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Photochemical Removal of Benzene Using 172 nm Xe_2 Excimer Lamp in N_2/O_2 Mixtures at Atmospheric Pressure

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The photochemical removal of benzene was investigated in N_2/O_2 mixtures (0–20% O_2) using a 172 nm Xe_2 excimer lamp at atmospheric pressure. After 20 min photoirradiation, about 97% of C_6H_6 (1000 ppm) in N_2/O_2 mixtures (10–20% O_2) was converted to HCOOH, CO, and CO_2. In the 172 nm photolysis of C_6H_6, not only direct photolysis by VUV photons but also reactions of $O(^3P,^1D)$ and O_3 can take part in the decomposition of C_6H_6. To examine effects of direct photolysis, C_6H_6 was decomposed in N_2, whereas the contribution of O_3 was studied by observing the $O_3 + C_6H_6$ reaction. The contribution of $O(^1D)$ was examined by reducing the total pressure to suppress the collisional quenching of $O(^1D)$ by N_2/O_2 mixtures. It was found that the $O(^3P) + C_6H_6$ reaction plays a significant role in the initial stage of the removal reaction of C_6H_6.

Volatile organic compounds (VOCs) are common air pollutants and can be found in both outdoor and indoor settings. Exposure to VOCs might cause toxic effects to central nervous system and internal organs, and might cause symptoms such as headache, respiratory tract irritation, dizziness, and nausea, known as the sick building syndrome. For VOCs emission sources of high concentrations, catalytic treatments such as catalytic incineration, catalytic combustion, and photocatalytic oxidation have been well developed.[1] However, these treatments require high temperatures (200–500 °C) for successful operation. Various types of discharges have been investigated for VOC removal through oxidation at room temperature: corona discharges,[2–4] atmospheric pressure glow discharges,[5–7] and dielectric barrier discharges.[8–10] However, plasma activation tends to be less selective than catalytic processes, and undesirable by-products may be formed. Especially the formation of carbon monoxide, nitrogen oxides, hydrogen cyanide, and polymeric deposits was often reported in discharges of hydrocarbon/air mixtures. Combinations of plasma and heterogeneous catalysts including photocatalysts have also been investigated with the aim of obtaining a synergetic effect.[11–17] In many cases improved results as compared to plasma treatment only were reported, consisting in enhancements of the VOC conversion or/and shifts of the product distribution toward total oxidation. Recently, catalytic oxidation of VOC with ozone over heterogeneous catalysts and with OH radical, ozone-UV, and TiO_2 under photoirradiation have also been studied.[18,19]

We have recently used vacuum ultraviolet (VUV) excimer lamps to remove NO, NO_2, N_2O, SO_2, and CO_2.[20–25] In the present study, we use a 172 nm Xe_2 excimer lamp as a new photochemical removal method of a typical VOC such as benzene operating at room temperature without using any catalysts or electric discharge. One advantage of the photochemical method is that the apparatus is simpler than plasma–catalyst hybrid systems because expensive novel metal catalysts and photocatalysts are unnecessary. The other advantage is that the formation of nitrogen oxides and hydrogen cyanide is negligible because N_2 cannot be decomposed under 172 nm light irradiation. Not only direct VUV photolysis, but also reactions of $O(^3P,^1D)$ and O_3 with C_6H_6 can contribute to the removal of benzene. The major purpose of this study is the clarification of dominant active species for the 172 nm photolysis of C_6H_6. To examine effects of direct VUV photolysis, C_6H_6 was decomposed in N_2, whereas the contribution of O_3 was studied by observing the $O_3 + C_6H_6$ reaction. The contribution of $O(^1D)$ was examined by reducing the total pressure to suppress the collisional quenching of $O(^1D)$ by N_2/O_2 mixtures. On the basis of above results, dominant active species for the removal of C_6H_6 under 172 nm photolysis are determined and decomposition processes of C_6H_6 to HCOOH, CO, and CO_2 are discussed.

Experimental

The VUV photolysis apparatus used in this work is shown in Figure 1. The inside volume of the photolysis chamber was 185 cm^3. Lights from an unfocused 172 nm Xe_2 lamp (USHIO, UER20H172: 50 $mW\,cm^{-2}$, 155–200 nm range) was used to remove benzene at room temperature. The flux of photons in our 172 nm lamp was estimated to be 4.33×10^{16} photons $cm^{-2}\,s^{-1}$. Experiments were carried out in a closed batch system or a flow system. The total pressure was maintained at atmospheric pressure in most experiments and the benzene concentration diluted in pure N_2/O_2 mixtures (0–20% O_2) was 1000 ppm (v/v) in the batch experiments and 250 ppm in the flow experiments. It was introduced through mass flowmeters. In the batch system, outlet gases before and after photoirradiation were analyzed by a HORIBA gas

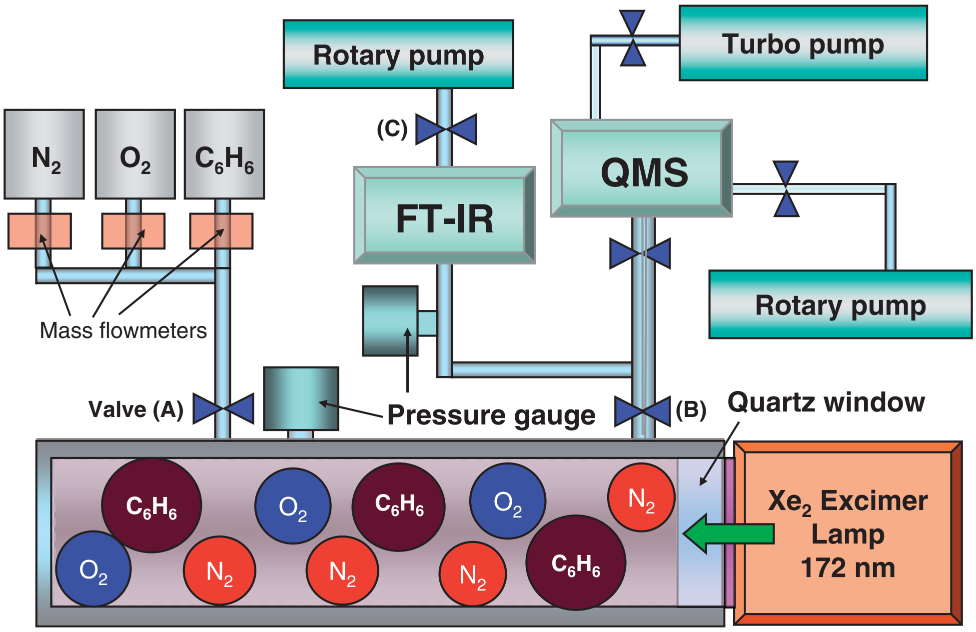


Figure 1. Photochemical chamber used for removal of C_6H_6 by 172 nm photons in N_2 and $O(^3P,^1D)$ and O_3 in N_2/O_2 mixtures.

analysis system (FG122-LS) equipped with an FTIR spectrometer and an ANELVA gas analysis system (M-200GA-DTS) equipped with a quadrupole mass spectrometer. On the other hand, outlet gases were analyzed online using the FTIR spectrometer in the flow experiments. A low-sensitivity mass spectrometer was used for the determination of the N_2/O_2 ratios of buffer gases, whereas a high-sensitivity FTIR system was used for the detection of C_6H_6, O_3, and other products. The light path length and the volume of the analyzing chamber in FTIR were 2.4 m and 300 cm^3, respectively. The spectra were measured in the 700–4000 cm^{-1} region with an optical resolution of 4 cm^{-1}. The concentrations of C_6H_6, CO, and CO_2 were calibrated using standard samples supplied from gas companies. The concentrations of O_3 and HCOOH were evaluated by reference to the standard spectral data supplied by HORIBA. We determined the residual amount of C_6H_6, $[C_6H_6]/[C_6H_6]_0$, from gas analyses. Here, $[C_6H_6]_0$ is the initial concentration of C_6H_6.

