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Simultaneous Removal of NO₂ and C₆H₆ in an NO₂/C₆H₆ Mixture in Air by 172-nm Xe₂ Excimer Lamp at Atmospheric Pressure

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NO₂ and C₆H₆ in an NO₂(200 ppm)/C₆H₆(200 ppm) mixture were simultaneously removed in air at atmospheric pressure using a 172-nm vacuum ultraviolet (VUV) Xe₂ excimer lamp. Reactants and products before and after photoirradiation were analyzed using an FTIR spectrometer. Results show that NO₂ and C₆H₆ were finally converted to HNO₃ and CO₂, respectively, by 172-nm photolysis of the NO₂/C₆H₆ mixture. Although the removal rate of NO₂ in the NO₂/C₆H₆ mixture was nearly the same as that of pure NO₂ in air, the C₆H₆ removal delayed until a sufficient reduction of NO_x (NO₂, NO, and NO₃) concentrations. In order to obtain information on these results, computer simulation of decomposition processes was carried out. The delay of the C₆H₆ removal in the NO₂/C₆H₆ mixture was explained by 42–82 times larger reaction rate constants of the O(³P) + NO_x reactions than that of the O(³P) + C₆H₆ reaction.

Key words: NO_x, VOC, Excimer lamp, VUV photolysis, Air pollution

1. Introduction

Nitrogen oxides (NO_x = NO + NO₂) and volatile organic compounds (VOCs) are major pollutants in the atmosphere, being a precursor to photochemical smog, acid rain, and ozone accumulation. The most general removal methods of NO_x are based on catalytic reduction of NO_x to elemental nitrogen by gaseous reducing agents, which are either selective (ammonia or ammonium compounds) or nonselective (NO_x, carbon monoxide, and hydrocarbons).¹⁻³⁾ In the selective catalytic reduction process, NO_x is reduced by ammonia over a catalyst to form harmless N₂ and H₂O vapor without creating any secondary pollutants. Non-selective catalytic reduction requires injection of expensive NH₃ or other reducing agents without catalysts.

VOCs are recognized as major contributors to air pollution, either through their toxic nature

or as participants in atmospheric photochemical reactions. They are emitted from different outdoor sources (motor vehicles, incomplete combustion in industrial processes) and from indoor sources.^{4,5)} Current methods to remove VOC from indoor air include plasma oxidation, photocatalytic oxidation, and adsorption by activated carbons.⁶⁻¹²⁾

The plasma discharge method is also used in domestic air cleaners for NO_x and VOC removal. Radicals formed by plasma discharge act as major active species for NO_x and VOC removal.¹³⁾ However, these radicals also oxidize nitrogen and oxygen simultaneously, respectively generating NO_x and ozone.¹⁴⁾ Therefore, the development of a new effective removal method of NO_x and VOC is highly anticipated.

Vacuum ultraviolet (VUV) photolysis of air pollutants is a new promising method for NO_x and VOC removal. Advantages of the VUV photolysis method are that it involves low-temperature operation in air at atmospheric pressure using a simple apparatus and no expensive catalysts. In general, when NO_x and VOCs are decomposed using electric discharge in air, toxic NO_x are formed because collisions of fast electrons generated in discharges with

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N₂ give active N atoms, which provide NO_x by collisions with O₂. In this respect, an additional advantage of 172-nm photochemical method is that no NO_x are emitted because active nitrogen is not generated under 172-nm photoirradiation of N₂.

We have studied removal of such typical NO_x and VOC as NO₂ and C₆H₆ in air using a side-on type of 172-nm excimer lamp.^{15,16)} NO₂ was dominantly converted to HNO₃ after photolysis, whereas C₆H₆ was converted to CO₂ via HCOOH and CO intermediates. Photochemical oxidants are the product of chemical reactions that occur between NO_x and VOCs. Typical photochemical oxidants are ozone (O₃), hydrogen peroxide (H₂O₂), and peroxyacetyl nitrate (PAN). These photochemical oxidants are cause for concern, as they can have negative effects on human, plant, and animal health. Therefore, simultaneous removal techniques of NO_x and VOCs in air at atmospheric conditions are required.

