

Photochemical Removal of C₂H₄ in N₂ or Air by Using a 172 nm Xe₂ Excimer Lamp at Atmospheric Pressure

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The photochemical removal of ethylene was investigated in N₂ or air using a head-on or side-on type of 172 nm vacuum ultraviolet (VUV) Xe₂ excimer lamp at atmospheric pressure. C₂H₄ was selectively converted to 1-butene via photo-dimerization reaction in N₂, whereas C₂H₄ was finally oxidized to CO₂ via HCHO, HCOOH, and CO intermediates in air. When the head-on lamp was replaced with the side-on one with a larger irradiation area, the removal rate of C₂H₄ in air was increased by a factor of 8.2. It was found that the O(³P) + C₂H₄ reaction plays a major role in the initial stage of the oxidation of C₂H₄ under 172 nm VUV irradiation in air. Major reaction pathways from C₂H₄ to 1-butene or CO₂ under 172 nm VUV photolysis in N₂ or air are discussed.

Key words: VUV photolysis, 172 nm Xe₂ excimer lamp, C₂H₄, O(³P) atoms, O₃, 1-butene, Dimerization, Oxidation, CO₂, Air, Atmospheric pressure

1. Introduction

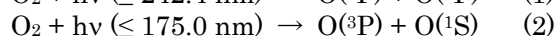
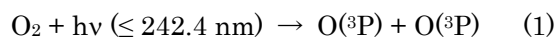
Ethylene is a plant hormone, which evolves from fruits and vegetables and accelerates ripening in stored postharvest fruits and vegetables.^{1,2)} The presence of a small amount of C₂H₄ causes premature spoilage and substantial food waste in industry. Therefore, removal of C₂H₄ during storage of fruits and vegetables is required to extend their freshness date.

Extensive studies have been conducted using effective and economically reasonable techniques for elimination of C₂H₄ from air during storage of fruits and vegetables. Conventional C₂H₄ removal techniques are air ventilation, low-temperature storage,³⁾ the use of different adsorber/absorbers,⁴⁾ the use of potassium permanganate (KMnO₄),⁵⁾ and ozone and catalytic oxidation.⁶⁾ UV and/or VUV photolysis is an emerging technique for C₂H₄ postharvest management.^{7,8)} Photolysis generally employs UV light sources, such as low-pressure and medium-pressure mercury lamps with approximately 85% output UV light at 254 nm and 15% output VUV light at 185 nm. This technique has demonstrated promising

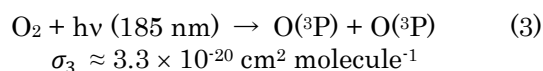
C₂H₄ removal capabilities and was successful in prolonging the shelf-life of apples and fruits.

We have recently used 172 nm VUV excimer lamps to remove such hydrocarbons and aldehydes as CH₄, C₆H₆, CH₃CHO, and C₂H₃CHO.⁹⁻¹⁴⁾ They could efficiently be decomposed and oxidized to CO₂ in air at atmospheric pressure without using any expensive noble-metal catalysts. In the present study, we attempted to use a 172 nm Xe₂ excimer lamp as a new photochemical removal method of C₂H₄ in air at atmospheric pressure.

Previous photolysis of C₂H₄ was carried out by using a mixture of 254 nm + 185 nm light in air.^{1,2,7,8)} The threshold wavelengths for the formation of O(³P) and O(¹D) from photolysis of O₂ are as follows.¹⁵⁾



On the basis of these facts, O₂ cannot be decomposed into O(³P) + O(³P) at 254 nm, whereas it can be decomposed into O(³P) + O(³P) at 185 nm with a small absorption cross section.¹⁵⁾

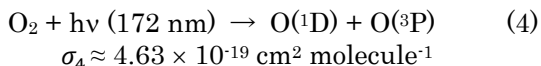


On the other hand, O₂ is selectively decomposed into O(¹D) + O(³P) at 172 nm with a larger absorption cross section.^{15,16)}

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Since absorption cross section of (4) is 14 times larger than that of (3), 172 nm light is expected to be more suitable than 185 nm one for C₂H₄ removal. In addition, the inert rare gas lamp is a more eco-friendly light source than the toxic mercury lamp. Therefore, mercury-free process is strongly desired as a practical photochemical removal technique.

The major purpose of this study is to obtain fundamental information on photochemical reactions of C₂H₄ under irradiation of 172 nm Xe₂ excimer lamps in air. Not only direct VUV photochemical reactions of C₂H₄, but also reactions of O(³P,¹D) and O₃ with C₂H₄ may contribute to the removal of C₂H₄. To examine effects of direct VUV photochemical reactions, C₂H₄ is decomposed in N₂.