We have also studied the $O_3 + C_6H_6$ reaction at room temperature using the same apparatus. Initially, $O(^3P,^1D)$ and O_3 were prepared from the 172 nm photolysis of air in the photolysis chamber. After O_3 was partly stored in the FTIR cell in Figure 1, the photolysis chamber was evacuated in vacuum. Then O_3 was introduced again to the chamber. Under such conditions, the short-lived $O(^3P,^1D)$ disappeared and only O_3 with a long lifetime was present as an active species. After then a C_6H_6/N_2 mixture was introduced to the chamber and the $O_3 + C_6H_6$ reaction was monitored on line using FTIR measurements. The initial concentrations of C_6H_6, O_2, and O_3 in a C_6H_6/air mixture was 1000 ppm, 10%, and 1.4%, 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 (Taiyo Sanso Inc.), and C_6H_6 (Nippon Sanso Inc.: 2000 ppm in high purity N_2). C_6H_6 was diluted in N_2 or air (1–20%) before use.

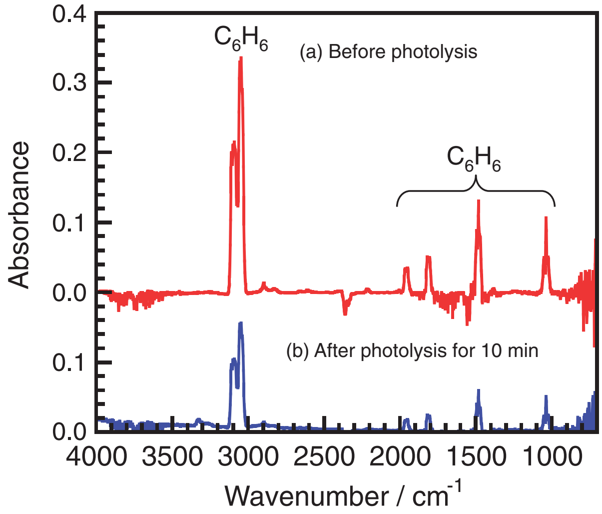


Figure 2. FTIR spectra of C_6H_6 (1000 ppm) in N_2 before and after photoirradiation for 10 min.

Results and Discussion

C_6H_6 Removal in N_2. Under 172 nm photolysis of C_6H_6 in N_2, only VUV photons can initially participate in the removal of C_6H_6. Figures 2a and 2b show FTIR spectra of C_6H_6 (1000 ppm) in N_2 before and after 172 nm photoirradiation. After photoirradiation for 10 min, C_6H_6 peaks decrease in intensity by ≈55%, and no other prominent peaks are observed. When 172 nm light was irradiated to the C_6H_6/N_2 mixture for 30 min, a brown polymer was deposited on the quartz window, so that little VUV light entered into the reaction chamber. Early experiments on the photolysis of benzene assigned the major products as fulvene, 1,3-hexadien-5-yne, and polymers, with the minor products including methane, ethane, ethylene, hydrogen, and acetylene.[26–32] In these experiments the primary photolysis products could undergo collisional deactivation with the buffer gas and also participate in secondary reactions. Although detailed photolysis channels of C_6H_6 at 172 nm has not been known, ring opening reaction followed by polymerization reactions must occur at 172 nm under our experimental conditions. The removal rate of C_6H_6 ($-d[C_6H_6]/dt$) in N_2 after 10 min is slower by a factor of about 30% than that in an N_2/O_2 mixture (20% O_2) as shown later. The deposition of polymer on the quartz window interfered with the detailed photolysis experiments of C_6H_6, and O_2 is generally present in exhausted gases involving C_6H_6. Therefore, we made detailed experiments in the presence of O_2.

C_6H_6 Removal in N_2/O_2 Mixtures. Under 172 nm photolysis of C_6H_6 in N_2/O_2 mixtures, not only the contribution of VUV photons but also that of $O(^3P,^1D)$ and O_3 may be present under our experimental conditions. In the presence of O_2, the absorption of the 172 nm light by O_2 becomes significant. In general, the total photon energy absorbed by such a mixture as C_6H_6, N_2, and O_2 during passing through the decomposition chamber, E_{total}, was calculated from the relation:

$$E_{\text{total}} = E_0 - E_0 \exp\left(-l \sum_i \sigma_i N_i\right) \tag{1}$$

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.

$$E_i = E_{\text{total}} \times \frac{\sigma_i N_i}{\sum_i \sigma_i N_i} \tag{2}$$

N_2 does not absorb 172 nm photons.[33] σ_{PhH} and σ_{O_2} at 172 nm were reported to be 6.5×10^{-21} and 4.6×10^{-19} $\text{cm}^2\,\text{molecule}^{-1}$, respectively.[33–35] When we calculated the $E_{\text{PhH}}/(E_{\text{PhH}} + E_{O_2})$ and $E_{O_2}/(E_{\text{PhH}} + E_{O_2})$ values at 172 nm using these values at O_2 concentrations of 1, 10, and 20%, they are 0.14 and 99.86%, 1.4×10^{-2} and 99.99%, and 7.1×10^{-3} and 99.993%, respectively. These values suggest that nearly all photons are initially absorbed by O_2 even at an O_2 concentration of 1% because of a very small ratios of $\sigma_{\text{PhH}}/\sigma_{O_2} = 0.014$ and $N_{\text{PhH}}/N_{O_2} = 0.1$. Thus, it is concluded that direct VUV photolysis is insignificant in N_2/O_2 mixtures (1–20% O_2) at atmospheric pressure and that $O(^3P,^1D)$ and/or O_3 can take part in the removal of C_6H_6 in N_2/O_2 mixtures under our conditions.