In this study we attempted simultaneous removal of NO₂ and C₆H₆ in an NO₂/C₆H₆ mixture in air by 172-nm photolysis. Air dominantly consists of N₂(80%) and O₂(20%). Although 172-nm photons are not absorbed by N₂, they are absorbed by O₂ through Schumann–Runge continuum.¹⁷⁾ After photoabsorption, O₂ is selectively dissociated into the ground-state O(³P) atom and the metastable-state O(¹D) atom: O₂ + hν (172 nm) → O(³P) + (¹D).¹⁹⁾ O₃ molecules are generated by the subsequent three-body reactions: O(³P) + O₂ + N₂ (or O₂) → O₃ + N₂ (or O₂). Therefore, in addition to direct VUV photodegradation, reactions of O(³P,¹D) and O₃ can participate in removal of an NO₂/C₆H₆ mixture. On the basis of our precious studies,^{15,16)} most important active species in the 172-nm photolysis of pure

NO₂ and C₆H₆ were found to be OH + NO₂ and O(³P) + C₆H₆ are major pathways for the formation of HNO₃ and CO₂ in the initial step. In the present study, removal mechanisms are discussed on the basis of computer simulation of reaction processes.

2. Experimental

Fig. 1 portrays a schematic diagram of side-on type of 172-nm excimer lamp used for this study. Table 1 presents the major performance of the side-on lamp (SL). The input power of the SL was 20 W. Experiments were conducted using the SL at a chamber volume of 235.5 cm³ or 39.3 cm³ where the chamber thicknesses was 3 cm or 0.5 cm, respectively.

Light from an unfocused 172-nm Xe₂ lamp (155–200 nm range, UER20H172; Ushio Inc.) was irradiated into the photolysis chamber through a quartz window. Experiments were conducted using a closed batch chamber at atmospheric pressure. The concentration of NO₂ and C₆H₆ diluted in an N₂/O₂ mixture (20% O₂) was both 200 ppm (v/v). Outlet gases from the photolysis chamber were analyzed using a gas analysis system (FG122-LS; Horiba Ltd.) equipped with an FTIR spectrometer. The spectra in the 700–4000 cm⁻¹ region were monitored. The concentrations of CO, CO₂, HCOOH, and NO₂ were calibrated using standard gases. On the other hand, the HNO₃, N₂O₅, and O₃ concentrations were evaluated by reference to standard spectral data supplied from Horiba Ltd. Thereby, the residual amounts of NO₂ and C₆H₆, C_t/C₀, were inferred from absorbance of FTIR peaks. Here, C₀ is the initial concentration of NO₂ or C₆H₆.

The following gases were used: N₂ (purity >99.9998%; Taiyo Nippon Sanso (TNS) Corp.) O₂ (purity >99.99995%; TNS Corp.), NO₂ (2000 ppm in high-purity N₂; TNS Corp., and C₆H₆ (TNS: 2000 ppm in high purity N₂). FTIR data indicated a small amount of H₂O (300 ppm) is

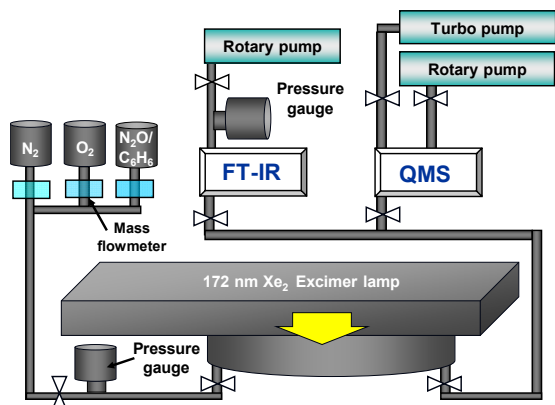
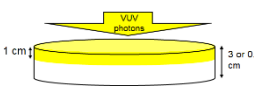


Fig. 1. Side-on type of 172-nm photolysis apparatus.

Table 1. Performance of photolysis chamber using a side-on lamp

VUV irradiation	
Input power	20 W
Irradiance	10 mW/cm ²
Window area	78.5 cm ²
Photon numbers/s	6.83 × 10 ¹⁷ photons/s
Chamber volume	235.5 or 39.3 cm ³

involved in the photolysis chamber as an impurity.

3. Results and discussion

3.1 Removal of NO_2 and C_6H_6 in an $\text{NO}_2/\text{C}_6\text{H}_6$ mixture by 172-nm photolysis in air

Fig. 2 shows FTIR spectra observed before and after 172-nm photolysis of an $\text{NO}_2/\text{C}_6\text{H}_6$ mixture in air (20% O_2) for 15 s at a chamber depth of 3 cm. Before photolysis, a strong NO_2 peak at about 1600 cm^{-1} and a weaker C_6H_6 peak at about 3200 cm^{-1} are observed. After 15 s photoirradiation, although the NO_2 peak disappears, the C_6H_6 peak becomes slightly weak. In addition, N_2O_5 , HNO_3 , HCOOH , CO , CO_2 , and O_3 peaks appear. All of these product peaks have been observed by photolysis of either pure NO_2 or C_6H_6 ^{15,16)} so that no new product peaks, arising from the reactions between NO_2 and C_6H_6 , were observed.

