH_3)_2C{=}C(CH_3)_2 + O \rightarrow (CH_3)_2CC(CH_3)O + CH_3 \quad (21)$$

A reference spectrum of the 1,2,2-trimethylvinoxy radical was measured when reacting chlorine atoms with 3-methyl-2-butanone (methyl isopropyl ketone), as shown in Figure 8.

$$(CH_3)_2CHCOCH_3 + Cl \rightarrow (CH_3)_2CC(CH_3)O + HCl \quad (22)$$

The spectrum in Figure 3b (spectrum F) and that of Figure 8 seem to be identical. Therefore, it is concluded that the 1,2,2-trimethylvinoxy radical is produced by reaction 21.

Summary of LIF Spectra of Methyl Substituted Vinoxy Radicals. A summary of the spectra of methyl substituted vinoxy radicals is given in Table 1. LIF spectra of all five methyl substituted vinoxy radicals were observed in the 330−370 nm region. In the jet-cooled LIF spectra of 1-methylvinoxy and of a cis/trans mixture of 2-methylvinoxy reported by Williams, Zingher, and Weisshaar,[16] the band origins appear to be at 27 250 and 29 096 cm^{-1}, respectively. As shown in Table 1, the band heads of the 1- and 2-methylvinoxy radicals observed in the present study at 296 ± 4 K appear at 27 170 and 28 800 cm^{-1}, respectively. These red shifts may be caused by hot bands.

The $\tilde{B} \leftarrow \tilde{X}$ transition of the unsubstituted vinoxy radical[19] originate at 28 784 cm^{-1}. Comparing this to the substituted radicals shows that the band origin shifts to the red by about 1500 cm^{-1} for a methyl group in the 1-position and to the blue by about 300 cm^{-1} for a methyl in the 2-position.[16] These shifts appear in all five radicals shown in Table 1, although the exact band origins (zero−zero band position) are obscured by hot bands.[20] Further, as shown in Figures 4−8, the band shapes of the LIF spectra of three radicals having a methyl group at the 1-position (1-methylvinoxy, 1,2-dimethylvinoxy, and 1,2,2-trimethylrinoxy) seem to be broader than the two radicals having only one methyl group at the 2-position. It has been reported[21] that the structure of ground state vinoxy is closer to the $^{\bullet}CH_2{-}CHO$ carbonyl structure than to the oxy radical structure $CH_2{=}CHO^{\bullet}$. We expect that the vinoxy radical having a methyl group at the 1-position would be closer to the oxy radical (or diradical) structure than the unsubstituted vinoxy radical because the methyl group is an electron-donating substituent. This speculation is consistent with the observations of the CH_2CFO radical reported previously.[8] Since the fluorine is an electron-withdrawing substituent, the C−C−O skeleton of the CH_2CFO radical shows a tight carbonyl structure ($^{\bullet}CH_2CFO$). Further jet-cooled spectroscopic and theoretical studies are desired in order to clarify the spectroscopic charactristics of the substituted vinoxy radicals.

Williams, Zingher, and Weisshaar[17] measured the fluorescence lifetimes of the $\tilde{B}$ state of the 1- and 2-methylvinoxy radicals. The fluorescence lifetimes were 131−26 and 191−75 ns, depending on the vibrational mode. These fluorescence lifetimes are close to those of the unsubstituted vinoxy radical (154−98 ns).[22] This suggests that the fluorescence efficiencies (or detection sensitivities by LIF) of these three radicals are similar. Measurements of the fluorescence lifetimes of the other three methyl substituted radicals are in progress in this laboratory.

Summary of O + Olefin Reactions. The present findings concerning the reaction mechanisms forming methyl substituted vinoxy radicals in olefin + O reactions are summarized in Table 2.

It is known[23−27] that interaction of a ground state oxygen atom, $O(^3P)$, with an olefin may in principle lead to any of the following three types of chemical change: (1) “abstraction” by the O atom of a H atom from the olefin, (2) “addition” of the O atom to the olefin, and (3) “replacement” by the O atom of a hydrogen atom or radical (CH_3 in this study) from the olefin. ”Replacement” itself is initially an addition, combined with subsequent or simultaneous fragmentation of the resulting adduct.