Major photochemical reaction pathways of C₂H₄ in N₂ or air are discussed. All reaction rate constants and branching ratios of products used for discussion have been measured at about 300 K.¹⁷⁾

2. Experimental

VUV photolysis apparatus used in this work was the same as that reported previously.^{10,11)} Lights from an unfocused head-on type or side-on type 172 nm Xe₂ lamp were used to remove C₂H₄ at room temperature. Most experiments were conducted using the head-on lamp (input power 20 W, irradiance 50 mW/cm², UER20H172; Ushio Inc). In addition, the side-on lamp (input power 20 W, irradiance 10 mW/cm², UER20H172; Ushio Inc) was used.

Experiments were carried out in a closed batch system. The total pressure was maintained at atmospheric pressure and the C₂H₄ concentration was 500 or 714 ppm in the experiments using the head-on or side-on lamps, respectively. Sample gases before and after photoirradiation were analyzed by a HORIBA gas analysis system (FG122-LS) equipped with an FTIR spectrometer. The IR spectra were measured in the 980–4000 cm⁻¹ region with an optical resolution of 4 cm⁻¹. The concentrations of C₂H₄, HCHO, HCOOH, CO, CO₂, and O₃ were determined from peak intensities of each FTIR band. The concentrations of C₂H₄, HCHO, CO, and CO₂ were calibrated using their standard samples supplied from gas companies. The concentrations of O₃ and HCOOH were evaluated by reference to the standard spectral

data supplied by HORIBA Ltd.

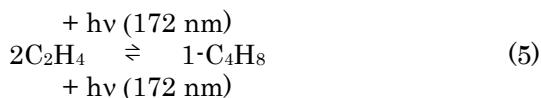
The following gases were used without further purification: N₂ (Taiyo Nissan Inc.: purity >99.9998%), O₂ (Nippon Sanso Inc.: >99.99995%), C₂H₄ (Nippon Sanso Inc.: 3000 ppm in high purity N₂). C₂H₄ was diluted in N₂ or air (20% O₂) before use.

3. Results and discussion

3.1 C₂H₄ removal in N₂

C₂H₄ removal in N₂ was attempted using a head-on lamp. N₂ has no absorption at 172 nm.¹⁵⁾ On the other hand, C₂H₄ absorbs 172 nm photons with an absorption cross section of $1.2 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$.¹⁸⁾ Therefore, photochemical removal of C₂H₄ by 172 nm VUV light may be possible in a C₂H₄/N₂ mixture. Figures 1(a)–1(d) show FTIR spectra of C₂H₄ (500 ppm) in N₂ before and after photoirradiation for 1, 3, and 5 min, respectively. Before photoirradiation, we can identify a strong C₂H₄ band in the 980–1100 cm⁻¹ region with a peak at 995 cm⁻¹ and a weak C₂H₄ band in the 2900–3200 cm⁻¹ region with a peak at 2989 cm⁻¹ (Fig. 1(a)).¹⁹⁾ After photoirradiation for 1 min, the main C₂H₄ band reduces its intensity by 28% (Fig. 1(b)). It should be noted that a weak new peak appears near 3000 cm⁻¹ region. By comparison with reported IR spectra of isomers of butenes,¹⁹⁾ it was ascribed to 1-butene band. The formation of 1-butene by VUV photolysis of C₂H₄ at 147 nm had been reported by Hara et al.²⁰⁾

Figure 2 shows the dependence of concentrations of C₂H₄ and 1-C₄H₈ on the irradiation time in the 0–10 min range. The C₂H₄ concentration decreases from 500 ppm to 200 ppm with increasing the irradiation time in the 0–5 min range, whereas the 1-C₄H₈ concentration increases from zero ppm to about 150 ppm in the same time range. Thus, photo-dimerization dominantly occurs in this time range. It should be noteworthy that the concentrations of C₂H₄ and 1-C₄H₈ are essentially independent on the irradiation time in the 5–10 min range. On the basis of above findings, forward photochemical dimerization reaction leading to 1-C₄H₈ and backward photodissociation reaction leading to C₂H₄ reactant equilibrate with each other under 172 nm photoirradiation in N₂ after 5 min irradiation.



More detailed reaction mechanism is discussed in Sec. 3.3.1.

