九州大学大学院総合理工学報告
第 46 巻 第 1 号 19-25 頁 令和 6 年 9 月

Engineering Sciences Reports, Kyushu University
Vol. 46, No. 1, pp. 19-25, SEP, 2024

Photochemical Removal of CH_4 in Air Using a 172 nm Xe_2 Excimer Lamp at Atmospheric Pressure

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(Received June 20, 2024, accepted July 17, 2024)

The photochemical removal of methane was investigated in N_2 or air using a head-on or side-on type 172 nm Xe_2 excimer lamp at atmospheric pressure. No photolysis of CH_4 was observed in N_2 because CH_4 does not absorb 172 nm photons. On the other hand, 34% of CH_4 (1000 ppm) was decomposed in air after 30 min photoirradiation using the head-on lamp. When the side-on type lamp with a larger irradiation area was used, the removal rate of CH_4 was increased by a factor of about 6. In the 172 nm photolysis of CH_4 in air, not only the $O(^3P,^1D) + CH_4$ reactions but also the $O_3 + CH_4$ reaction can take part in the initial oxidation of CH_4. The contribution of $O(^1D)$ was examined by reducing the total pressure to suppress the collisional quenching of $O(^1D)$ by the buffer N_2/O_2 gases. The contribution of O_3 was studied by observing the $O_3 + CH_4$ reaction. It was found that the $O(^1D) + CH_4$ reaction plays a major role in the initial stage of the oxidation of CH_4 under 172 nm VUV irradiation. Major oxidation pathways from CH_4 to CO_2 under 172 nm VUV photolysis in air are discussed.

Key words: *VUV photolysis, 172 nm Xe_2 excimer lamp, CH_4, $O(^1D)$ atoms, O_3, Oxidation, Air, Atmospheric pressure*

1. Introduction

The concentration of CH_4 in the atmosphere in 2022 is 1.91 ppm, which is lower than that of CO_2 (417 ppm) by a factor of 218.[1-4] However, the global warming potential (GWP) of CH_4 is 84–87 on a 20-year scale and 27–36 on a 100-year time scale in comparison of the standard value for CO_2 (GWP = 1).[4] The much larger GWP values of CH_4 dominantly originate from its shorter lifetime than that of stable CO_2 in the atmosphere. The large GWP values of CH_4 indicate that CH_4 traps far more heat than CO_2 in the atmosphere even though its concentration is low. Actually, recent studies have shown that CH_4 contributes about 0.5 ^{o}C (or nearly half) of the observed 1.1 ^{o}C present-day warming above the pre-industrial temperature.[4] Therefore, it is highly desirable to develop a new removal technique of CH_4 without using expensive metallic catalysts.

We have recently used vacuum ultraviolet (VUV) excimer lamps to remove NO, NO_2, N_2O, SO_2, C_6H_6, CH_3CHO, and C_2H_3CHO.[5-16] They could efficiently be decomposed and oxidized in air at atmospheric pressure without using any expensive metallic catalysts. In the present study, we attempted to use a 172 nm Xe_2 excimer lamp as a new photochemical removal method of CH_4 operating at room temperature without using any catalysts. The major purpose of this study is to obtain fundamental information on photochemical decomposition of CH_4 under 172 nm VUV irradiation and the clarification of dominant active species for oxidation of CH_4. Not only direct VUV photolysis of CH_4, but also reactions of $O(^3P,^1D)$ and O_3 with CH_4 may contribute to the removal of CH_4. To examine effects of direct VUV photolysis, CH_4 was decomposed in N_2 atmosphere, whereas the contribution of $O(^1D)$ was examined by reducing the total pressure to suppress the collisional quenching of $O(^1D)$ by the buffer N_2/O_2 gas mixtures. The contribution of O_3 was studied by observing the $O_3 + CH_4$ reaction in the same apparatus. On the basis of above experiments, dominant active species for the removal of CH_4 under 172 nm photolysis are determined and major oxidation processes

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of CH_4 to CO and CO_2 are discussed. All reported reaction rate constants used for discussion[17] have been measured at 298 K.

2. Experimental

VUV photolysis apparatus used in this work was the same as that reported previously.[12,13] Lights from an unfocused head-on type or side-on type 172 nm Xe_2 lamp was used to remove CH_4 at room temperature. Most experiments were conducted using the head-on lamp (50 mW/cm^2, 155–200 nm range, UER20H172; Ushio Inc).