In Fig 3 is shown the dependence of concentrations of (a) NO_2 and C_6H_6 , (b) HCOOH , CO , and CO_2 , and (c) N_2O_5 , HNO_3 , and O_3 on the irradiation time. NO_2 is decomposed completely within 5 s, whereas the decomposition of C_6H_6 occurs more slowly and it takes about 50 s until its complete decomposition. The HCOOH and CO concentrations have peaks at 50–60 s, whereas the CO_2 concentration increases with increasing the irradiation time. These results indicate that HCOOH and CO intermediates are finally converted to CO_2 . The N_2O_5 concentration has a peak at 5 s and decreases rapidly above that. On the other hand, the HNO_3 concentration increases until about 100 s and then levels off above thereafter. It is therefore reasonable to assume that N_2O_5 is efficiently converted to HNO_3 under our condition. The O_3 concentration increases from

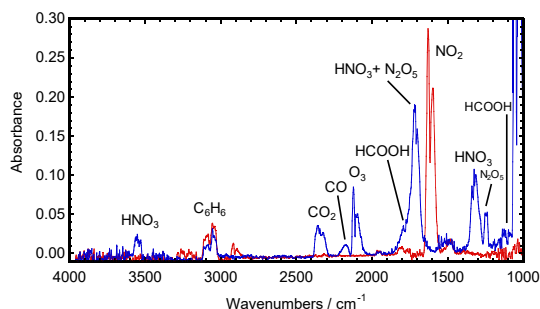


Fig. 2. FTIR spectra observed before (red line) and after 172-nm photolysis (blue line) of an $\text{NO}_2/\text{C}_6\text{H}_6$ mixture in air (20% O_2) for 15 s.

zero to 31,000 ppm with increasing the irradiation time from zero to 300 s.

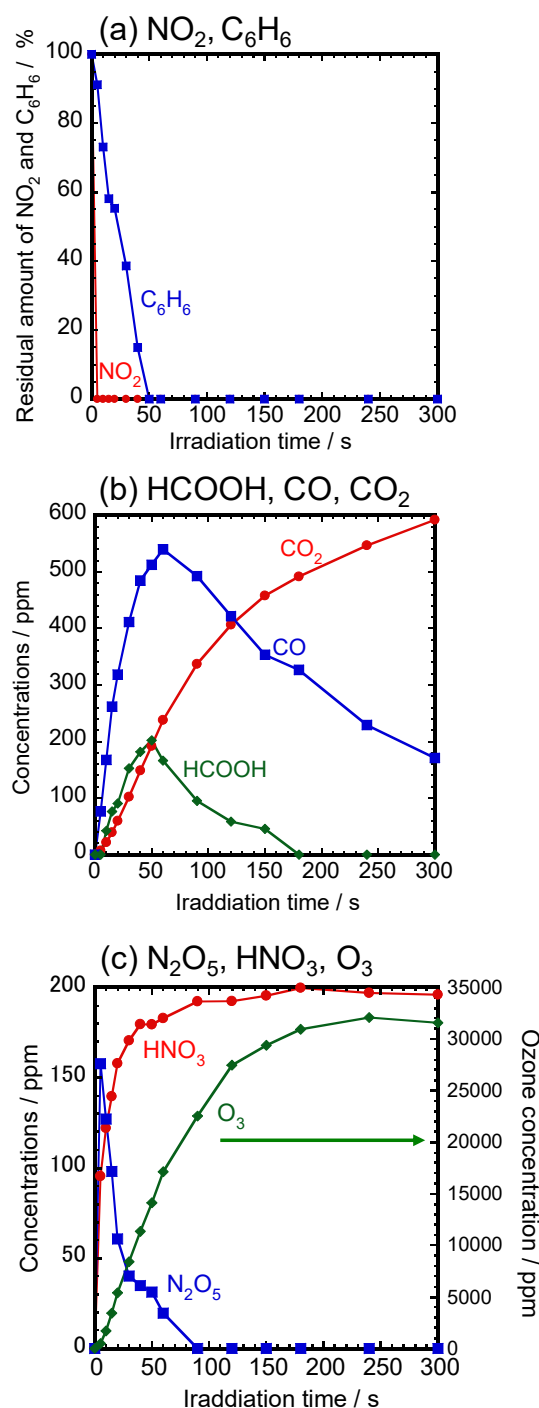


Fig. 3. Dependence of (a) residual amounts of NO_2 and C_6H_6 , (b) concentrations of HCOOH , CO , and CO_2 , and (c) concentrations of N_2O_5 , HNO_3 , and O_3 on the irradiation time in removal of NO_2 and C_6H_6 in an $\text{NO}_2/\text{C}_6\text{H}_6$ mixture by 172-nm excimer lamp in air (20% O_2). The chamber depth was 3 cm.