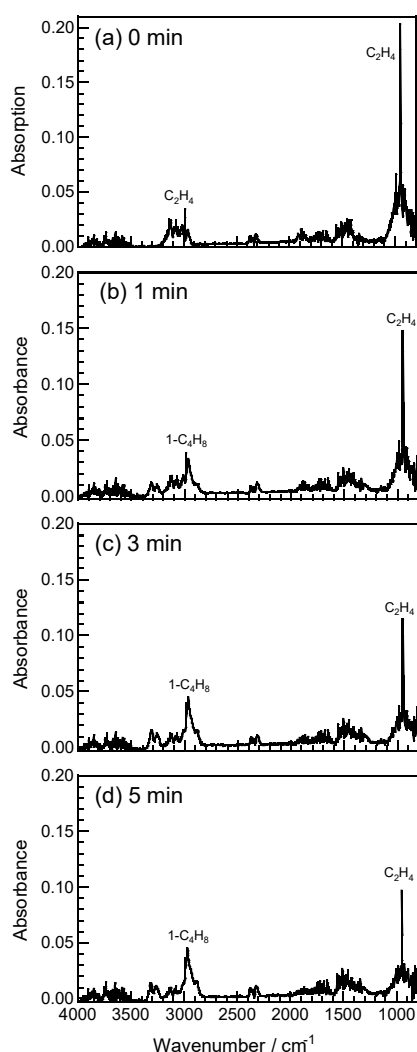


Fig. 1. (a) FTIR spectra of C_2H_4 in N_2 (a) before photoirradiation and (b)–(d) after photoirradiation for 1, 3, and 5 min, respectively. Spectra were measured using a head-on lamp.

3.2 C_2H_4 removal in air

C_2H_4 removal in air was examined using head-on and side-on lamps. Figures 3(a)–3(d) show FTIR spectra of C_2H_4 (500 ppm) in air (20% O_2) before and after photoirradiation for 1, 3, and 5 min, respectively. These spectra were measured using the head-on lamp. Before photoirradiation, strong and weak C_2H_4 bands are observed in the 980 – 1100 cm^{-1} and 2900 – 3200 cm^{-1} regions, respectively. After photoirradiation for 1 min, the C_2H_4 peak reduced its intensity by 66%, whereas new CO_2 ,

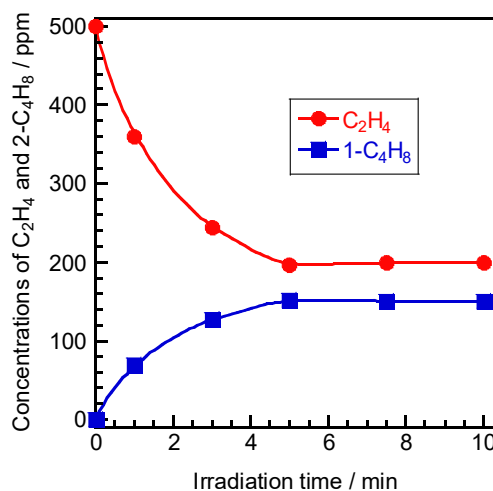


Fig. 2. Dependence of concentrations of C_2H_4 and $1-C_4H_8$ in N_2 on the irradiation time measured using a head-on lamp.

CO , $HCHO$, $HCOOH$, and O_3 bands are observed. With increasing the photoirradiation time from 1 min to 5 min, the C_2H_4 peak disappears, and the intensities of CO_2 and O_3 bands increase, whereas CO , $HCHO$, and $HCOOH$ bands decrease.

Figure 4 shows the dependence of concentrations of C_2H_4 , CO , CO_2 , $HCHO$, $HCOOH$, and O_3 on the irradiation time in the 0–10 min range. The concentration of C_2H_4 rapidly decreases from 500 ppm to 48 ppm with increasing the irradiation time until 2 min, and then slowly decreases to zero at 5 min. The concentration of CO increases to 525 ppm until 3 min, and then slowly decreases to 440 ppm in the 3–10 min range. The concentration of CO_2 increases almost linearly to 753 ppm until 10 min. The concentrations of $HCHO$ and $HCOOH$ increase to 101 and 242 ppm at 1 min, and then slowly decrease in the 1–10 min range. These time profiles suggest that CO , $HCHO$, and $HCOOH$ are slowly converted to CO_2 under the operation condition. The concentration of O_3 increases to 2.4% after 10 min.