Quandt et al.[16] studied the OH product of the abstraction reaction of $O(^3P)$ atom with 10 alkenes by LIF under single-collision conditions. They reported that $O(^3P)$ atoms do not abstract vinylic C−H bonds because they are stronger than O−H bonds. Also, of all the C−H bonds in an alkyl chain attached to a C atom of a double bond, only the allylic C−H bonds appear to be attacked.

The addition reaction has been suggested[15,16] to proceed as follows: The O atom attaches itself to the less substituted carbon atom forming a triplet biradical (ketocarbene). There is a barrier to the release of a H atom, and the rate of release must compete with the rate of intersystem crossing. In the O + C_2H_4 reaction, the vinoxy radical is thought to be produced by this direct release of a H atom, reaction 1, because the yield of vinoxy radicals is pressure independent.[2,4] If a H atom is not released, intersystem

TABLE 1: Summary of Laser-Induced Fluorescence of Methyl Substituted Vinoxy Radicals

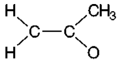
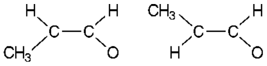
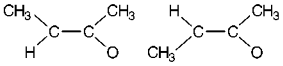
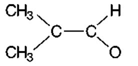
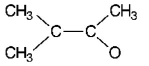
radical	observed range (cm^{-1}) at 298 K (band profile)	radical source ($h\nu$ = 193 nm)
 (1-methylvinoxy)	27170−30200 (relatively broad)	$ClCH_2COCH_3 + h\nu$ $CH_3COCH_3 + h\nu$ $CH_3COCH_2COCH_3 + h\nu$ $CH_2{=}C(CH_3)OCH_3 + h\nu$ $CH_3COCH_3 + Cl$ $CH_3COCH_3 + F$
 (2-methylvinoxy (cis/trans))	28800−30300 (sharp)	$CH_3CH{=}CHOC_2H_5 + h\nu$ $CH_3CH_2CHO + Cl$
 (1,2-dimethylvinoxy (cis/trans))	27300−30200 (broad)	$CH_3CHClCOCH_3 + h\nu$ $CH_3CH_2COCH_3 + Cl$
 (2,2-dimethylvinoxy)	29400−29900 (sharp)	$(CH_3)_2CHCHO + Cl$
 (1,2,2-trimethylvinoxy)	27500−30300 (broad)	$(CH_3)_2CHCOCH_3 + Cl$

TABLE 2: Methyl Substituted Vinoxy Radicals Formed in O + Olefin Reactions[a]

	methyl substituted vinoxy radicals		
olefin + O reaction	observed as major route	observed as minor route	not observed
$(CH_3)HC{=}CH_2 + O$ (propene)	$\underline{CH_2CHO} + CH_3$ (5a)	$\underline{CH_3CHCHO} + H$ (5c)	$\underline{CH_2C(CH_3)O} + H$ (5b)
$(CH_3)HC{=}CH(CH_3) + O$ (*cis*- and *trans*-2-butene)	$\underline{CH_3CHCHO} + CH_3$ (6a) $\underline{CH_2C(CH_3)O} + CH_3$ (6b)		$\underline{CH_3CHC(CH_3)O} + H$ (6c)
$(CH_3)_2C{=}CH_2 + O$ (isobutene)	$\underline{CH_2C(CH_3)O} + CH_3$ (16a) $\underline{CH_3CHCHO} + CH_3$ (16b)	$\underline{(CH_3)_2CCHO} + H$ (16c)	
$(CH_3)_2C{=}CH(CH_3) + O$ (2-methyl-2-butene)	$\underline{(CH_3)_2CCHO} + CH_3$ (17a) $\underline{CH_3CHC(CH_3)O} + CH_3$ (17b)		$\underline{(CH_3)_2CC(CH_3)O} + H$ (17c)
$(CH_3)_2C{=}C(CH_3)_2 + O$ (2,3-dimethyl-2-butene)	$\underline{(CH_3)_2CC(CH_3)O} + CH_3$ (21)		

[a] The number in parentheses indicates the number of the reaction in the text.