Experiments were carried out in a closed batch system. The total pressure was maintained at atmospheric pressure and the CH_4 concentration diluted in an N_2/O_2 mixture (20% O_2) was 1000 or 730 ppm in most experiments. It was introduced through mass flowmeters. Sample gases before and after photoirradiation were analyzed by a HORIBA gas analysis system (FG122-LS) equipped with an FTIR spectrometer and an ANELVA gas analysis system (M-200GA-DTS) equipped with a quadrupole mass spectrometer. A low-sensitivity mass spectrometer was used for the determination of the N_2/O_2 ratio of buffer gases, whereas a high-sensitivity FTIR system was used for the detection of CH_4, O_3, CO, and CO_2. The light path length and the volume of the analyzing chamber in FTIR were 2.4 m and 300 cm^3, respectively. The IR spectra were measured in the 1000–4000 cm^{-1} region with an optical resolution of 4 cm^{-1}. The concentrations of CH_4, CO, and CO_2 were calibrated using standard samples supplied from gas companies. The concentration of O_3 was evaluated by reference to the standard spectral data supplied by HORIBA.

We have also studied the O_3 + CH_4 reaction at room temperature using the same apparatus. $O(^3P,^1D)$ and O_3 were initially prepared from the 172 nm photolysis of air in the photolysis chamber. After O_3 was partly stored in the FTIR cell for gas analysis, the photolysis chamber was evacuated in vacuum. Then O_3 was introduced again to the photolysis chamber. Under such conditions, short lived $O(^3P,^1D)$ atoms disappeared and only long-lived O_3 molecules survived as an active species. After then a CH_4/N_2 mixture was introduced to the chamber, and the reactants and products of the O_3 + CH_4 reaction were monitored online using the FTIR spectrometer. The initial concentrations of CH_4, O_2, and O_3 in a CH_4/air mixture was 1000 ppm, 20%, and 1.1%, respectively, and the total pressure was 50 kPa.

The following gases were used without further purification: N_2 (Taiyo Nissan Inc.: purity >99.9998%), O_2 (Nippon Sanso Inc.: >99.99995%), CH_4 (Nippon Sanso Inc.: 3000 ppm in high purity N_2). CH_4 was diluted in N_2 or air (20% O_2) before use.

3. Results and discussion

3.1 An attempt of CH_4 removal in N_2

N_2 has no absorption at 172 nm.[18,19] Therefore, only CH_4 may absorb 172 nm photons in a CH_4/N_2 mixture. In order to examine the contribution of direct 172 nm VUV photolysis of CH_4, CH_4 removal was studied in N_2. Figure 1(a) shows an FTIR spectrum of CH_4 (1000 ppm) in N_2 before photoirradiation, where two strong CH_4 peaks are observed in the 1200–1400 and 2800–3200 cm^{-1} regions. The variation of the main CH_4 peak intensity, which is proportional to the CH_4 concentration, was monitored as a function of irradiation time