Figures 5(a)–5(d) show FTIR spectra of C_2H_4 (714 ppm) in air before and after photoirradiation for 5, 30, and 90 s, respectively. These spectra were obtained using the side-on lamp. Before photoirradiation, C_2H_4 bands are observed in the 980 – 1100 cm^{-1} and 2900 – 3200 cm^{-1} regions. It should be noteworthy that the removal rate of C_2H_4 is strongly enhanced by using the side-on lamp. After photoirradiation for only 5 s, the C_2H_4 peak reduced its intensity by 52%, whereas new CO_2 , CO , $HCHO$,

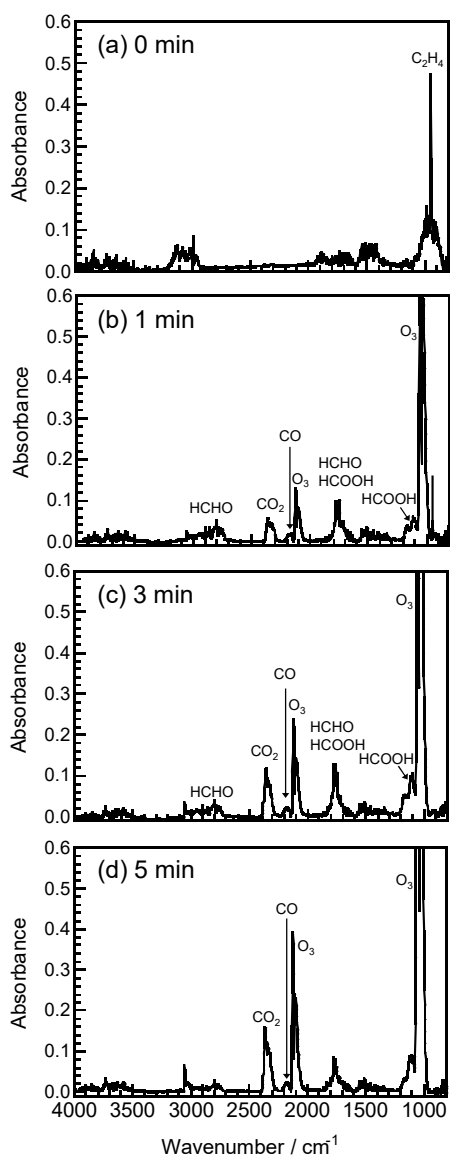


Fig. 3. (a) FTIR spectra of C₂H₄ in air (a) before photoirradiation and (b)–(d) after photoirradiation for 1, 3, and 5 min, respectively. Spectra were measured using a head-on lamp.

HCOOH, and O₃ bands appear. With increasing the photoirradiation time from 5 s to 30 s, the C₂H₄ peak disappears and the intensities of HCOOH, CO₂ and O₃ bands increase. At 90 s CO₂ and O₃ bands further increase, whereas CO, HCHO, and HCOOH bands become weak.

Figure 6(a) shows the dependence of concentrations of C₂H₄, CO, CO₂, HCHO, HCOOH, and O₃ on the irradiation time in the 0–300 s range. An expanded plot below 100 s is given in Fig. 6(b), where variations of

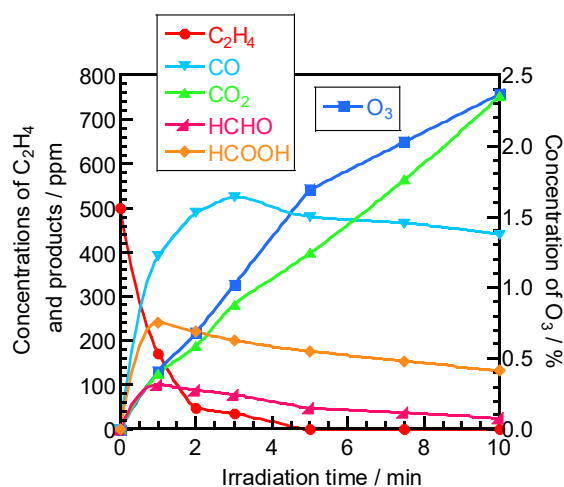


Fig. 4. Dependence of concentrations of C₂H₄, products, and O₃ in air on the irradiation time measured using a head-on lamp.

concentrations of C₂H₄ and HCHO at short times can be confirmed. It should be noted that the concentration of C₂H₄ rapidly decreases to zero after only 15 s irradiation. The concentrations of HCHO and HCOOH have peaks at 10 s and 30 s, respectively. The maximum concentration of HCOOH is 3.4 times higher than that of HCHO. The concentrations HCHO and HCOOH become zero at 45 s and 90 s, respectively. The concentrations of CO increase to 663 ppm in the 0–30 s range and then slowly decrease to zero in the 30–300 s range. The concentration of CO₂ rapidly increases to 540 ppm until 90 s and slowly increases to 628 ppm in the 90–300 s range. These time profiles of products suggest that major oxidation of C₂H₄ occur through HCHO → HCOOH → CO → CO₂. The concentration of O₃ rapidly increases to 1.7% in the 0–90 s range and then slowly increases to 1.9% in the 90–300 s range.