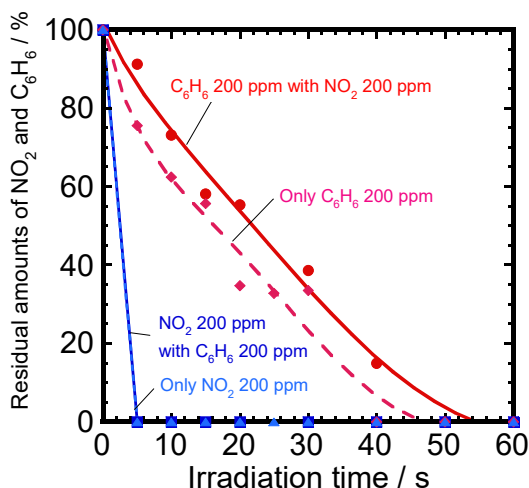


Fig. 4. Dependence of residual amounts of NO₂ and C₆H₆ on the irradiation time in pure NO₂ or C₆H₆ and NO₂/C₆H₆ mixture under 172-nm photolysis in air (20% O₂). The chamber depth was 3.0 cm.

In order to examine effects of mixing NO₂ with C₆H₆, dependence of residual amounts of NO₂ and C₆H₆ on the irradiation time in the NO₂/C₆H₆ mixture was compared with that in pure NO₂ and C₆H₆ (Fig. 4). It should be noted that the removal rate of NO₂ in the NO₂/C₆H₆ mixture is nearly identical to that of pure NO₂. On the other hand, the removal rate of C₆H₆ in the NO₂/C₆H₆ mixture is slower than that of pure C₆H₆, so that the removal curve of C₆H₆ in the NO₂/C₆H₆ mixture shifts to longer irradiation time in comparison with that of pure C₆H₆ by about 10 s.

3.2 Simulation of removal processes of NO₂ and C₆H₆ in an NO₂/C₆H₆ mixture by 172-nm photolysis in air

In our previous studies on 172-nm photolysis of pure NO₂ and C₆H₆, we succeeded in reproducing dependence of their removal amounts on the irradiation time by model calculations.^{15,16} In this study, removal of an NO₂/C₆H₆ mixture is kinetically simulated by solving simultaneous differential equations using Runge–Kutta methods. Table A1 (Appendix) gives experimental parameters used for the simulation. For the simulation, we assumed that such active species as 172-nm photons, O(³P), and O₃ were distributed uniformly within the reaction chamber. At a short chamber length of 0.5 cm, incident light is attenuated by only 7.23% at 20% O₂.^{15,16} Therefore, we conducted removal experiments

of the NO₂/C₆H₆ mixture at 0.5 cm with a small reaction volume (39.3 mL), where the above assumption is expected to be well established. The obtained experimental data for NO₂, C₆H₆, and HNO₃ are presented in Fig. 5(a). The concentration of NO₂ decreases to zero below 5 s, whereas that of C₆H₆ decreases to zero at 10 s. The HNO₃ concentration increases from zero to about 200 ppm after about 30 s.

Table 2 shows elementary reactions used for the simulation. They consist of 172-nm photolysis of O₂ leading to O(¹D) + O(³P) atoms (1),¹⁸ relaxation of O(¹D) to O(³P) (2a)–(2b), three-body reactions leading to O₃ (3a)–(3b), VUV photolysis of O₃ (4a)–(4b), dissociation of O₃ (5)–(7), three-body recombination of O(³P) (8a)–(8b), VUV photolysis of NO₂, (9), NO_x + O₃ reactions (10)–(12), NO_x + O(³P) reactions (13)–(17), other NO_x reactions (18)–(21), and