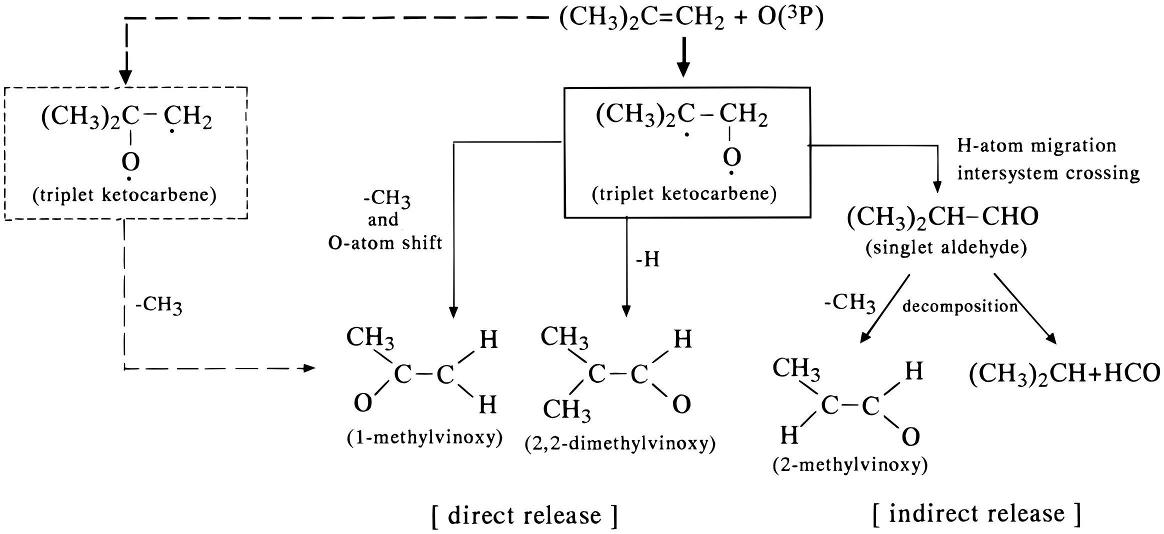


Figure 9. Reaction scheme for the O + isobutene reaction. See the text and ref 28.

crossing occurs and a H atom migrates to the adjacent C atom, forming an energized singlet state aldehyde, R′RCH−CH=O. The aldehyde dissociates unimolecularly forming the pair of radicals R′• and the substituted vinoxy RCH=CH−O• or the pair R′RCH and HCO. In the case of the O + C_3H_6 reaction, the formation of the vinoxy radical is explained by this unimolecular decomposition of the energized aldehyde because at least some part of the vinoxy production fraction is pressure dependent (the fraction seems to increase with the decrease in pressure).[2,15] The fractions of vinoxy production in the $C_2H_4 + O$[2,4] and $C_3H_6 + O$[2,15] reactions have been reported to be 0.4 and 0.5−0.2 (pressure dependent), respectively.

In the present study, several new methyl substituted vinoxy radicals were found in reactions of O + alkenes, although the absolute yields of these radicals were not determined. The radicals presented in Table 2 satisfy the following generalizations about the reaction pathways after addition of the O atom to the less substituted carbon atom.

(1) The direct release of a methyl radical is evident after forming a triplet ketocarbene. The formation of 2-methylvinoxy in reaction 6a, 1-methylvinoxy in reaction 16a, 2,2-dimethylvinoxy in reaction 17a, and 1,2,2-trimethylvinoxy in reaction 21 can be explained by the direct release of a methyl radical. These processes were judged to be major observable routes, based on LIF intensities. This is expected because a C−CH_3 bond has a slightly smaller bond energy than a C−H bond. In the case of the O + isobutene reaction (reaction 18a), an O atom shift might occur after the release of a methyl radical (see Figure 9).[28]

