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Photochemical Removal of CH₄ in Air Using a 172 nm Xe₂ Excimer Lamp at Atmospheric Pressure

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The photochemical removal of methane was investigated in N₂ or air using a head-on or side-on type 172 nm Xe₂ excimer lamp at atmospheric pressure. No photolysis of CH₄ was observed in N₂ because CH₄ does not absorb 172 nm photons. On the other hand, 34% of CH₄ (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 CH₄ was increased by a factor of about 6. In the 172 nm photolysis of CH₄ in air, not only the O(³P,¹D) + CH₄ reactions but also the O₃ + CH₄ reaction can take part in the initial oxidation of CH₄. The contribution of O(¹D) was examined by reducing the total pressure to suppress the collisional quenching of O(¹D) by the buffer N₂/O₂ gases. The contribution of O₃ was studied by observing the O₃ + CH₄ reaction. It was found that the O(¹D) + CH₄ reaction plays a major role in the initial stage of the oxidation of CH₄ under 172 nm VUV irradiation. Major oxidation pathways from CH₄ to CO₂ under 172 nm VUV photolysis in air are discussed.

Key words: VUV photolysis, 172 nm Xe₂ excimer lamp, CH₄, O(¹D) atoms, O₃, Oxidation, Air, Atmospheric pressure

1. Introduction

The concentration of CH₄ in the atmosphere in 2022 is 1.91 ppm, which is lower than that of CO₂ (417 ppm) by a factor of 218.¹⁻⁴⁾ However, the global warming potential (GWP) of CH₄ is 84–87 on a 20-year scale and 27–36 on a 100-year time scale in comparison of the standard value for CO₂ (GWP = 1).⁴⁾ The much larger GWP values of CH₄ dominantly originate from its shorter lifetime than that of stable CO₂ in the atmosphere. The large GWP values of CH₄ indicate that CH₄ traps far more heat than CO₂ in the atmosphere even though its concentration is low. Actually, recent studies have shown that CH₄ contributes about 0.5 °C (or nearly half) of the observed 1.1 °C present-day warming above the pre-industrial temperature.⁴⁾ Therefore, it is highly desirable to develop a new removal technique of CH₄ without using expensive metallic catalysts.

We have recently used vacuum ultraviolet (VUV) excimer lamps to remove NO, NO₂, N₂O, SO₂, C₆H₆, CH₃CHO, and C₂H₃CHO.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 Xe₂ excimer lamp as a new photochemical removal method of CH₄ operating at room temperature without using any catalysts. The major purpose of this study is to obtain fundamental information on photochemical decomposition of CH₄ under 172 nm VUV irradiation and the clarification of dominant active species for oxidation of CH₄. Not only direct VUV photolysis of CH₄, but also reactions of O(³P,¹D) and O₃ with CH₄ may contribute to the removal of CH₄. To examine effects of direct VUV photolysis, CH₄ was decomposed in N₂ 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 N₂/O₂ gas mixtures. The contribution of O₃ was studied by observing the O₃ + CH₄ reaction in the same apparatus. On the basis of above experiments, dominant active species for the removal of CH₄ under 172 nm photolysis are determined and major oxidation processes

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of CH₄ to CO and CO₂ are discussed. All reported reaction rate constants used for discussion¹⁷⁾ 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 Xe₂ lamp was used to remove CH₄ at room temperature. Most experiments were conducted using the head-on lamp (50 mW/cm², 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 CH₄ concentration diluted in an N₂/O₂ mixture (20% O₂) 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 N₂/O₂ ratio of buffer gases, whereas a high-sensitivity FTIR system was used for the detection of CH₄, O₃, CO, and CO₂. The light path length and the volume of the analyzing chamber in FTIR were 2.4 m and 300 cm³, respectively. The IR spectra were measured in the 1000–4000 cm⁻¹ region with an optical resolution of 4 cm⁻¹. The concentrations of CH₄, CO, and CO₂ were calibrated using standard samples supplied from gas companies. The concentration of O₃ was evaluated by reference to the standard spectral data supplied by HORIBA.