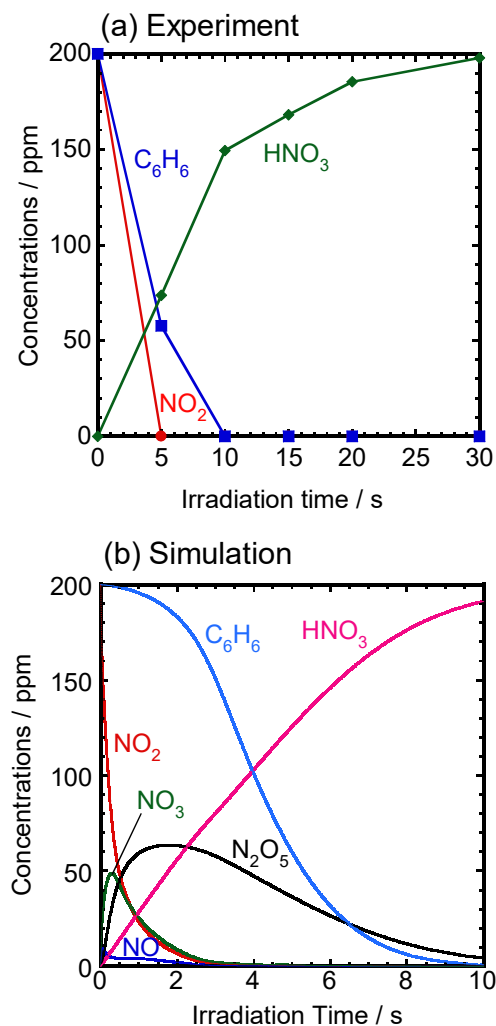


Fig. 5. Dependence of reagents and products on the irradiation time obtained by (a) experiment and (b) simulation. The chamber depth was 0.5 cm.

Table 2

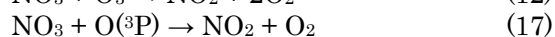
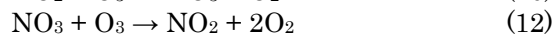
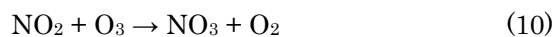
Reactions considered for the simulation of simultaneous removal of NO₂ and C₆H₆ in the NO₂/C₆H₆ mixture by 172-nm photolysis in air.

Chemical equations		
$O_2 + hv \rightarrow O(^3P) + O(^1D)$	σ_1	(1)
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	k_{2a}	(2a)
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	k_{2b}	(2b)
$O(^3P) + O_2 + O_2 \rightarrow O_3 + O_2$	k_{3a}	(3a)
$O(^3P) + O_2 + N_2 \rightarrow O_3 + N_2$	k_{3b}	(3b)
$O_3 + hv \rightarrow O(^3P) + O_2$	σ_{4a}	(4a)
$O_3 + hv \rightarrow 3O(^3P)$	σ_{4b}	(4b)
$O_3 \rightarrow O_2 + O(^3P)$	k_5	(5)
$O_3 + O_3 \rightarrow 3O_2$	k_6	(6)
$O(^3P) + O_3 \rightarrow 2O_2$	k_7	(7)
$2O(^3P) + O_2 \rightarrow O_2 + O_2$	k_{8a}	(8a)
$2O(^3P) + N_2 \rightarrow O_2 + N_2$	k_{8b}	(8b)
$NO_2 + hv \rightarrow NO + O(^3P)$	σ_9	(9)
$NO_2 + O_3 \rightarrow NO_3 + O_2$	k_{10}	(10)
$NO + O_3 \rightarrow NO_2 + O_2$	k_{11}	(11)
$NO_3 + O_3 \rightarrow NO_2 + 2O_2$	k_{12}	(12)
$NO_2 + O(^3P) \rightarrow NO_3$	k_{13}	(13)
$NO_2 + O(^3P) + N_2$ $\rightarrow NO_3 + N_2$	k_{14a}	(14a)
$NO_2 + O(^3P) + O_2$ $\rightarrow NO_3 + O_2$	k_{14b}	(14b)
$NO_2 + O(^3P) \rightarrow NO + O_2$	k_{15}	(15)
$NO + O(^3P) \rightarrow NO_2$	k_{16}	(16)
$NO_3 + O(^3P) \rightarrow NO_2 + O_2$	k_{17}	(17)
$NO_2 + NO_3 \rightarrow N_2O_5$	k_{18}	(18)
$NO_2 + NO_3$ $\rightarrow NO + NO_2 + O_2$	k_{19}	(19)
$NO + NO_3 \rightarrow 2NO_2$	k_{20}	(20)
$N_2O_5 + H_2O \rightarrow 2HNO_3$	k_{21}	(21)
$H_2O + hv \rightarrow OH + O(^3P)$	σ_{22}	(22)
$NO_2 + OH \rightarrow HNO_3$	k_{23}	(23)
$2N_2O_5 \rightarrow 4NO_2 + O_2$	k_{24}	(24)
$N_2O_5 + O(^3P) \rightarrow 2NO_2 + O_2$	k_{25}	(25)
$C_6H_6 + hv \rightarrow \text{products}$	σ_{26}	(26)
$O(^3P) + C_6H_6 \rightarrow \text{Products}$	k_{27}	(27)
$O_3 + C_6H_6 \rightarrow \text{Products}$	k_{28}	(28)