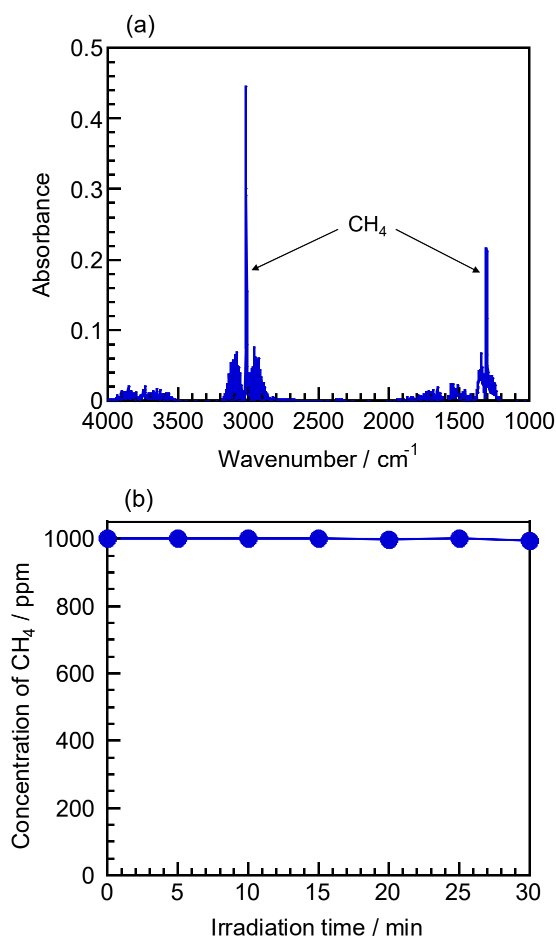


Fig. 1. (a) FTIR spectrum of CH_4 in N_2 before photoirradiation. (b) dependence of concentration of CH_4 on the irradiation time.

in the 0–30 min range. The CH_4 concentration was essentially independent on the irradiation time as shown in Fig. 1(b). This shows that CH_4 is not decomposed under 172 nm VUV photoirradiation. According to reported photoabsorption spectrum of CH_4, CH_4 has essentially no absorption (< 10^{-20} cm^2) at 172 nm.[20] Little change in the concentration of CH_4 after photoirradiation for 30 min is consistent with the absence of absorption of CH_4 at 172 nm.

3.2 CH_4 removal in air

The photolysis of CH_4 at 172 nm in air was examined in an N_2/O_2 mixture at an O_2 concentration of 20%. As an example, Figs. 2(a) and 2(b) show FTIR spectra of CH_4 (1000 ppm) before and after 30 min photoirradiation, respectively. Before photolysis, two CH_4 peaks are observed as in the case of N_2 atmosphere. After photolysis for 30 min, these CH_4 peaks decrease in intensity by 34% and new strong CO_2 and O_3 peaks and a very weak CO peak are observed. Figure 3 shows the concentrations of CH_4, CO, CO_2, and O_3 as a function of the irradiation time. The concentration of CH_4 decreases to 655 ppm almost linearly with increasing the irradiation time until 30 min. The concentration of CO increases to 57 ppm until 15 min and then slowly decreases to 46 ppm in the 15–30 min range. The concentration of CO_2 increases almost linearly to 269 ppm until 30 min. The concentration of CO_2 is higher than that of CO in all time range and the $[CO_2]/[CO]$ concentration ratio increases from 1.4 to 5.9 with increasing the irradiation time from 5 min to 30 min. These time profiles suggest that CO is slowly converted to CO_2 under the operation condition. The concentration of O_3 rapidly increases to 1.3% until 15 min irradiation and then decreases to 1.1% in the 15–30 min range.

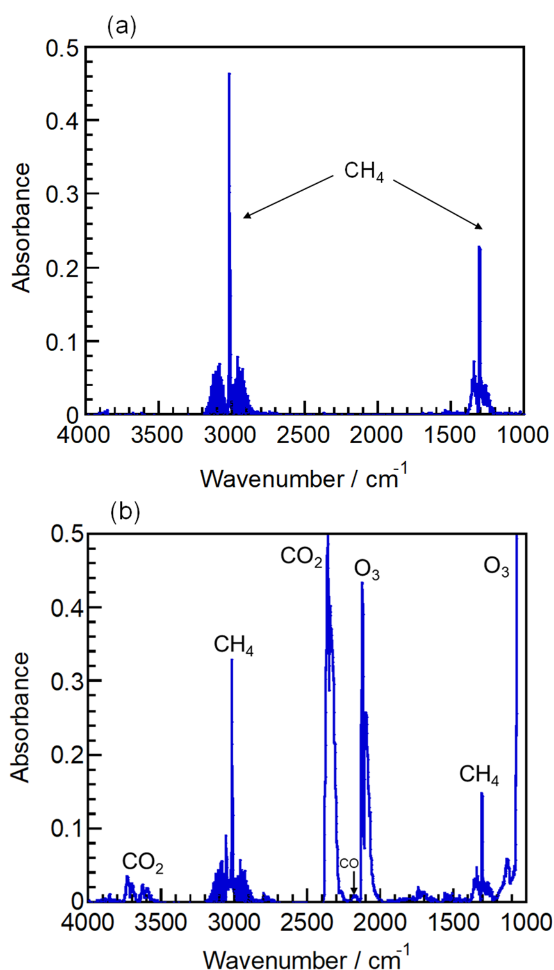


Fig. 2. (a) FTIR spectrum of CH_4 in air (a) at a total pressure of 100 kPa before and (b) after photoirradiation for 30 min.