We have also studied the O₃ + CH₄ reaction at room temperature using the same apparatus. O(³P,¹D) and O₃ were initially prepared from the 172 nm photolysis of air in the photolysis chamber. After O₃ was partly stored in the FTIR cell for gas analysis, the photolysis chamber was evacuated in vacuum. Then O₃ was introduced again to the photolysis chamber. Under such conditions, short lived O(³P,¹D) atoms disappeared and only long-lived O₃ molecules survived as an active species. After then a CH₄/N₂ mixture was introduced to the chamber, and the reactants and products of the O₃ + CH₄ reaction were monitored online using the FTIR spectrometer. The initial concentrations of CH₄, O₂, and O₃ in a CH₄/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: N₂ (Taiyo Nissan Inc.: purity >99.9998%), O₂ (Nippon Sanso Inc.: >99.99995%), CH₄ (Nippon Sanso Inc.: 3000 ppm in high purity N₂). CH₄ was diluted in N₂ or air (20% O₂) before use.

3. Results and discussion

3.1 An attempt of CH₄ removal in N₂

N₂ has no absorption at 172 nm.^{18,19)} Therefore, only CH₄ may absorb 172 nm photons in a CH₄/N₂ mixture. In order to examine the contribution of direct 172 nm VUV photolysis of CH₄, CH₄ removal was studied in N₂. Figure 1(a) shows an FTIR spectrum of CH₄ (1000 ppm) in N₂ before photoirradiation, where two strong CH₄ peaks are observed in the 1200–1400 and 2800–3200 cm⁻¹ regions. The variation of the main CH₄ peak intensity, which is proportional to the CH₄ concentration, was monitored as a function of irradiation time

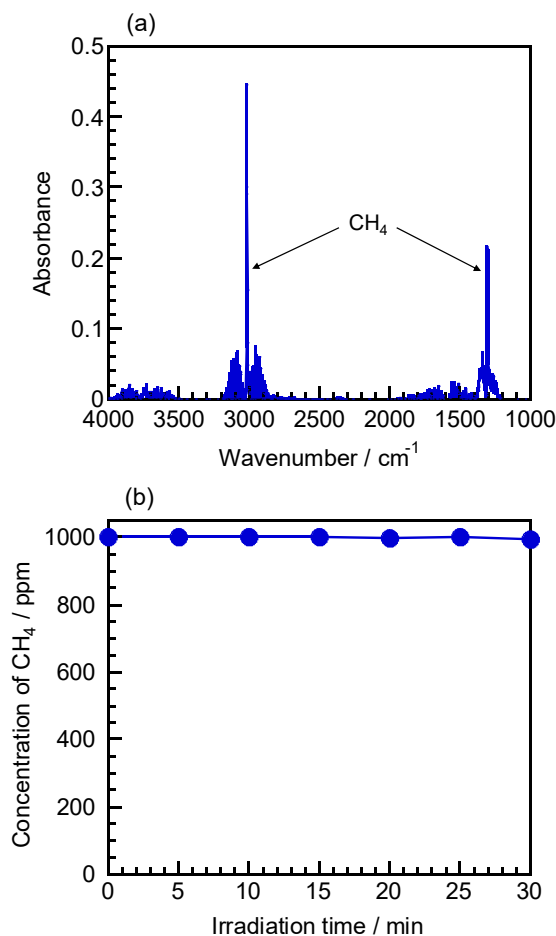


Fig. 1. (a) FTIR spectrum of CH₄ in N₂ before photoirradiation. (b) dependence of concentration of CH₄ on the irradiation time.

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 ($< 10^{-20} \text{ cm}^2$) 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 $[\text{CO}_2]/[\text{CO}]$ 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.