VUV photolysis of H₂O (22), and other NO_x reactions (23)–(25). 172-nm photolysis of C₆H₆ (26) and reactions of C₆H₆ (27)–(28) were also considered.

In the simulation, we used the same reaction rate constants and spectroscopic data as those used in our previous studies.^{15,16} Most of kinetic and spectroscopic data were obtained from Refs. 17–19. The temperature rise of 0.026 K/s in the photolysis chamber after photoirradiation was assumed for the simulation of simultaneous removal of NO₂ and C₆H₆ in the NO₂/C₆H₆ mixture because the temperature of the reaction chamber increases concomitantly with increasing photoirradiation time. The validity of this assumption was confirmed from the time evolution of O₃ in air in our photolysis chamber.¹⁵ Fig. 5(b) shows simulation data for NO₂, NO, NO₃, N₂O₅, HNO₃, and C₆H₆ in the NO₂/C₆H₆ mixture.

In our removal model of NO₂, NO₂ molecules are oxidized to NO₃ by collisions with O₃, whereas NO₃ molecules are reduced to NO₂ by collisions with O₃ and O(^3P).



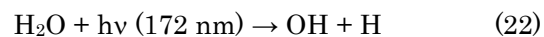
N₂O₅ molecules are formed by the NO₂ + NO₃ reaction.



It was further converted to HNO₃ by the N₂O₅ + H₂O reaction.



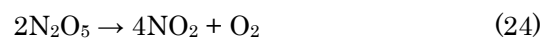
In addition, reactions of OH radicals, formed by 172-nm photolysis of H₂O, are considered.



The NO₂ + OH reaction gives HNO₃.



N₂O₅ formed by the oxidation of NO₂ is reduced again to NO₂ by the first-order reaction.



N₂O₅ is also decomposed by the reaction with O(^3P).

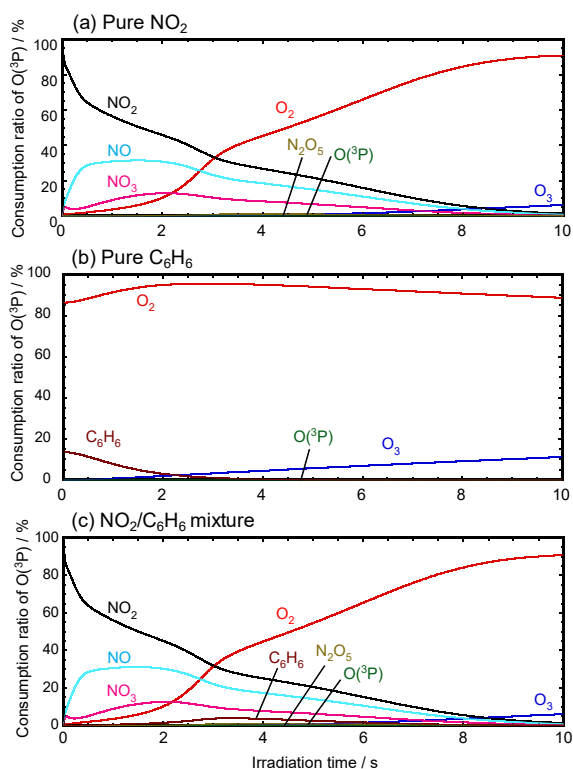
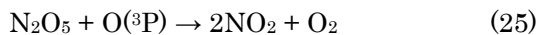


Fig. 6. Dependence of consumption ratio of O(³P) in (a) pure NO₂, (b) pure C₆H₆, and (c) NO₂/C₆H₆ mixture on the irradiation time under 172-nm photolysis. Data were obtained by model calculations. The chamber depth was 0.5 cm.