The photolysis of C_6H_6 at 172 nm was carried out in N_2/O_2 mixtures at O_2 concentration range of 1–20%. As an example, Figures 3a–3c show FTIR spectra of C_6H_6 (1000 ppm) at an O_2 concentration of 20% before and after 1 and 20 min 172 nm photoirradiation, respectively. Before photolysis, in addition to a strong C_6H_6 peak at 3000–3070 cm^{-1}, several weak C_6H_6 peaks are observed at 1000–2000 cm^{-1}. After photolysis for 1 min, these C_6H_6 peaks decrease in intensity by 17% and new peaks of CO, CO_2, HCOOH, and O_3 are observed. After photoirradiation for 20 min, the C_6H_6 peaks further decrease, whereas CO_2 and O_3 peaks increase significantly. Satoh et al.[4] have recently studied the removal of C_6H_6 using corona discharge. Although their FTIR spectra were similar to those found in this study, weak peaks of hazardous N_2O and HCN molecules were observed in their experiments. The main energy carrier in electric discharge is energetic electrons, which have sufficient kinetic energies to dissociate and ionize N_2 molecules. Therefore, secondary reactions of active N, N^+, and N_2^+ with O_2 and hydrocarbons gave such hazardous compounds. A great advantage of the present photochemical method is that such hazardous N_2O and HCN gases are not emitted under 172 nm photolysis of $C_6H_6/N_2/O_2$ mixtures, because N_2 is inert to 172 nm light.

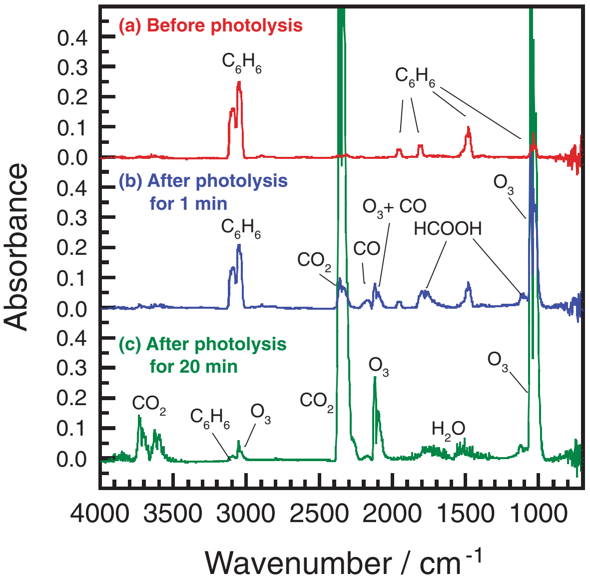


Figure 3. FTIR spectra of C_6H_6 (1000 ppm) in an N_2/O_2 mixture (20% O_2) before and after photoirradiation for 1 and 20 min.

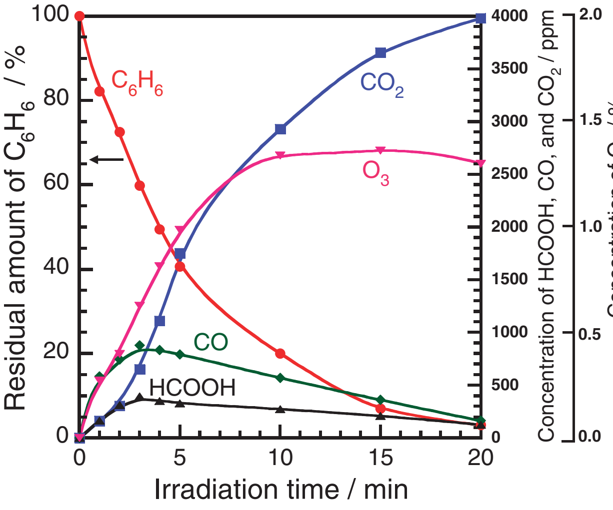


Figure 4. Dependence of the residual amount of C_6H_6 and the concentrations of products and O_3 on the irradiation time of Xe_2 excimer lamp in an N_2/O_2 (20% O_2) mixture. The initial C_6H_6 concentration was 1000 ppm.

Figure 4 shows the residual amount of C_6H_6 and the concentrations of HCOOH, CO, CO_2, and O_3 as a function of the irradiation time at an O_2 concentration of 20%. The residual amount of C_6H_6 decreases exponentially to 3% with increasing the irradiation time up to 20 min. The concentrations of HCOOH and CO increase in the 0–3 min range and then slowly decrease in the 3–20 min range. The maximum concentration of CO at 3 min is higher than that of HCOOH by a factor of 2.2. The similar time profile between HCOOH and CO indicates that decomposition of HCOOH → $CO + H_2O$ is insignificant. The concentration of CO_2 initially increases more slowly until 3 min and increases rapidly above that. The concentration of CO_2 becomes higher than those of HCOOH and CO in the 2–3 min range and CO_2 becomes a dominant product above 5 min. This time profile suggests that C_6H_6 is finally converted to CO_2 via CO and HCOOH through consecutive reactions. The concentration of O_3 increases to about 1.3% in the 0–10 min range and levels off in the 10–20 min range. The initial removal rate of C_6H_6 below 5 min is fast even though the concentration of O_3 is low. This implies that the contribution of O_3 is insignificant for the removal of C_6H_6.

The carbon balance between C_6H_6 and products was estimated to be 74% at 20 min in Figure 4. Such a low carbon balance was also found in the decomposition of benzene in a corona discharge at atmospheric pressure by Satoh et al.[4] They reported that carbon balance was 43 and 76% at oxygen concentrations of 0.2 and 20%, respectively, so that 57 and 24% of carbon atoms from decomposed benzene are deposited on the electrode and discharge chamber. Thus, in our experiments non-volatile compounds are also formed and deposited on the chamber as in the case of their discharge experiments and/or some by-products in gas phase which are difficult to be detected by FTIR spectroscopy are present. If 172 nm photons are irradiated to non-volatile compounds deposited on the chamber in the presence of O_2, carbon atoms in non-volatile compounds will be efficiently converted to CO_2. To examine effects of non-volatile compounds deposited on the chamber, the photochemical removal of benzene was studied using a side-on type chamber.[36] In this apparatus, 172 nm photons, $O(^3P,^1D)$, and O_3 can react with deposition products on the chamber, because the distance from the entrance window of the VUV light to the wall of chamber was only 3 cm. In this experiment, carbon balance after 20 min increased to 86%, although it was still lower than 100%. On the basis of the above facts, it is reasonable to assume that the low carbon balance arises both from the deposition of non-volatile compounds on the present long chamber and from the presence of other by-products which are difficult to detect by FTIR spectroscopy.

To further study effects of the concentration of O_2, C_6H_6 was decomposed at lower O_2 concentrations of 1 and 10%. When C_6H_6 was decomposed at lower O_2 concentrations of 1 and 10%, the same product and O_3 peaks were observed in the FTIR spectra. At a low O_2 concentration of 1%, some polymer was deposited on the windows after photoirradiation for 5 min as in the case of N_2 atmosphere, so that experiments were carried out below 5 min. Figures 5 and 6 show the dependence of the residual amount of C_6H_6 and the concentrations of products and O_3 on the irradiation time. For comparison the results obtained at 20% are also shown. The removal rate of C_6H_6 below 5 min increases by 8 and 23% with decreasing the O_2 concentration from 20% to 10 and 1%, respectively. With decreasing the O_2 concentration from 20% to 10 and 1%, the light transmittance distance above 99.8% increases from ≈2 cm to ≈4 and >25 cm, respectively, as shown in Figure S1 (Supporting Information). This indicates that the VUV light penetrates inside the photolysis chamber with decreasing O_2 concentration so that reaction volume increases with decreasing O_2 concentration. This is one reason why decomposition rate slightly increases with decreasing O_2 concentration.