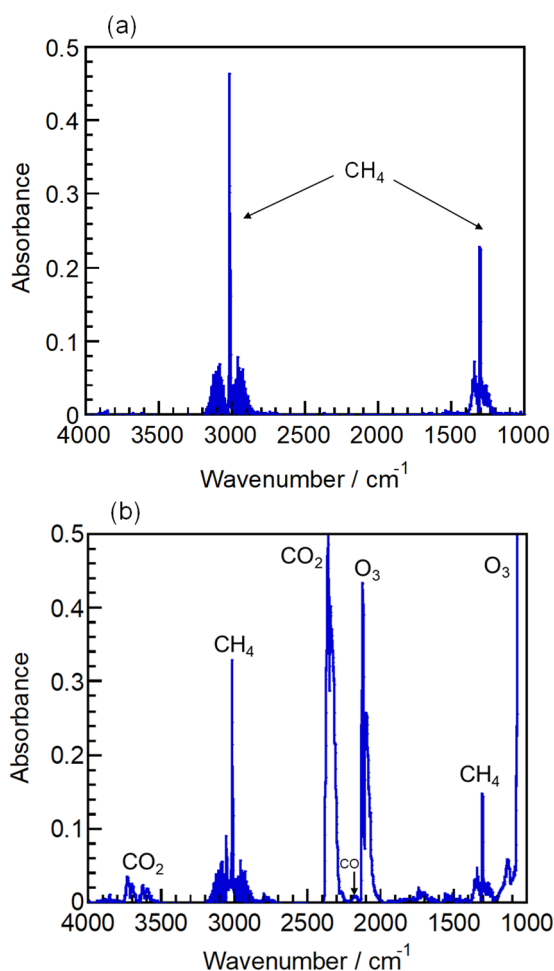


Fig. 2. (a) FTIR spectrum of CH_4 in air (a) at a total pressure of 100 kPa before and (b) after photoirradiation for 30 min.

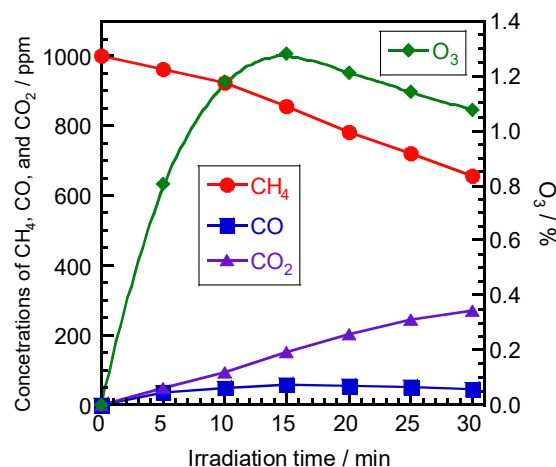


Fig. 3. Dependence of concentrations of CH_4 , CO , CO_2 , and O_3 on the irradiation time measured using a head-on lamp.

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

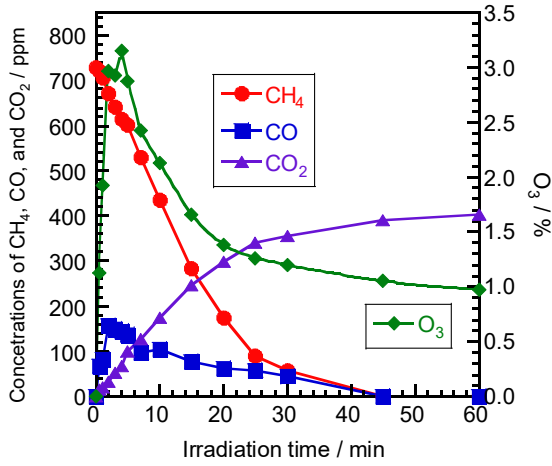
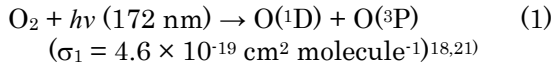


Fig. 4. Dependence of concentrations of CH₄, CO, CO₂, and O₃ on the irradiation time measured using a side-on lamp.

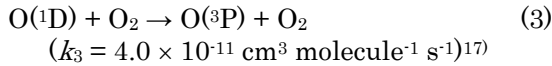
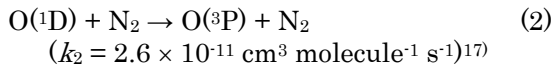
the 0–4 min range and decreases to 0.98% in the 4–60 min range. The decomposition rate of CH₄ by using the side-on lamp (0.077 min⁻¹) is 6.0 times faster than that by using the head-on lamp (0.0128 min⁻¹) in the 0–30 min range. The window area of the side-on lamp, from which VUV enters into the photolysis 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% O₂ 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 CH₄ using the side-on lamp.

3.3 Effects of O(¹D)

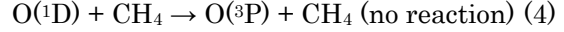
In a CH₄/N₂/O₂ mixture (20% O₂), O₂ initially absorbs all of 172 nm photons and selectively dissociates into O(¹D) + O(³P), because CH₄ and N₂ have no absorption in this wavelength.