In our removal model for the NO₂/C₆H₆ mixture (Fig. 5(b)), NO₂ is decomposed below about 3 s. NO₃ and NO are formed below 2 s and disappear at about 3 s. The N₂O₅ concentration increases to about 60 ppm at about 2 s and decreases to 4 ppm at 10 s. On the other hand, the concentration of HNO₃, which is the dominant product in this model, increases gradually from zero to 190 ppm until 10 s. A reasonable agreement is found between the calculated and experimental data for time profiles of the NO₂, HNO₃, and N₂O₅ concentrations, indicating that NO₂ removal proceeds dominantly through our proposed removal model.

Fig. 5(b) also shows removal profile of C₆H₆ calculated taking account of all reactions processes given in Table 2. In our removal model of C₆H₆, C₆H₆ molecules are decomposed by the O(³P) + C₆H₆ reaction. A satisfactory agreement between the experimental and simulation data is obtained for the C₆H₆ removal in the NO₂/C₆H₆ mixture, implying

that our simulation model is applicable to reproduce the removal profile of C₆H₆ in the NO₂/C₆H₆ mixture

Fig. 6 shows the dependence of the consumption ratio of O(³P) on the irradiation time in pure NO₂ or C₆H₆, and NO₂/C₆H₆ mixture obtained by simulations. Results show that the time profile of consumption ratio of O(³P) obtained from the NO₂/C₆H₆ mixture is nearly identical to that obtained from pure NO₂, except for the time profile of consumption ratio of O(³P) by C₆H₆. Below about 3 s, O(³P) atoms are dominantly consumed by NO₂, NO, and NO₃. Although the consumption ratio of O(³P) by O₂ is small below 2 s, it gradually increases above 2 s and it becomes larger than those of NO₂, NO, and NO₃ above about 3 s.

It should be noted that the time profile of consumption ratio of O(³P) by C₆H₆ in the NO₂/C₆H₆ mixture is different from that in pure C₆H₆. The consumption ratio of the O(³P) + C₆H₆ reaction rapidly decreases from 14% to 1.1% in the short 0–3 s range in pure C₆H₆, whereas it occupies only 1.5–4.0 % in the 2–6 s range in the NO₂/C₆H₆ mixture. On the basis of above facts, O(³P) atoms are initially consumed by NO_x in the NO₂/C₆H₆ mixture, so that the consumption of O(³P) by C₆H₆ delays by 4±2 s in the NO₂/C₆H₆ mixture.

We discuss below the reason why the time profile of consumption ratio of O(³P) by C₆H₆ in the NO₂/C₆H₆ mixture is different from that in pure C₆H₆ using known reaction rate constants of related reactions. Removal of NO₂ and C₆H₆ occurs competitively in the NO₂/C₆H₆ mixture. The reaction rate constant of the O(³P) + C₆H₆ reaction ($k_{27} = 4.04 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) is smaller than those of the O(³P) + NO₂ reactions ($k_{13} + k_{15} = 3.33 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) by a factor of 82.¹⁹ It is also smaller than those of the O(³P) + NO reaction ($k_{16} = 2.99 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) and O(³P) + NO₃ reaction ($k_{17} = 1.70 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$) by factors of 74 and 42, respectively.¹⁹ Therefore, O(³P) atoms are initially consumed by reactions with such NO_x as NO₂, NO, and NO₃. The O(³P) + C₆H₆ reaction occurs after the NO₂, NO, and NO₃ concentrations become low, where the initial NO₂ concentration is reduced to about half. The consumption of O(³P) by NO_x in the initial stage is attributed to the main reason why the C₆H₆ removal delayed until a sufficient reduction of NO_x.

For the practical use of our removal method, a flow system, by which continuous removal of NO₂/C₆H₆ is possible, is required. On the basis of the present results, a long reaction chamber

is necessary for the simultaneous removal of NO_2 and C_6H_6 in the $\text{NO}_2/\text{C}_6\text{H}_6$ mixture using a flow system, where NO_2 must be removed to some extent upstream and the C_6H_6 is removed downstream at low NO_2 concentrations.

4. Summary and Conclusion

NO_2 and C_6H_6 in an $\text{NO}_2/\text{C}_6\text{H}_6$ mixture were simultaneously removed in air at atmospheric pressure using a 172-nm Xe_2 excimer lamp. Reactants and products before and after photoirradiation demonstrated that NO_2 and C_6H_6 were finally converted to HNO_3 and CO_2 , respectively. Although the removal rate of NO_2 in the $\text{NO}_2/\text{C}_6\text{H}_6$ mixture was nearly the same as that of pure NO_2 in air, the C_6H_6 removal delayed until the NO_2 concentration is reduced to about half. In order to obtain information on these results, computer simulation of removal processes of NO_2 and C_6H_6 in the $\text{NO}_2/\text{C}_6\text{H}_6$ mixture was carried out. The delay of the C_6H_6 removal in the $\text{NO}_2/\text{C}_6\text{H}_6$ mixture was explained by much larger reaction rate constants of the $\text{O}(^3\text{P}) + \text{NO}_x$ reactions than that of the $\text{O}(^3\text{P}) + \text{C}_6\text{H}_6$ reaction. The present results give fundamental information on the development of photochemical removal apparatus of mixtures of NO_x/VOC .