The initial pseudo-first-order decomposition rate of C₂H₄ by using the side-on lamp in the 0–10 s range (0.159 s⁻¹) is 8.2 times faster than that by using the head-on lamp in the 0–120 s range (0.0195 s⁻¹). The window area of the side-on lamp, from which VUV enters into the photolysis chamber, is 9.8 times wider than that of the head-on one.^{10,11} Therefore, the fraction of photoirradiation volume in the reaction chamber at 20% O₂ increases from 4.3% to 33.3% by changing excimer lamp from the head-on type to the side-on one.¹¹ This is a major reason for the significant enhancement of removal rate of C₂H₄ using the side-on lamp.

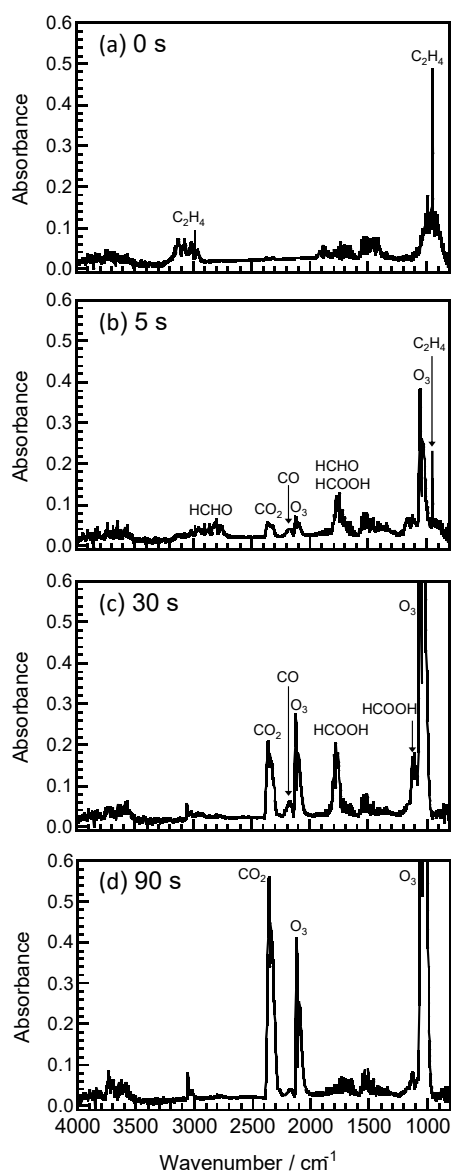


Fig. 5. (a) FTIR spectra of C₂H₄ in air (a) before photoirradiation and (b)–(d) after photoirradiation for 5, 30, and 90 s, respectively. Spectra were measured using a side-on lamp.

3.3 Possible removal mechanisms of C₂H₄ under 172 nm photolysis in N₂ or air

3.3.1 C₂H₄ Removal Mechanism in N₂

We found that 1-C₄H₈ is selectively formed by 172 nm VUV photolysis of C₂H₄ in N₂. The most probable formation and decomposition processes of 1-C₄H₈ are as follows.