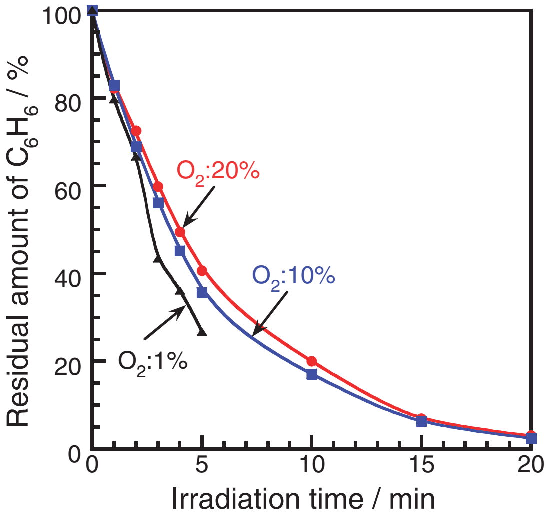


Figure 5. Dependence of the residual amount of C_6H_6 on the irradiation time of Xe_2 excimer lamp in an N_2/O_2 mixture at O_2 concentrations of 1, 10, and 20%. The initial C_6H_6 concentration was 1000 ppm.

The concentration of O_3 rapidly increases in the 0–10 min range and levels off in the 10–20 min at O_2 concentrations of 10 and 20%. This behavior implies that the formation of O_3 through three-body recombination processes (3a) and (3b) was equilibrated with its decomposition processes (4) and (5) above 10 min.[33,37,38]

$$O + O_2 + N_2 \rightarrow O_3 + N_2 \ (4.82 \times 10^{-33}\,cm^6\,molecule^{-2}\,s^{-1}) \quad (3a)$$

$$O + O_2 + O_2 \rightarrow O_3 + O_2 \ (1.0 \times 10^{-32}\,cm^6\,molecule^{-2}\,s^{-1}) \quad (3b)$$

$$O_3 + h\nu \rightarrow O(^3P,^1D) + O_2 \quad (4)$$

$$O_3 + O(^3P) \rightarrow 2O_2 \ (8.0 \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}) \quad (5)$$

The concentration of O_3 was about 0.08, 0.7, and 1.3% at O_2 concentrations of 1, 10, and 20%, respectively. No significant differences are found among the time profiles in the reagent C_6H_6 and products HCOOH, CO, and CO_2 at O_2 concentrations of 1 and 10% in the short time range of 0–5 min. The concentrations of HCOOH and CO in the 5–20 min range at an O_2 concentration of 10% are lower than those at 20%, whereas that of CO_2 at 10% is slightly higher than that at 20%. This implies that conversion of C_6H_6 to CO_2 via HCOOH and CO at 10% is higher than at 20% by a factor of about 3% at 20 min. At an O_2 concentration of 1%, the conversion of C_6H_6 is lower than that at 10 and 20%. When the concentration of CO_2 was measured as a function of irradiation time at an O_2 concentration of 5%, it was just between the data at 10 and 20% (not shown in Figure 6). On the basis of this finding, the conversion of C_6H_6 to CO_2 has a maximum at about 10%.

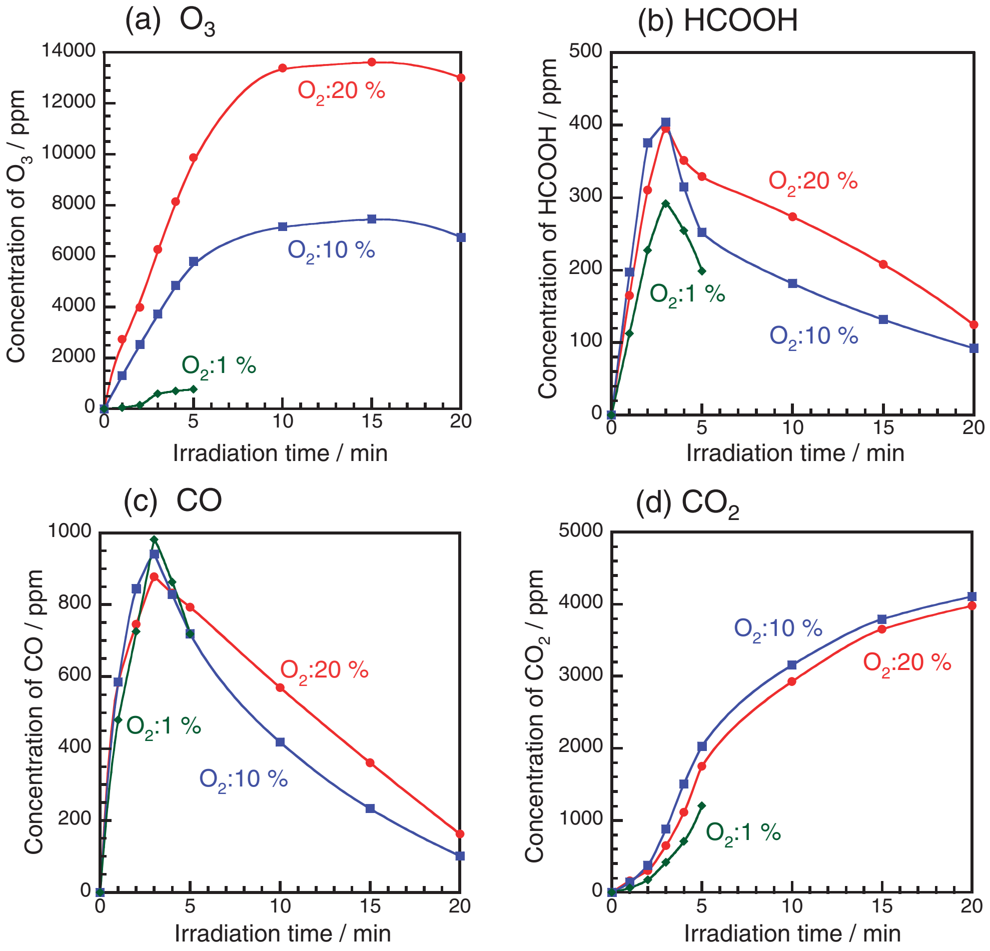


Figure 6. Dependence of the concentrations of O_3, HCOOH, CO, and CO_2 on the irradiation time of Xe_2 excimer lamp in an N_2/O_2 mixture at O_2 concentrations of 1, 10, and 20%. The initial C_6H_6 concentration was 1000 ppm.