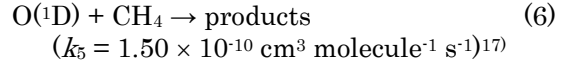
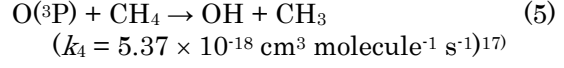
It is known that O(¹D) atoms are rapidly quenched to the ground O(³P) atoms by collisions with N₂ and O₂ atoms in air.



On the other hand, quenching reaction of O(¹D) to O(³P) by CH₄ does not occur.^{22,23)}



Although the reaction of O(³P) with CH₄ is extremely slow, that of O(¹D) with CH₄ is fast.



Thus, the O(¹D) + CH₄ reaction (6) will be an important reaction for CH₄ removal. However, quenching reactions of O(¹D) by N₂/O₂ gases (2) and (3) compete with the O(¹D) + CH₄ reaction (6). To reduce the relative contribution of reactions (2) and (3) to that of (6), we attempted to enhance the decomposition of CH₄ by decreasing the total pressure at a constant CH₄ partial pressure. For example, Figs. 5(a) and 5(b) show FTIR spectra of CH₄ in air before

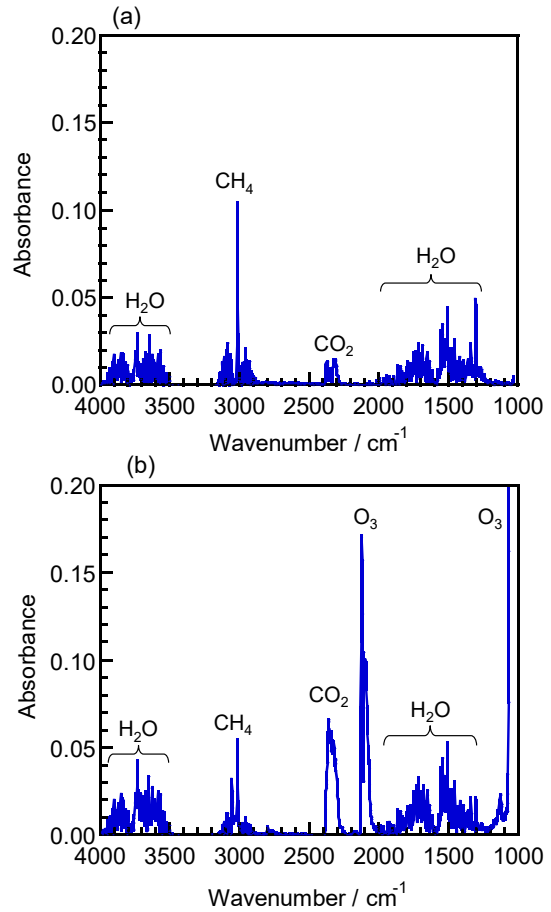


Fig. 5 (a) FTIR spectrum of CH₄ in air at a total pressure of 40 kPa (a) before photoirradiation and (b) after photoirradiation for 30 min.

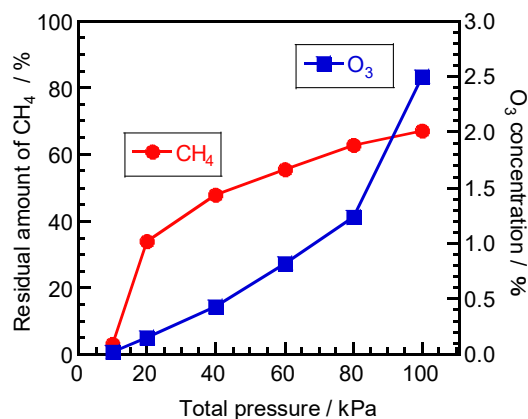
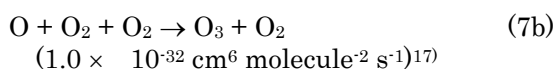
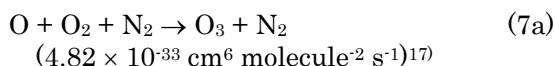


Fig. 6. Dependence of residual amount of CH₄ and O₃ concentration on the total pressure after 30 min photoirradiation.

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 CH₄ constant (150 ppm at 100 kPa). In this condition, 52% of CH₄ is decomposed after 30 min photoirradiation. This value is 53% larger than that at 100 kPa (Fig. 2). We determined the residual amount of CH₄, $[\text{CH}_4]/[\text{CH}_4]_0$, from gas analyses. Here, $[\text{CH}_4]_0$ is the initial concentration of CH₄. Figure 6 shows the dependence of the residual amount of CH₄ and the concentration of O₃ on the total pressure. It should be noted that the residual amount of CH₄ 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 CH₄ 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 CH₄ in our conditions.