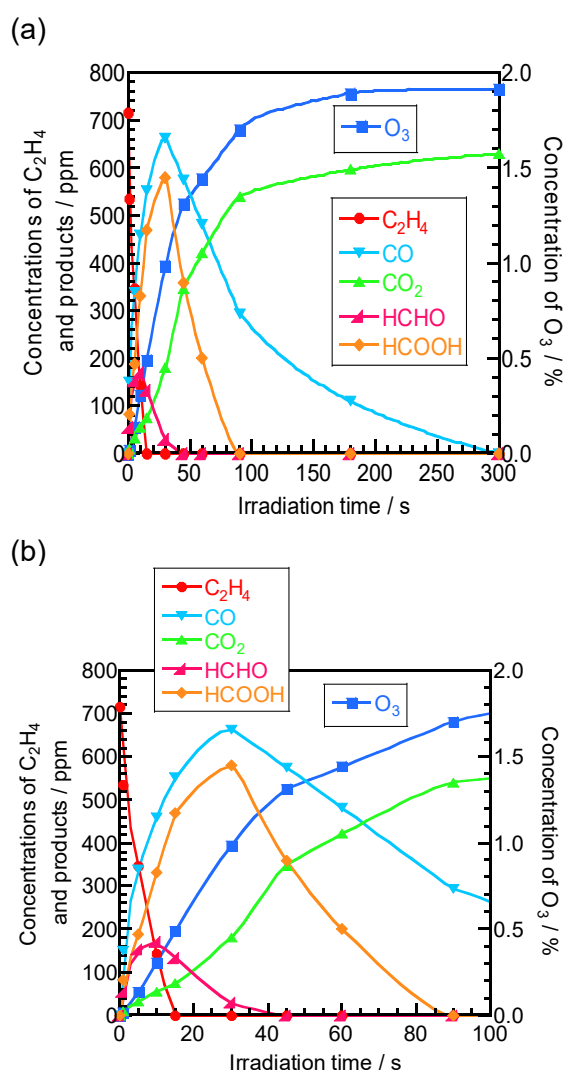
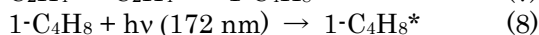
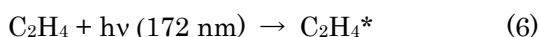


Fig. 6. Dependence of concentrations of C₂H₄, products, and O₃ in air on the irradiation time measured using a side-on lamp in the (a) 0–300 s and (b) 0–100 s ranges.

Experimental data suggest that the formation and decomposition of 1-C₄H₈ under 172 nm photoirradiation become equilibrium after 5 min irradiation. FTIR data indicated that 1-C₄H₈ is selectively formed and no 2-C₄H₈ is produced in process (7).

3.3.2 C₂H₄ Removal Mechanism of in Air

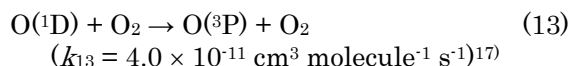
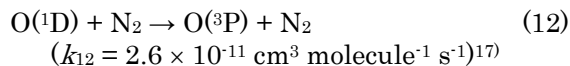
Under 172 nm photolysis of C₂H₄ (500 or 714 ppm) in an N₂/O₂ mixture (20% O₂), the absorption of the 172 nm light is absorbed by C₂H₄ and O₂. In general, the total photon energy absorbed by such a mixture as C₂H₄ and O₂ during passing through the decomposition chamber, E_{total} , was calculated from the relation:

$$E_{total} = E_0 - E_0 \exp(-l \sum_i \sigma_i N_i) \quad (10)$$

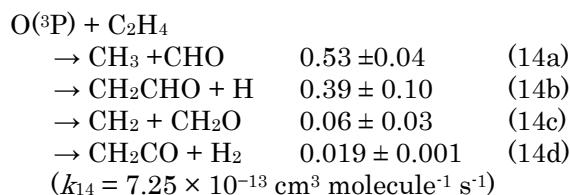
Here, E_0 , l , σ_i , and N_i are the energy of excimer lamp, the length of decomposition chamber, absorption cross section of a molecule i , and its number density, respectively. Photon energy absorbed by a molecule i , E_i , is obtained from the relation.

$$E_i = E_{total} \times \frac{\sigma_i N_i}{\sum_i \sigma_i N_i} \quad (11)$$

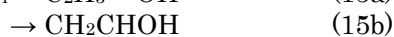
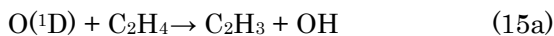
$\sigma_{C_2H_4}$ and σ_{O_2} values at 172 nm were reported to be 1.2×10^{-17} and 4.63×10^{-19} cm² molecule⁻¹, respectively.^{15,18} When we calculated $E_{C_2H_4} / (E_{C_2H_4} + E_{O_2})$ and $E_{O_2} / (E_{C_2H_4} + E_{O_2})$ values at 172 nm using these values at C₂H₄ concentrations of 500 and 714 ppm, they are 6.1 and 93.9% and 8.5 and 91.5%, respectively. These values suggest that most photons are initially absorbed by O₂, because the O₂ concentration is 400 and 280 times higher than C₂H₄ at 500 and 714 ppm, respectively. Thus, photolysis of C₂H₄ in air starts from selective photolysis of O₂ into O(¹D) + O(³P) under 172 nm photoirradiation, as shown in reaction (4). Metastable O(¹D) atoms are rapidly quenched to the ground O(³P) atoms by collisions with N₂ and O₂ atoms in air.