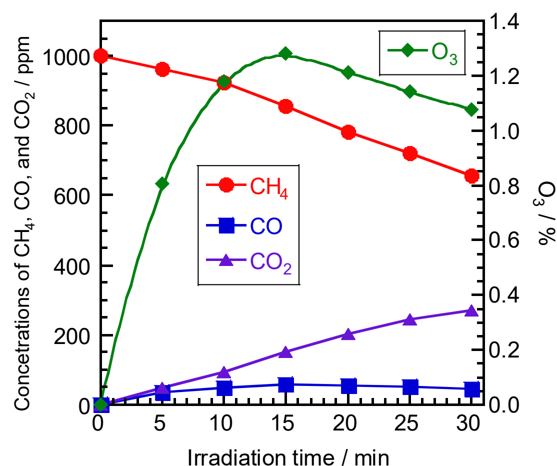


Fig. 3. Dependence of concentrations of CH_4, CO, CO_2, and O_3 on the irradiation time measured using a head-on lamp.

CH_4 (730 ppm) removal in air was also studied by using a side-on lamp. The result obtained in the 0–60 min range is shown in Fig. 4. The concentration of CH_4 linearly decreases to 89 ppm until 25 min and slowly decreases to zero at 45 min. The concentration of CO increases to 158 ppm in the 0–2 min range and then slowly decreases to zero in the 2–45 min range. The concentration of CO_2 rapidly increases to 350 ppm until 25 min and slowly increases to 402 ppm in the 25–60 min range. These time profiles of CO and CO_2 indicate that CO is converted to CO_2 during photolysis. The concentration of O_3 rapidly increases to 3.2% in

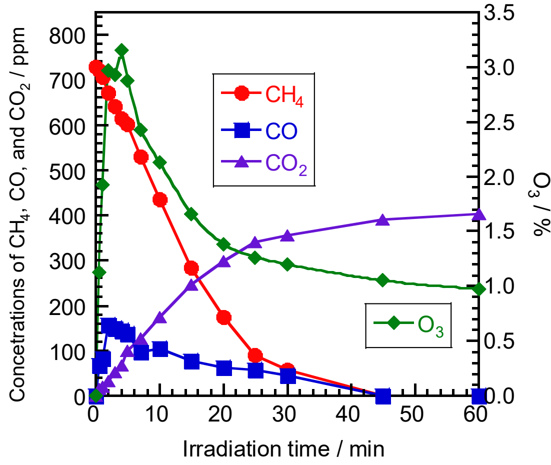
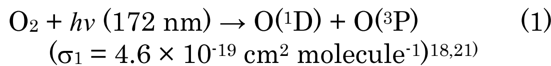


Fig. 4. Dependence of concentrations of CH_4, CO, CO_2, and O_3 on the irradiation time measured using a side-on lamp.

the 0–4 min range and decreases to 0.98% in the 4–60 min range. The decomposition rate of CH_4 by using the side-on lamp (0.077 min^{-1}) is 6.0 times faster than that by using the head-on lamp (0.0128 min^{-1}) in the 0–30 min range. 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.[12,13] Therefore, the fraction of photoirradiation volume in the reaction chamber at 20% O_2 increases from 4.3% to 33.3% by changing excimer lamp from the head-on type to the side-on one.[12] This is a major reason for the significant enhancement of removal rate of CH_4 using the side-on lamp.

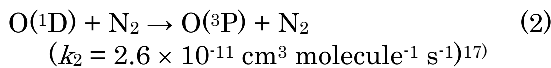
3.3 Effects of $O(^1D)$

In a $CH_4/N_2/O_2$ mixture (20% O_2), O_2 initially absorbs all of 172 nm photons and selectively dissociates into $O(^1D) + O(^3P)$, because CH_4 and N_2 have no absorption in this wavelength.

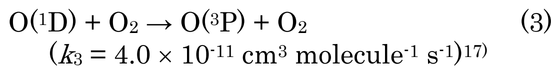


$$O_2 + h\nu \text{ (172 nm)} \rightarrow O(^1D) + O(^3P) \quad (1)$$
$$(\sigma_1 = 4.6 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1})^{18,21)}$$

It is known that $O(^1D)$ atoms are rapidly quenched to the ground $O(^3P)$ atoms by collisions with N_2 and O_2 atoms in air.