The concentration of O₃ decreases rapidly with decreasing the total pressure, because three-body recombination reactions (7a) and (7b) leading to O₃ are greatly suppressed with decreasing the total pressure.

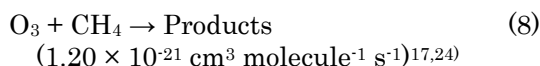


The removal rate of CH₄ increases with decreasing the total pressure, even though the O₃ concentration decreases rapidly. This suggests that O₃ molecules will not be major

active species for CH₄ removal in air. To confirm this prediction, the O₃ + CH₄ reaction was actually studied in the next section.

3.4 Effects of O₃

It is known that the upper limit of the rate constant of O₃ with CH₄ is extremely small at 298 K in N₂ atmosphere.



We have studied the contribution of reaction (8) by isolating O₃ in the reaction chamber. Figures 7(a) and 7(b) show FTIR spectra observed after the O₃ + CH₄ reaction for 1 and 180 min, respectively, where reactant peaks of CH₄ and O₃, a product peak of CO₂, and impurity peaks of H₂O are observed. Figure 8 shows the dependence of residual amount of CH₄ and the concentration of O₃ on the reaction time. The concentration of O₃ decreases from

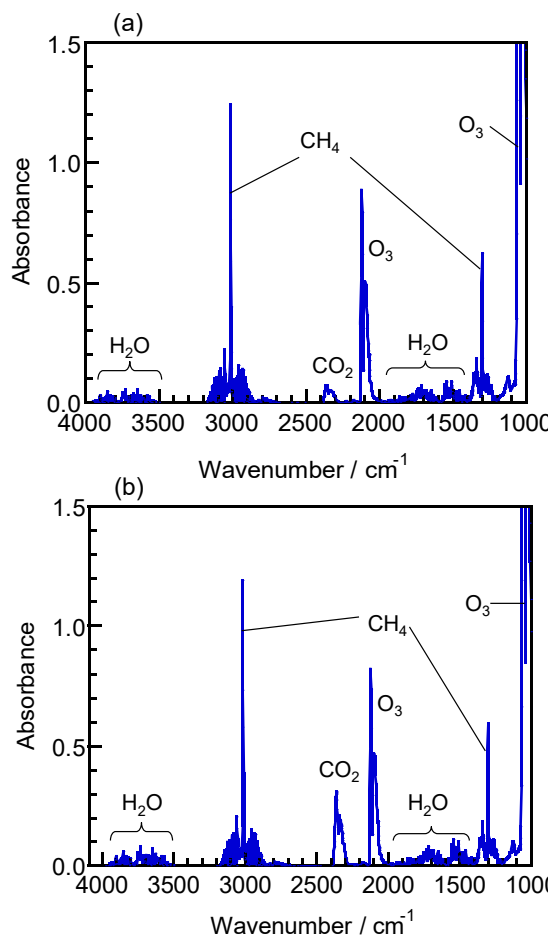


Fig. 7. (a) FTIR spectrum of CH₄ resulting from the O₃ + CH₄ reaction at reaction times of (a) 1 min and (b) 180 min.

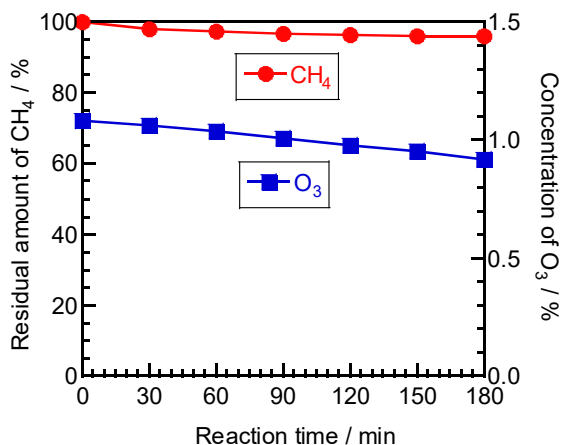


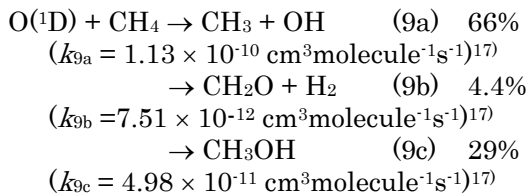
Fig. 8. Dependence of residual amount of CH₄ and concentration of O₃ in the O₃ + CH₄ reaction at thermal energy

1.08% to 0.92% with increasing the reaction time from 0 min to 180 min. The residual amount of CH₄ 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.