The rate constants and product branching ratios of the O(³P)/C₂H₄ reaction have been measured.^{17,21}



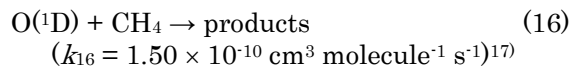
This implies that major primary products involving carbon atom are CH₃, CHO, and CH₂CHO. The rate constant and products of the O(¹D)/C₂H₄ reaction have been measured.^{17,21-25}



$$(k_{15} = 2.19 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$

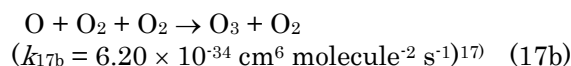
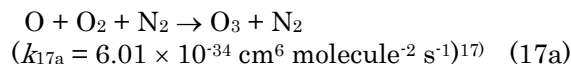
The main channels of the O(¹D)/C₂H₄ reaction are H abstraction reactions leading to C₂H₃ + OH radicals and C–H insertion channel to form highly excited vinylalcohol.^{22,23} It has also been predicted that the ethylene oxide is formed through a barrierless reaction channel (15c).²⁴ Although Miyoshi *et al.*²⁵ evaluated the branching ratio of (15a) to be 0.54±0.03, branching ratios of reactions (15b) and (15c) have not been reported. The O(¹D)/C₂H₄ reaction is faster than the O(³P)/C₂H₄ reaction by a factor of 302. However, the initial concentration of C₂H₄ (714 ppm) is much smaller than those of N₂ (80%) and O₂ (20%). When the relative contribution of the O(¹D)/C₂H₄ reaction (15) to quenching reactions (12) + (13) is evaluated using rate constants and initial concentrations, it is smaller than that of the latter ones by a factor of 184. Therefore, it is expected that the O(¹D)/C₂H₄ reaction is insignificant for the C₂H₄ removal in air under the present experimental condition.

We have recently studied CH₄ removal in air using the same apparatus and a similar initial CH₄ concentration (730 ppm) as that of C₂H₄ in this study.¹⁴ In the case of CH₄, major active species for the decomposition of CH₄ is O(¹D) with an excitation energy of 1.967 eV.¹⁵ The rate constant of the O(¹D)/CH₄ reaction is 32% smaller than that of the O(¹D)/C₂H₄ reaction.

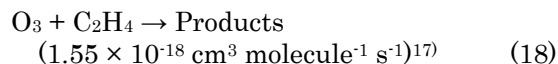


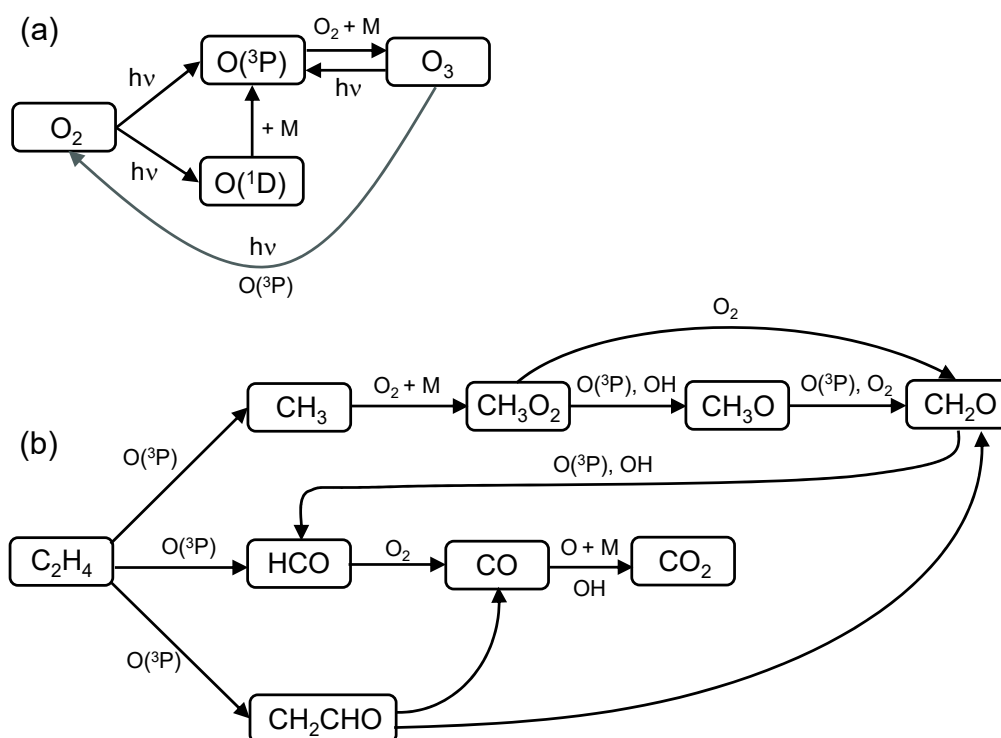
In the case of CH₄ removal by O(¹D) using the side-on lamp, it takes about 45 min for the complete removal of CH₄ in air.¹⁴ On the other hand, it takes only 15 s for the complete removal of C₂H₄. This fact also supports that major active species is not minor O(¹D) atoms but major O(³P) atoms in the case of the C₂H₄ removal in air.