Effects of O(^{1}D). We have recently examined the removal of N_2O by 172 nm photolysis in N_2 or N_2/O_2 mixtures.[25] In an N_2/O_2 mixture (20% O_2), O_2 absorbs most of photons leading to O(^{1}D) + O(^{3}P).[33,35]

$$O_2 + h\nu(172\,\text{nm}) \rightarrow O(^1D) + O(^3P)\ (4.6 \times 10^{-19}\,\text{cm}^2\,\text{molecule}^{-1}) \quad (6)$$

Therefore the following direct photolysis is insignificant as in the case of C_6H_6 in the N_2/O_2 mixture.

$$N_2O + h\nu(172\,\text{nm}) \rightarrow N_2 + O(^1D) \quad (7)$$

It is known that the metastable O(^{1}D) atoms can decompose N_2O through the following fast reactions, whereas the ground state O(^{3}P) atoms, O_2, and O_3 are inert for N_2O at 298 K.[37,38]

$$O(^1D) + N_2O \rightarrow N_2 + O_2\ (4.4 \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (8a)$$

$$\rightarrow 2NO\ (7.2 \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (8b)$$

$$O(^3P) + N_2O \rightarrow 2NO\ (<1.66 \times 10^{-16}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (9)$$

$$O_2 + N_2O \rightarrow \text{no reaction} \quad (10)$$

$$O_3 + N_2O \rightarrow \text{no reaction} \quad (11)$$

Reaction (8) competes with quenching reactions (12) and (13).[37,38]

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2\ (2.6 \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (12)$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2\ (4.0 \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (13)$$

To reduce the relative contribution of reactions (12) and (13) to that of (8), we attempted to enhance the conversion of N_2O by decreasing the total pressure. When the total pressure of N_2O/air was reduced from 100 to 20 kPa keeping the absolute amount of N_2O constant (100 ppm), the residual amount of N_2O decreases from 58 to 19%. The above results for N_2O in air implies that the effects of O(^{1}D) can be examined by reducing the total pressure of the N_2/O_2 mixture. Thus, we used a similar technique to examine the effects of O(^{1}D) in this study.

In the 172 nm photolysis of C_6H_6 (250 ppm) in an N_2/O_2 mixture (20% O_2), O_2 initially absorbs 99.998% of 172 nm photons and selectively dissociates into O(^{1}D) + O(^{3}P).[33,35] Although the rate constant of the O(^{3}P) + C_6H_6 reaction has been measured,[37] that of the O(^{1}D) + C_6H_6 reaction has not been reported to the best of our knowledge.

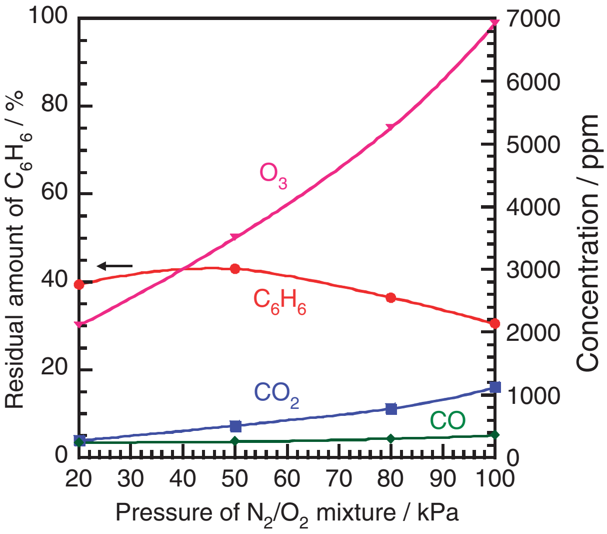


Figure 7. Dependence of the residual amount of C_6H_6 and the concentrations of CO, CO_2, and O_3 in an N_2/O_2 mixture on the total pressure after 5 min photoirradiation at constant amounts of C_6H_6 and O_2 in the N_2/O_2 mixture. The initial O_2 and C_6H_6 concentrations were 5% and 400 ppm, respectively.

$$O(^3P) + C_6H_6 \rightarrow \text{products } (3.16 \times 10^{-14}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (14)$$

$$O(^1D) + C_6H_6 \rightarrow \text{products} \quad (15)$$

The $O(^1D) + C_6H_6$ reaction (15) competes with quenching reactions of $O(^1D)$ by N_2 and O_2 (12) and (13).

We studied the contribution of $O(^1D)$ by reducing the total pressure. Figure 7 shows the dependence of the residual amount of C_6H_6, and the concentrations of CO, CO_2, and O_3 on the total pressure after 5 min photoirradiation keeping the absolute amounts of C_6H_6 and O_2 constant. The residual amount of C_6H_6 increases from 31 to 43% with decreasing the total pressure from 100 to 50 kPa and slightly decreases from 43 to 40% with decreasing the total pressure from 50 to 20 kPa. The CO, CO_2, and O_3 concentrations decrease from 362 to 244 ppm, from 1130 to 280 ppm, and from 6930 to 2110 ppm with decreasing the total pressure from 100 to 20 kPa. No significant decrease in the residual amount of C_6H_6 with decreasing the total pressure from 100 to 20 kPa indicates that the $O(^1D)$ atoms do not play an important role for the removal of C_6H_6 in our conditions.

Effects of O_3. We have measured the dependence of the concentration of O_3 in an N_2/O_2 mixture (10% O_2) on the time without the addition of C_6H_6 to examine the self-decomposition of ozone in our system. Within 30 min no appreciable change in the concentration of O_3 (1.4%) was found. These results indicate that the self-decomposition of ozone is very slow under our conditions. This fact is consistent with the very small rate coefficient of the self-decomposition of O_3[37] and a very long lifetime of O_3 in troposphere (1–2 weeks in summer and 1–2 months in winter).[1]

$$O_3 \rightarrow O_2 + O(^3P) \ (4.38 \times 10^{-26}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) \quad (16)$$

It is known that O_3 reacts with C_6H_6 and primary ozonides are formed, though its rate constant is extremely small in the gas phase.[37]

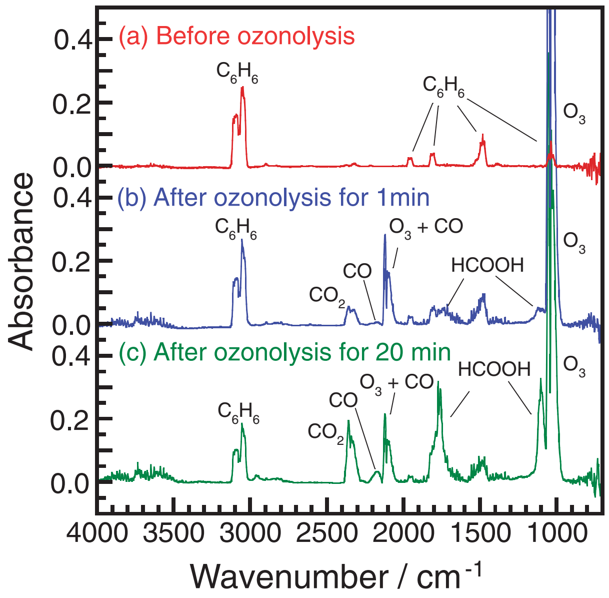


Figure 8. FTIR spectra obtained from the $O_3 + C_6H_6$ (1000 ppm) reaction in an N_2/O_2 mixture (10% O_2) at the reaction times of 0, 1, and 20 min at a total pressure of 50 kPa.