(2) The direct release of a hydrogen atom is significant in some reactions as minor observable routes. The 2-methylvinoxy radical in reaction 5c and 1,2-dimethylvinoxy in reaction 16c should be produced by the direct release of a H atom. However, formation of 1,2-dimethylvinoxy in reaction 6c or 1,2,2-trimethylvinoxy in reaction 17c could not be found. These results are in good agreement with the results of the H atom formation yields studied under single-collision conditions by Quandt et al.[16] They observed the H atom product in reactions of ethylene, propene, 1-butene, and isobutene with O(^3P), but they did not observe H in the *cis*-2-butene or trimethylethylene systems. They proposed that no H atoms are formed if both carbon atoms are alkyl substituted; at least one unsubstituted carbon atom, i.e., a CH_2 group, is necessary to produce H atoms because a C−C bond has a smaller bond energy than a C−H bond and the H atoms can only be released from vinylic H atoms.

(3) Formation of vinoxy-type radicals by the decomposition of the energized aldehydes or ketones following a hydrogen atom migration are evident. The vinoxy radical formed in reaction 5a, 1-methylvinoxy in reaction 6b, 2-methylvinoxy in reaction 16b, and 1,2-dimethylvinoxy in reaction 17b should be produced through a methyl radical release from the energized methyl substituted aldehydes or ketones formed by a 1,2-shift of a hydrogen atom. In the unimolecular decomposition, the methyl radical should be preferentially expelled rather than a hydrogen atom because a C−C bond has a smaller bond energy than a C−H bond. The reaction scheme for the reaction of O(^3P) with isobutene is shown in Figure 9.

All of the reaction processes listed in Table 2 can be fit into the above three generalizations. Determination of the absolute branching ratios for each process (including possible pressure dependencies) awaits future studies.

Conclusions

(1) New LIF spectra were observed in the 330−370 nm region when reacting oxygen atoms with olefins such as propene, *cis*- and *trans*-2-butene, isobutene, 2-methyl-2-butene, or 2,3-dimethyl-2-butene.

(2) These spectra were assigned to the five expected methyl substituted vinoxy radicals: 1-methylvinoxy, 2-methylvinoxy, 1,2-dimethylvinoxy, 2,2-dimethylvinoxy, and 1,2,2-trimethylvinoxy radicals. Identification of these spectra were supported by using several sources of each radical, including photolysis or chlorine or fluorine atom reactions with ketones, aldehydes, or ethers.

(3) Formation of these radicals from the initial triplet carbene adduct were explained by the following three mechanisms: (1) the direct release of a methyl group, (2) the direct release of a hydrogen atom, and (3) formation of an energized singlet aldehyde or ketone by a 1,2-migration of a hydrogen atom, followed by decomposition.

Acknowledgment. The authors thank Professor Kyle D. Bayes for his helpful suggestions and comments. We thank Professor J. C. Weisshaar for sending the manuscript of 1- and 2-methylvinoxy work before publication. The support from the Project of the Global Environment Research Program for FY 1996−1998 of Japan Environment Agency is gratefully acknowledged.

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(20) As shown in Table 1, the shifts of band origins of the substituted vinoxy radicals from 28 784 cm^{-1} depend on the position (1- or 2-position) and number of methyl substituents. When two hydrogen atoms at the 2-position carbon are substituted with two methyl groups, the band origin shifts more to the blue than with one methyl substitution. If hydrogens at both the 1- and 2-position carbons are substituted, the red shift caused by the 1-position substitution is reduced due to the blue shift by the 2-position methyl substitution. Probably the value of the shift is additive, depending upon the position and number of methyl group. However, more quantitative results will require the real band origins without the disturbance of hot bands.

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(28) The mechanism shown in Figure 9 is caused by the assumption that the O atom attaches itself to the less substituted carbon atom. However, if initial addition of O to a more substituted carbon occurs, 1-methylvinoxy radicals can be produced by direct release of CH_3 without an O atom shift. At this stage, we have not enough reason to neglect the latter mechanism (see broken lines in Figure 9).