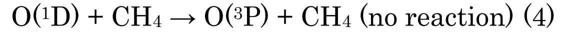


$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \quad (2)$$
$$(k_2 = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$



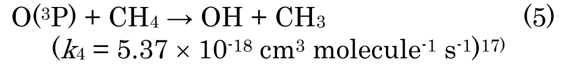
$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \quad (3)$$
$$(k_3 = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$

On the other hand, quenching reaction of $O(^1D)$ to $O(^3P)$ by CH_4 does not occur.[22,23]

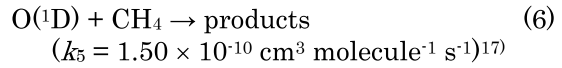


$$O(^1D) + CH_4 \rightarrow O(^3P) + CH_4 \text{ (no reaction)} \quad (4)$$

Although the reaction of $O(^3P)$ with CH_4 is extremely slow, that of $O(^1D)$ with CH_4 is fast.



$$O(^3P) + CH_4 \rightarrow OH + CH_3 \quad (5)$$
$$(k_4 = 5.37 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$



$$O(^1D) + CH_4 \rightarrow \text{products} \quad (6)$$
$$(k_5 = 1.50 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{17)}$$

Thus, the $O(^1D) + CH_4$ reaction (6) will be an important reaction for CH_4 removal. However, quenching reactions of $O(^1D)$ by N_2/O_2 gases (2) and (3) compete with the $O(^1D) + CH_4$ reaction (6). To reduce the relative contribution of reactions (2) and (3) to that of (6), we attempted to enhance the decomposition of CH_4 by decreasing the total pressure at a constant CH_4 partial pressure. For example, Figs. 5(a) and 5(b) show FTIR spectra of CH_4 in air before

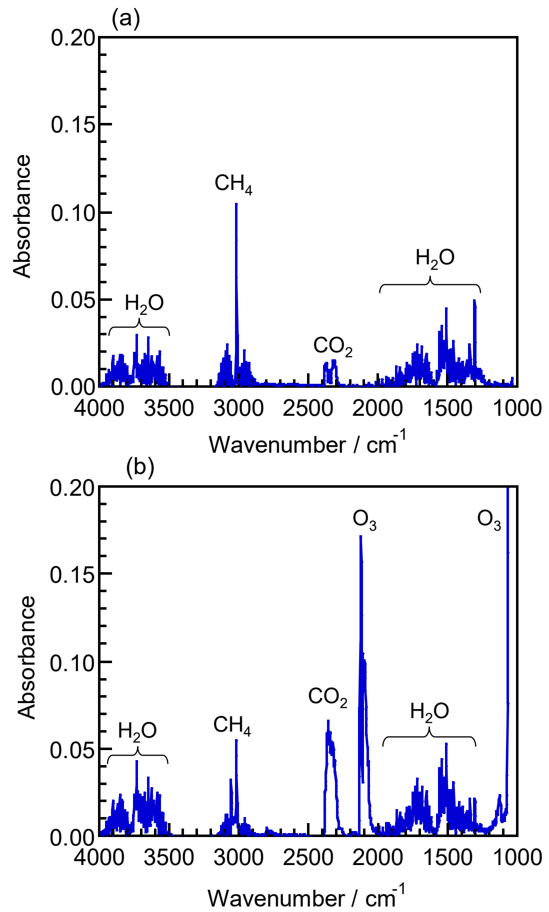


Fig. 5 (a) FTIR spectrum of CH_4 in air at a total pressure of 40 kPa (a) before photoirradiation and (b) after photoirradiation for 30 min.