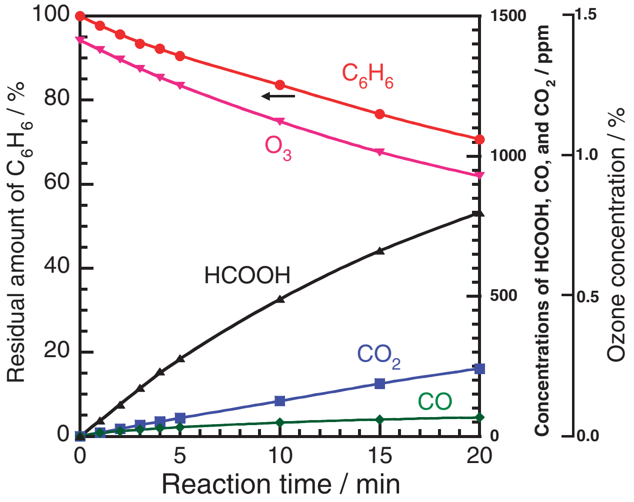
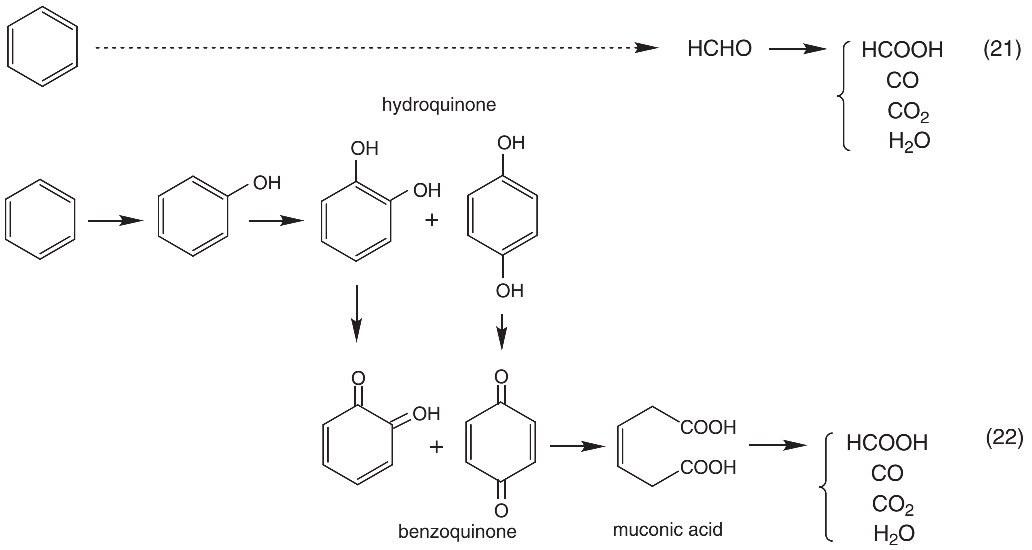


Figure 9. Dependence of the residual amount of C_6H_6 and the concentrations of products and O_3 in an N_2/O_2 mixture (10% O_2) in the $O_3 + C_6H_6$ (1000 ppm) reaction on the reaction time at a total pressure of 50 kPa.

$$O_3 + C_6H_6 \rightarrow \text{Products } (7.01 \times 10^{-23}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1} \text{ in } N_2) \quad (17)$$

We have studied the contribution of reaction (17) by isolating O_3 in the reaction chamber. Figure 8 shows FTIR spectra observed before and after $O_3 + C_6H_6$ reaction for 1 and 20 min, where the same product peaks (HCOOH, CO, and CO_2) as those observed in the 172 nm photolysis of C_6H_6 were detected (Figure 3). Figure 9 shows the dependence of the residual amount of C_6H_6 and the concentrations of HCOOH, CO, CO_2,



Scheme 1. Typical oxidation mechanisms of benzene to HCOOH, CO, and CO_2 by reactions with $O(^3P,^1D)$, O_2, and O_3.

and O_3 on the reaction time. The concentration of C_6H_6 decreases more slowly than that in the 172 nm photolysis of C_6H_6 (Figures 4 and 5). Although HCOOH, CO, and CO_2 are produced, the $[HCOOH]/[CO_2]$ ratio in the $O_3 + C_6H_6$ reaction is much higher than that in the 172 nm photolysis. This implies that the $O_3 + HCOOH$ reaction leading to CO_2 is slow in our conditions.

$$O_3 + HCOOH \rightarrow CO_2 + H_2O + O_2 \qquad (18)$$

Einaga et al.[18d] reported that reaction (18) is responsible for the formation of CO_2 in catalytic oxidation of benzene with ozone on alumina-supported manganese oxides in the presence of H_2O. Our present result implies that the rate constant of reaction (18) is very small without using heterogeneous catalysts.

When we monitored the concentration of C_6H_6 in N_2/O_2 mixtures in the absence of O_3, little change was observed. This indicated that C_6H_6 is not consumed in N_2/O_2 mixtures without the presence of O_3. The rate constant of O_3 with C_6H_6 was determined to be $k_{17} = 1.48 \times 10^{-20}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ from the following relation.

$$k_2 t = \frac{1}{[C_6H_6]_0 - [O_3]_0} \ln\left(\frac{[C_6H_6]_t[O_3]_0}{[C_6H_6]_0[O_3]_t}\right) \qquad (19)$$

This value is 211 times faster than the reported value of $7.01 \times 10^{-23}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.[37] In our conditions, primary ozonides are initially formed and multiple-step reactions of O_3 with unstable intermediates including ozonides leading to HCOOH, CO, and CO_2 occur. Since O_3 is consumed not only by the initial $O_3 + C_6H_6$ reaction but also various fast O_3 + intermediate reactions, the apparent removal rate of O_3 is larger than the reported value.

Possible Decomposition Mechanism of C_6H_6 under 172 nm Photolysis in N_2/O_2 Mixtures. We found that 172 photons and $O(^1D)$ and O_3 do not play a significant role for the removal of C_6H_6 in N_2/O_2 mixtures (1–20% O_2) under our experimental conditions. In addition direct photolysis is also insignificant for the removal of C_6H_6. It is therefore reasonable to assume that the most important active species for the removal of C_6H_6 in N_2/O_2 mixtures are the ground $O(^3P)$ atoms. The dominant source of $O(^3P)$ in the 172 nm photolysis of N_2/O_2 mixtures is the direct photolysis of O_2 (6) and the collisional quenching of $O(^1D)$ to $O(^3P)$ via processes (12) and (13). All $O(^3P,^1D)$ atoms arise from 172 photolysis of O_2 at 0 min, because the concentration of O_3 is initially zero. The largest contribution of $O(^3P,^1D)$ atoms from photolysis of $O_3 \rightarrow O(^3P,^1D) + O_2$ (4) arises at ≈15 min in Figure 4, where the concentrations of O_3 and O_2 were 1.4 and 18%, respectively. The absorption cross sections of O_2 and O_3 at 172 nm are 4.6×10^{-19} and $8.2 \times 10^{-19}\,\mathrm{cm^2\,molecule^{-1}}$, respectively.[33,35] From the relation (2), the $E_{O_2}/(E_{PhH} + E_{O_2} + E_{O_3})$ and $E_{O_3}/(E_{PhH} + E_{O_2} + E_{O_3})$ values were estimated to be 88 and 12%, respectively. $O(^1D)$ is rapidly quenched to $O(^3P)$ by reactions (12) and (13) under our conditions. Therefore, two $O(^3P)$ atoms are finally formed from photolysis of O_2 (6), whereas one $O(^3P)$ atom is finally formed from photolysis of O_3 (4). Thus the maximum contribution of $O(^3P)$ from photolysis of O_3 was estimated to be 6% under our conditions.