O₃ molecules are formed through the following three-body recombination reactions.



It is known that the rate constant of O₃ with C₂H₄ is very small at 298 K.





Scheme 1. (a) photolysis of O_2 and O_3 under 172 nm VUV irradiation. (b) Major oxidation processes of C_2H_4 under 172 nm VUV photolysis in air. M denotes the third-body N_2 and O_2 molecules.

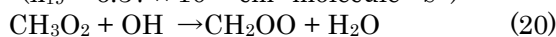
Therefore, O_3 will be unimportant active species in the C_2H_4 removal in the initial stage. As shown in Fig. 6, fast removal of C_2H_4 occurs just after irradiation of 172 nm light, where the concentration of O_3 is very low. This experimental observation supports the fact that O_3 molecules do not participate in the C_2H_4 removal in the initial stage.

Scheme 1(a) shows 172 nm photolysis of O_2 and O_3 in air. $O(^3P)$ atoms, which are dominant active species for C_2H_4 removal, are formed by photolysis of O_2 and O_3 and collisional quenching of $O(^1D)$. On the basis of known oxidation reactions of such major initial products as CH_3 , HCO , and CH_2CHO and their product branching ratios,¹⁷⁾ dominant two-body and three-body reaction pathways from these intermediates to CO and CO_2 are shown in Scheme 1(b). Although $HCHO$, $HCOOH$, and CO molecules are detected as intermediates of final product CO_2 in this study, short lived $C_xH_yO_z$ ($x \leq 2, y \leq 3, z \leq 2$) intermediates, shown in Scheme 1, will be formed as additional intermediates in oxidation processes.

Although we detected $HCOOH$ as an intermediate species, it was not shown in Scheme 1. Possible formation pathways of $HCOOH$ are as follows.



$$(k_{19} = 6.37 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$



$$(k_{20} = 1.65 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$



$$(k_{21} = 9.20 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$

Although OH radicals are not formed in the initial $O(^3P)/C_2H_4$ reaction (14), they will be formed during some secondary reactions and contribute to the formation of $HCOOH$. $O(^1D)$, OH , O_2 , and O_3 are not major active species in the decomposition of C_2H_4 in the initial stage. However, they will be important oxidants for $C_xH_yO_z$ intermediates shown in Scheme 1 and reactions (20) and (21). Although 172 nm photoabsorption and photodissociation data of $C_xH_yO_z$ intermediates shown in Scheme 1 have not been known, direct VUV photodissociation processes may also take part in the photolysis processes of these intermediates.

4. Summary and Conclusion

The photolysis of ethylene by using head-on and side-on types of 172 nm Xe_2 excimer lamps was studied in N_2 or air at atmospheric pressure. We found that C_2H_4 was selectively

converted to 1-C₄H₈ in N₂, whereas C₂H₄ was oxidized to CO₂ via HCO, HCOOH, and CO in air. In the presence of O₂, O(³P,¹D) and O₃ can be active species for the removal of C₂H₄. Results showed that O(³P) is the major active species under the 172 nm photolysis of C₂H₄ and the contributions of O(¹D) and O₃ are unimportant in the initial stage of the C₂H₄ decomposition. The removal rate of C₂H₄ by using the side-on lamp was 8.2 times faster than that using the head-on lamp because of larger irradiation volume in the reaction chamber. Photochemical removal of rate of C₂H₄ using the side-on lamp was 15 times faster than that of CH₄,¹⁴ for which minor O(¹D) atoms were the major active species. The present results demonstrate that mercury-free 172 nm Xe₂ excimer lamp is useful for C₂H₄ removal in air.

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