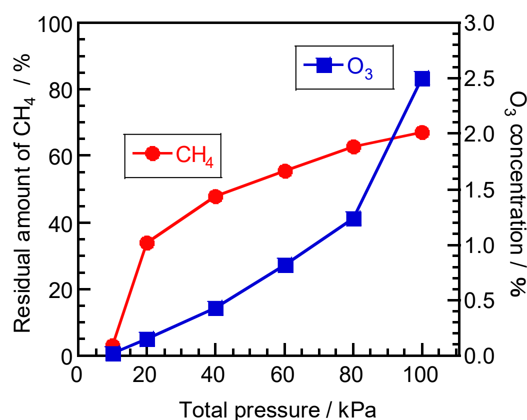
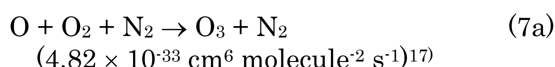


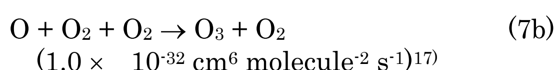
Fig. 6. Dependence of residual amount of CH_4 and O_3 concentration on the total pressure after 30 min photoirradiation.

photoirradiation and after photoirradiation for 30 min obtained by reducing the total gas pressure from 100 kPa to 40 kPa keeping the absolute amounts of CH_4 constant (150 ppm at 100 kPa). In this condition, 52% of CH_4 is decomposed after 30 min photoirradiation. This value is 53% larger than that at 100 kPa (Fig. 2). We determined the residual amount of CH_4, $[CH_4]/[CH_4]_0$, from gas analyses. Here, $[CH_4]_0$ is the initial concentration of CH_4. Figure 6 shows the dependence of the residual amount of CH_4 and the concentration of O_3 on the total pressure. It should be noted that the residual amount of CH_4 decreases from 67% to 34% with decreasing the total pressure from 100 to 20 kPa and rapidly decreases from 34% to 3% with further decreasing the total pressure from 20 kPa to 10 kPa. A significant decrease in the residual amount of CH_4 with decreasing the total pressure from 100 kPa to 10 kPa gives definite evidence that the $O(^1D)$ atoms play an important role for the removal of CH_4 in our conditions.

The concentration of O_3 decreases rapidly with decreasing the total pressure, because three-body recombination reactions (7a) and (7b) leading to O_3 are greatly suppressed with decreasing the total pressure.



$$O + O_2 + N_2 \rightarrow O_3 + N_2 \quad (7a)$$
$(4.82 \times 10^{-33}\ cm^6\ molecule^{-2}\ s^{-1})$[17]

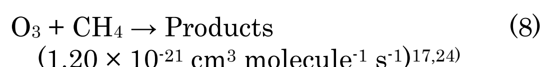


$$O + O_2 + O_2 \rightarrow O_3 + O_2 \quad (7b)$$
$(1.0 \times 10^{-32}\ cm^6\ molecule^{-2}\ s^{-1})$[17]

The removal rate of CH_4 increases with decreasing the total pressure, even though the O_3 concentration decreases rapidly. This suggests that O_3 molecules will not be major active species for CH_4 removal in air. To confirm this prediction, the $O_3 + CH_4$ reaction was actually studied in the next section.

3.4 Effects of O_3

It is known that the upper limit of the rate constant of O_3 with CH_4 is extremely small at 298 K in N_2 atmosphere.



$$O_3 + CH_4 \rightarrow Products \quad (8)$$
$(1.20 \times 10^{-21}\ cm^3\ molecule^{-1}\ s^{-1})$[17,24]

We have studied the contribution of reaction (8) by isolating O_3 in the reaction chamber. Figures 7(a) and 7(b) show FTIR spectra observed after the $O_3 + CH_4$ reaction for 1 and 180 min, respectively, where reactant peaks of CH_4 and O_3, a product peak of CO_2, and impurity peaks of H_2O are observed. Figure 8 shows the dependence of residual amount of CH_4 and the concentration of O_3 on the reaction time. The concentration of O_3 decreases from