It is known that the rate constant of the $O(^3P) + C_6H_6$ reaction is $3.16 \times 10^{-14}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ and the primary stable products are phenol, benzene oxide/oxepin, and a not identified compound with the probable composition C_6H_5O (Scheme S1 in Supporting Information).[37,39]

$$O(^3P) + C_6H_6 \rightarrow \text{Products } (3.16 \times 10^{-14}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}) \qquad (20)$$

The yields of phenol and benzene oxide/oxepin were determined to be 0.12 ± 0.02 and 0.26 ± 0.06, respectively.[39] The lack of FTIR peaks corresponding to these primary products implies that secondary oxidation reactions by $O(^3P,^1D)$, O_2, and O_3 are too fast to detect these products under our conditions. Although a detailed oxidation mechanism of C_6H_6 to HCOOH, CO, and CO_2 is not identified in this study, typical processes are shown in Scheme 1. It is expected that a lot of species are initially produced as predicted from theoretical calculations[40] and oxidized to CO, and CO_2. We cannot detect stable intermediates such as PhOH, hydroquinone, benzoquinone, and

HCHO in FTIR spectra. Therefore, it is reasonable to assume that oxidation of these species to HCOOH, CO, and CO_2 under 172 nm photolysis are much faster than that of C_6H_6 in N_2/O_2 mixtures. Actually, when we studied the removal of HCHO by 172 nm photolysis in N_2/O_2 mixtures, its oxidation to CO and CO_2 was much faster than that of C_6H_6.[41] This is consistent with our prediction that oxidation of benzene by $O(^3P,^1D)$ and O_3 is slow due to a high stability of benzene ring, however, once electrophilic O-addition onto C atom occurs, further oxidation to HCOOH, CO, and CO_2 takes place rapidly due to lower stability of intermediates for oxidation.

In our experiments, we found that CO and HCOOH are produced from 172 nm photolysis of C_6H_6 as intermediate species and they are finally oxidized to CO_2. CO is finally converted to CO_2 under our conditions. Possible oxidation processes are as follows.[37,38]

$$\mathrm{CO} + \mathrm{O}(^3\mathrm{P}) + \mathrm{N_2} \rightarrow \mathrm{CO_2} + \mathrm{N_2}\ (1.11 \times 10^{-35}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}) \quad (23)$$

$$\mathrm{CO} + \mathrm{O_3} \rightarrow \mathrm{CO_2} + \mathrm{O_2}\ (4.0 \times 10^{-25}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad (24)$$

Since the rate constant of reaction (24) is very small, the three-body reaction (23) is expected to be dominant process for the oxidation of CO to CO_2. Unfortunately little information on reactions of $O(^3P)$ and O_3 with HCOOH. However, we found that the conversion of HCOOH to CO and CO_2 in the presence of $O(^3P,^1D)$ and O_3 was faster than that in the presence of only O_3 (cf. Figures 4 and 9). Thus, it seems that $O(^3P,^1D)$ also play a significant role in the conversion of HCOOH to CO and CO_2.

In FTIR spectra of products, weak peaks of H_2O are observed at 1300–1800 cm^{-1} after photoirradiation for 20 min (Figure 3), indicating that H_2O is also produced as a by-product. H_2O is partly absorbed on the photolysis chamber, so that it was difficult to evacuate rapidly by pumping. In addition, it was difficult to measure the accurate concentration of H_2O, because a hygrometer could not be used in the presence of O_3 owing to damage of its sensor by O_3. Therefore, reliable quantitative data for the concentration of H_2O was not obtained in this study. Einaga et al.[18d] reported that the removal rate of C_6H_6 by the $O_3 + C_6H_6$ reaction on the catalysts leading to HCOOH, CO, and CO_2 increases by the addition of H_2O. It is known that OH can be formed via $O(^1D) + C_6H_6$ reaction[42] and 172 nm photolysis of H_2O,[33] and the $OH + C_6H_6$ reaction is fast and CO and HCOOH are known to be produced through the reaction.[37,38]

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{C_6H_6} \rightarrow \mathrm{OH} + \mathrm{C_6H_5} \quad (25)$$

$$\mathrm{H_2O} + h\nu(172\ \mathrm{nm}) \rightarrow \mathrm{OH} + \mathrm{H} \quad (26)$$

$$\left.\begin{aligned} \mathrm{OH} + \mathrm{C_6H_6} &\rightarrow \mathrm{CO} + \text{other products}\ (0.42 \pm 0.22) \\ &\rightarrow \mathrm{HCOOH} + \text{other products}\ (0.16 \pm 0.03) \\ &\rightarrow \mathrm{C_6H_5OH} + \text{other products}\ (0.24 \pm 0.08) \end{aligned}\right\} \\ (1.28 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \quad (27)$$

Since the $O(^3P) + C_6H_6 \rightarrow OH + C_6H_5$ reaction is endoergic by 12.2 $kcal\ mol^{-1}$ (1 $kcal\ mol^{-1}$ = 4.184 $kJ\ mol^{-1}$),[40] it is unimportant under our conditions at room temperature. The major products in reaction (27) agree with our present data and in our reaction system some OH radicals generated from processes (25) and (26) and other abstraction reactions of $O(^3P)$ with intermediate in the 172 nm photolysis of C_6H_6 are probably present. Although we found that the contribution of $O(^1D)$ is insignificant and that photolysis of H_2O by 172 nm will also be unimportant in the presence of high concentration of O_2 as discussed in the photolysis of C_6H_6, the fast $OH + C_6H_6$ reaction and some OH + intermediate reactions may participate in the removal of C_6H_6 under 172 nm photolysis in N_2/O_2 mixtures. In order to clarify the contribution of OH, a further detailed experimental study is required.