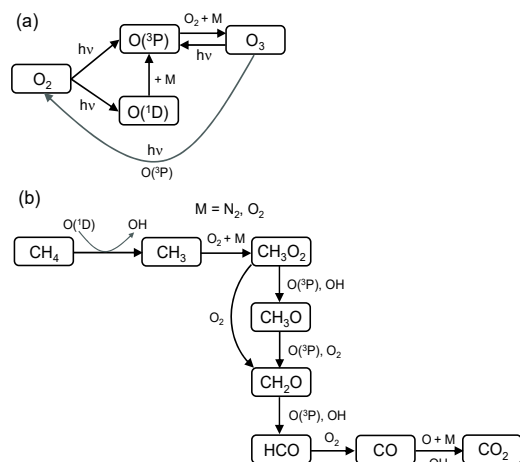
3.5 Possible oxidation mechanism of CH₄ under 172 nm photolysis in air

O(³P), O(¹D), and O₃ are formed by 172 nm photolysis of O₂ 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 CH₄ in air under our experimental conditions. The contributions of 172 nm photons and O(³P) are negligible and that of O₃ is very small. Active O(¹D) atoms arise exclusively from the direct 172 nm photolysis of O₂ (1) in the initial stage.

The rate constants of the O(¹D) + CH₄ reaction leading to CH₃, CH₂O, and CH₃O have been measured as.



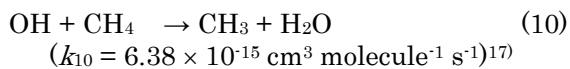
The branching fractions of the above three product channels indicate that major initial products are CH₃ + OH. On the basis of known oxidation reactions of CH₃ and their rate constants,^{17,25)} major two-body and three-body reaction pathways from CH₃ to CO and CO₂ are



Scheme 1. (a) photolysis of O₂ and O₃ under 172 nm VUV irradiation in air. (b) major oxidation processes of CH₄ 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 CO₂ in this study, short lived CH₃O₂, CH₃O, CH₂O, and HCO will be formed as intermediates.

OH radicals formed in process (9a) can react with CH₄, and CH₃ + H₂O are formed.



Since the rate constant of the OH + CH₄ reaction (10) is much smaller than that of the O(¹D) + CH₄ reaction (6), its contribution to initial decomposition of CH₄ to CH₃ 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 O₂ molecules do not participate in the initial decomposition of CH₄. However, they can contribute to the oxidation of such intermediates as CH₃, CH₃O₂, CH₃O, CH₂O, HCO, and CO as shown in Scheme 1(b). Present experimental data and reported kinetic data¹⁷⁾ suggest that O₃ molecules are less important than O(³P) and O₂ in the oxidation of CH₄ under 172 nm photoirradiation. Although 172 nm photoabsorption and photodissociation data of CH₃, CH₂O₂, CH₃O, CH₂O, 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 Xe₂ excimer lamps was studied to develop a new simple photochemical removal method of CH₄ without using any expensive catalysts at room temperature. No photolysis of CH₄ was observed in N₂, whereas CH₄ was oxidized to CO and CO₂ in air. In the presence of O₂, O(³P,¹D) and O₃ can be active species for the removal of CH₄. Effects of O(¹D) were examined by increasing the [O(¹D)]/[O(³P)] ratio at low total pressures. The contribution of O₃ was determined by observing CH₄ removal by the O₃ + CH₄ reaction using the same apparatus. Results showed that O(¹D) is the responsible active species under the 172 nm photolysis of CH₄ and the contributions of O(³P) and O₃ are unimportant in the initial stage of the CH₄ decomposition. The removal rate of CH₄ 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 CH₄ is more difficult than that of C₆H₆, CH₃CHO, and C₂H₃CHO,^{12,13,16} because its oxidation by the O(³P) + CH₄ and O₃ + CH₄ reactions are very slow and no direct photolysis of CH₄ occurs by 172 nm photons. These fundamental data provide valuable information for the design of practical removal apparatus CH₄ under VUV photolysis in air.

Acknowledgments

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