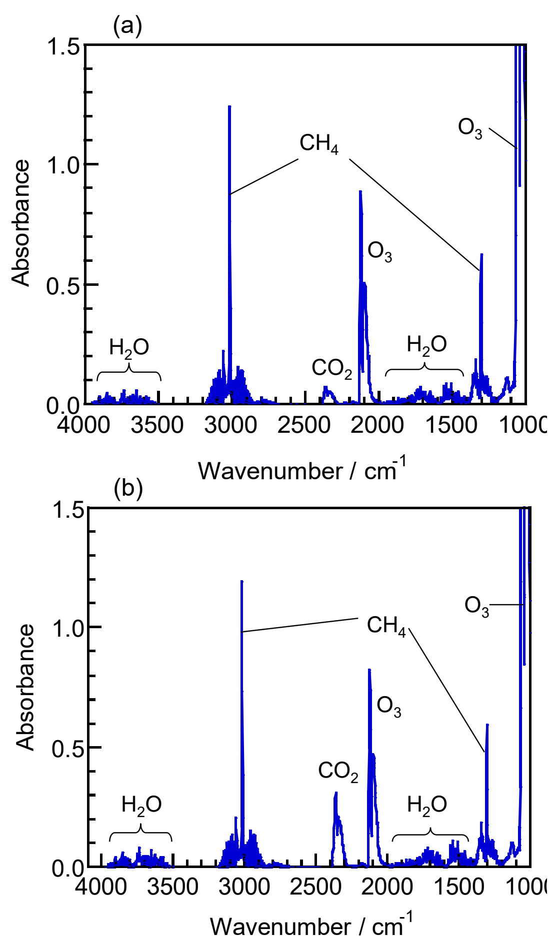


Fig. 7. (a) FTIR spectrum of CH_4 resulting from the $O_3 + CH_4$ reaction at reaction times of (a) 1 min and (b) 180 min.

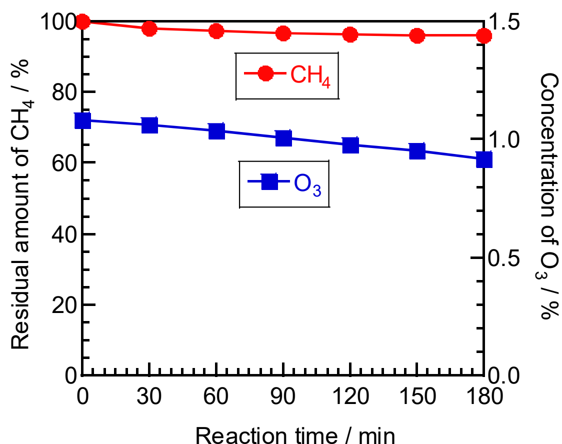


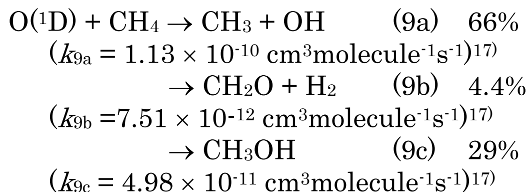
Fig. 8. Dependence of residual amount of CH_4 and concentration of O_3 in the O_3 + CH_4 reaction at thermal energy

1.08% to 0.92% with increasing the reaction time from 0 min to 180 min. The residual amount of CH_4 decreases more slowly from 100% to 96% after 180 min. Our present result implies that the rate constant of reaction (8) is very small, being consistent with the reported very small rate constant.

3.5 Possible oxidation mechanism of CH_4 under 172 nm photolysis in air

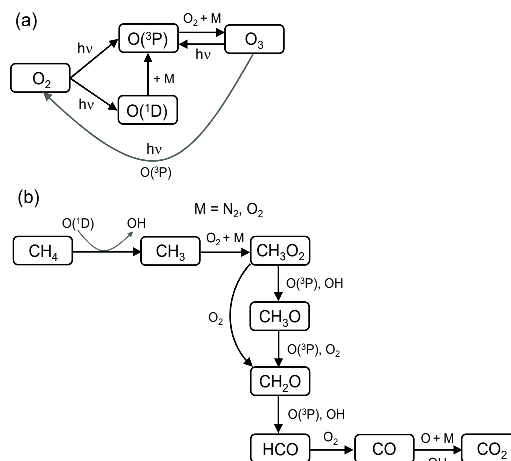
$O(^3P)$, $O(^1D)$, and O_3 are formed by 172 nm photolysis of O_2 in air as shown in Scheme 1(a). Among them, we found that the metastable $O(^1D)$ atoms with an excitation energy of 1.967 eV play a significant role for the removal of CH_4 in air under our experimental conditions. The contributions of 172 nm photons and $O(^3P)$ are negligible and that of O_3 is very small. Active $O(^1D)$ atoms arise exclusively from the direct 172 nm photolysis of O_2 (1) in the initial stage.