C_6H_6 Removal in a Flow System. For the actual application of the photochemical removal of C_6H_6, a flow system in which the continuous removal of VOC gas is possible is required. In this study, we attempted to apply a flow system for the removal of C_6H_6. Figure 10 shows the results obtained for the $C_6H_6/N_2/O_2$ system. Four kinds of flow experiment were carried out at a constant initial C_6H_6 concentration of 250 ppm in N_2/O_2 mixtures. The Xe_2 excimer lamp was switched on at 1 min and switched off at 15 min. In the flow system, the irradiation time corresponds to the length of time that C_6H_6 gas spends in the photolysis chamber being irradiated by 172 nm light. On the other hand, the average residence time of C_6H_6 in the photolysis chamber, τ, is defined as $\tau = V/v$, where V is the total volume of the photolysis chamber and v is the volumetric flow rate. In the first experiment, about 10% of C_6H_6 was decomposed to CO, CO_2, and HCOOH at a total flow rate of 1 $L\ min^{-1}$ (Figure 10a). The concentration of CO is higher than CO_2 by factors of 2.0–2.8, indicating incomplete oxidation in this flow system due to short residence time of gas (11 s). In the second experiment, the concentration of C_6H_6 was varied in the 200–800 ppm (Figure 10b). The residual amount of C_6H_6 increases from ≈90 to ≈98% with increasing the concentration of C_6H_6 from 200 to 800 ppm. In the third experiment, C_6H_6 was decomposed at O_2 concentrations 1, 10, and 20% (Figure 10c). With decreasing O_2 concentration, the residual amount of C_6H_6 decreases from ≈90 to ≈83%. This shows that a higher removal efficiently was obtained at a low concentration of O_2, being consistent with the experimental data in the batch system (Figure 5). In the fourth experiment, the total flow rate of C_6H_6 was varied in the 250–1000 $mL\ min^{-1}$ (Figure 10d). The residual amount of C_6H_6 decreases from ≈90 to ≈65% with decreasing the flow rate from 1000 to 250 $mL\ min^{-1}$. The residence time of C_6H_6 in the photolysis chamber is equal to the irradiation time of 172 nm light, so that the irradiation time of photons to C_6H_6 decreases with increasing flow rate. In the present experiments, the τ values were only about 11, 22, and 44 s at flow rates of 1000, 500, and 250 $mL\ min^{-1}$, respectively. The short residence time is a major reason why the conversion of C_6H_6 in an N_2/O_2 (O_2 20%) mixture in a flow system is restricted to 10–35%. On the basis of these results, the C_6H_6 removal in N_2/O_2 mixtures is possible in the flow system, although higher performance is required for practical application.

Conclusion

The removal of benzene by 172 nm photolysis was studied to develop a new simple photochemical removal method of VOC without using any expensive catalysts at room temperature. In

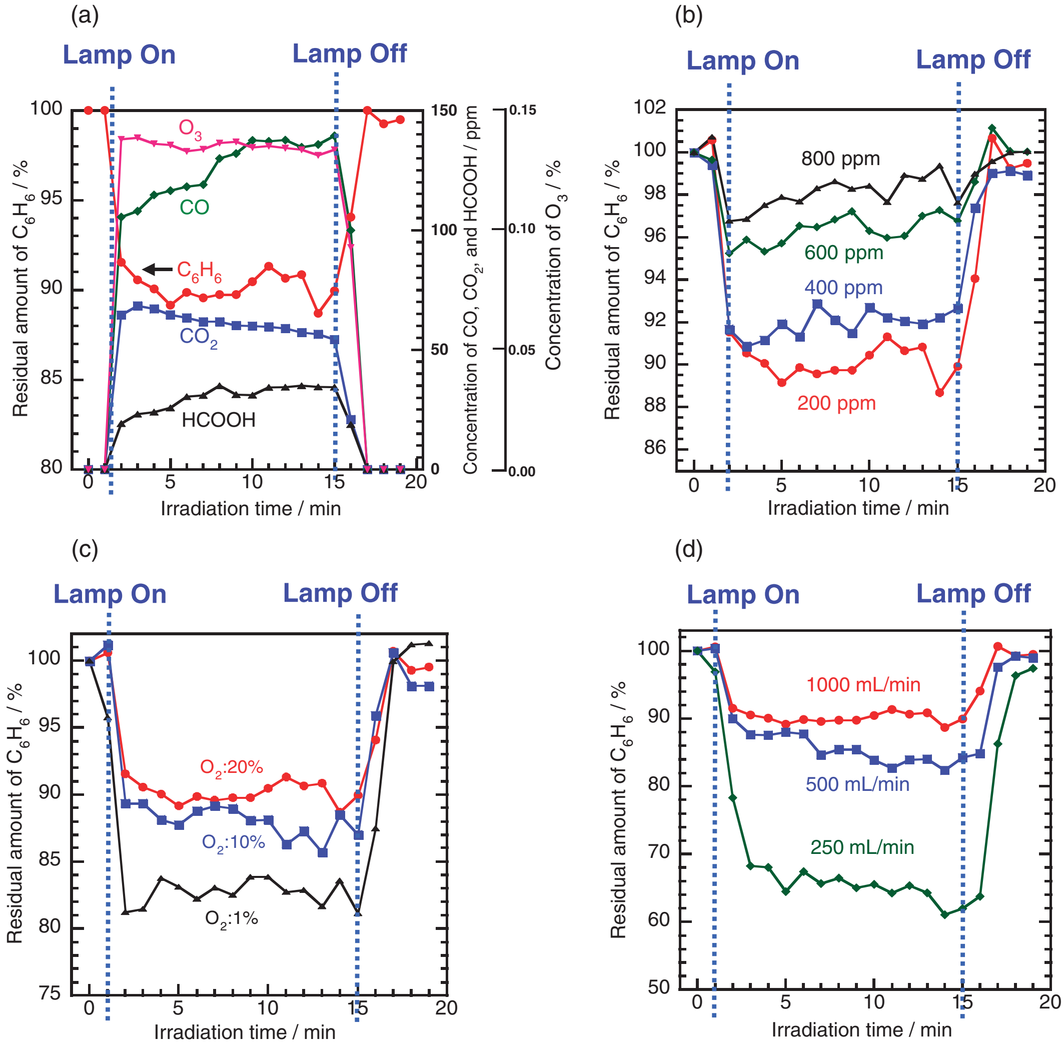


Figure 10. Dependence of the residual amount of C_6H_6 and the concentrations of products and O_3 on the reaction time in the flow system. Excimer lamp was switched on at 1 min and switched off at 15 min. (a) C_6H_6: 250 ppm, total flow rate: 1 L min^{-1}, N_2/O_2 mixture: O_2 20%, (b) C_6H_6: 200–800 ppm, total flow rate: 1 L min^{-1}, N_2/O_2 mixture: O_2 20%, (c) C_6H_6: 250 ppm, total flow rate: 1 L min^{-1}, N_2/O_2 mixture: O_2: 1–20%, (d) C_6H_6: 250 ppm, total flow rate: 250–1000 mL min^{-1}, N_2/O_2 mixture: O_2 20%.

N_2 atmosphere, C_6H_6 was decomposed by photolysis, whereas it was decomposed to HCOOH, CO, and CO_2 in N_2/O_2 mixtures. In the presence of O_2, $O(^3P,^1D)$ and O_3 can be active species for the removal of C_6H_6. It was found that $O(^3P)$ is the most important active species under the 172 nm photolysis of C_6H_6. This provides valuable information for the design of practical removal apparatus of C_6H_6 under VUV photolysis.

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Supporting Information

Dependence of light transmission rate on the distance from light source and possible reaction scheme of the reaction of $O(^3P)$ with C_6H_6 in the initial stage. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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