The rate constants of the $O(^1D)$ + CH_4 reaction leading to CH_3, CH_2O, and CH_3O have been measured as.



$$O(^1D) + CH_4 \rightarrow CH_3 + OH \quad (9a) \quad 66\%$$
$$(k_{9a} = 1.13 \times 10^{-10}\ cm^3 molecule^{-1} s^{-1})^{17)}$$
$$\rightarrow CH_2O + H_2 \quad (9b) \quad 4.4\%$$
$$(k_{9b} = 7.51 \times 10^{-12}\ cm^3 molecule^{-1} s^{-1})^{17)}$$
$$\rightarrow CH_3OH \quad (9c) \quad 29\%$$
$$(k_{9c} = 4.98 \times 10^{-11}\ cm^3 molecule^{-1} s^{-1})^{17)}$$

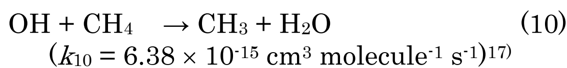
The branching fractions of the above three product channels indicate that major initial products are CH_3 + OH. On the basis of known oxidation reactions of CH_3 and their rate constants,[17,25] major two-body and three-body reaction pathways from CH_3 to CO and CO_2 are



Scheme 1. (a) photolysis of O_2 and O_3 under 172 nm VUV irradiation in air. (b) major oxidation processes of CH_4 under 172 nm VUV photolysis in air.

shown in Scheme. 1(b). Although only CO molecules are detected as an intermediate of the final product CO_2 in this study, short lived CH_3O_2, CH_3O, CH_2O, and HCO will be formed as intermediates.

OH radicals formed in process (9a) can react with CH_4, and CH_3 + H_2O are formed.



$$OH + CH_4 \rightarrow CH_3 + H_2O \quad (10)$$
$$(k_{10} = 6.38 \times 10^{-15}\ cm^3\ molecule^{-1}\ s^{-1})^{17)}$$

Since the rate constant of the OH + CH_4 reaction (10) is much smaller than that of the $O(^1D)$ + CH_4 reaction (6), its contribution to initial decomposition of CH_4 to CH_3 will be small. As shown in Scheme 1(b), OH radicals can take part in the oxidation of some intermediate species. Therefore, they may take part in the oxidation of some intermediates. $O(^3P)$ atoms and O_2 molecules do not participate in the initial decomposition of CH_4. However, they can contribute to the oxidation of such intermediates as CH_3, CH_3O_2, CH_3O, CH_2O, HCO, and CO as shown in Scheme 1(b). Present experimental data and reported kinetic data[17] suggest that O_3 molecules are less important than $O(^3P)$ and O_2 in the oxidation of CH_4 under 172 nm photoirradiation. Although 172 nm photoabsorption and photodissociation data of CH_3, CH_2O_2, CH_3O, CH_2O, and HCO intermediates have not been known, direct photodissociation processes may also take part in the oxidation processes of above intermediates shown in Scheme 1(b).

4. Summary and Conclusion

The photolysis of methane by using 172 nm Xe_2 excimer lamps was studied to develop a new simple photochemical removal method of CH_4 without using any expensive catalysts at room temperature. No photolysis of CH_4 was observed in N_2, whereas CH_4 was oxidized to CO and CO_2 in air. In the presence of O_2, $O(^3P,^1D)$ and O_3 can be active species for the removal of CH_4. Effects of $O(^1D)$ were examined by increasing the $[O(^1D)]/[O(^3P)]$ ratio at low total pressures. The contribution of O_3 was determined by observing CH_4 removal by the $O_3 + CH_4$ reaction using the same apparatus. Results showed that $O(^1D)$ is the responsible active species under the 172 nm photolysis of CH_4 and the contributions of $O(^3P)$ and O_3 are unimportant in the initial stage of the CH_4 decomposition. The removal rate of CH_4 by using the side-on lamp was about 6 times faster than that using the head-on lamp because of larger irradiation volume in the reaction chamber. Photochemical removal of CH_4 is more difficult than that of C_6H_6, CH_3CHO, and C_2H_3CHO,[12,13,16] because its oxidation by the $O(^3P) + CH_4$ and $O_3 + CH_4$ reactions are very slow and no direct photolysis of CH_4 occurs by 172 nm photons. These fundamental data provide valuable information for the design of practical removal apparatus CH_4 under VUV photolysis in air.

Acknowledgments

This work was supported by NEDO (2008–2009), and City Area Project from Fukuoka Prefecture (2009).

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