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References

- 1) M. Devadas, O. Krocher, M. Elsener, A. Wokaun, N. Soger, M. Pfeifer, and Y. Demel, *Appl. Catal. B Environ.*, 67, 187 (2006).
- 2) R. M. Heck, R. J. Farrauto, and S. T. Gulati, *Catalytic air pollution control: commercial technology*, Vol. 522. (2009). Wiley, Hoboken.
- 3) T. Ye, D. Chen, Y. Yin, J. Liu, and X. Zeng, *Catalysts*, 7, 258 (2017).
- 4) R. Pal, K. H. Kim, Y. J. Hong, and E. C. Jeon, *J. Hazard. Mater.*, 153, 1122 (2008).
- 5) D. A. Sarigiannis, S. P. Karakitsios, A. Gotti, I. L. Liakos, and A. Katsoyiannis, *Environ. Int.*, 37, 743 (2011).
- 6) M. Balcerek, K. Pielech-Przybylska, P. Patelski, U. Dziekońska-Kubczak, and T. Jusel, *Food. Addit. Contam. Part A*, 34, 714 (2017).
- 7) H. L. Chen, J. M. Lee, S. H. Chen, M. B. Chang, S. J. Yu, and S. N. Li, *Environ. Sci. Technol.*, 43, 2216 (2009).
- 8) Y. El-Sayed and T. J. Bandosz, *Langmuir*, 18, 3213 (2002).
- 9) T. Hayashi, M. Kumita, and Y. Otani, *Environ. Sci. Technol.*, 39, 5436 (2005).
- 10) J. H. Mo, Y. P. Zhang, Q. Xu, J. J. Lamson, and R. Zhao, *Atmos. Environ.*, 43, 2229 (2009).
- 11) M. Tomatis, H. H. Xu, J. He, and X. D. Zhang, *J. Chem.*, 8324826 (2016).
- 12) A. M. Vandenbroucke, R. Morent, N. De Geyter, and C. Leys, *J. Hazard. Mater.*, 195, 30. (2011).
- 13) M. Okubo, T. Yamamoto, T. Kuroki, and H. Fukumoto, *IEEE Trans. Ind. Appl.*, 37, 1505 (2001).
- 14) N. Sano, T. Nagamoto, H. Tamon, T. Suzuki, and M. Okazaki, *Ind. Eng. Chem. Res.*, 36, 3783 (1997).
- 15) M. Tsuji, T. Kawahara, K. Uto, N. Kamo, M. Miyano, J.-I. Hayashi, and T. Tsuji, *Environ. Sci. Pollut. Res.*, 25, 18980 (2018).
- 16) M. Tsuji, T. Kawahara, K. Uto, J.-I. Hayashi, and T. Tsuji, *Int. J. Environ. Sci. Technol.*, in press (2019). <https://doi.org/10.1007/s13762-018-2131-y>.
- 17) H. Okabe, *Photochemistry of small molecules*, Wiley, New York (1978).
- 18) J. B. Nee and P. C. Lee, *J. Phys. Chem. A*, 101, 6653 (1997).
- 19) R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson Jr, J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data*, 26, 1329 (1997). Updated data were obtained from NIST Chemical Kinetics Database on the Web, Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data Version 2017.07. <http://kinetics.nist.gov/kinetics/index.jsp>

Appendix

Table A1. Parameters used for the simulation of simultaneous removal of NO_2 and C_6H_6 in the $\text{NO}_2/\text{C}_6\text{H}_6$ mixture by 172-nm photolysis in air.

Absorption cross section of O_2 at 172 nm	$\sigma_1 = 4.63 \times 10^{-19}$ [cm ² /molecule]
Absorption cross section of O_3 at 172 nm	$\sigma_4 = 8.16 \times 10^{-19}$ [cm ² /molecule]
Branching fraction of photolysis of O_3 at 172 nm	4a : 4b =
$\text{O}_3 + h\nu$	0.9 : 0.1
$\rightarrow \text{O}(^3\text{P}) + \text{O}_2$ (4a)	
$\rightarrow 3\text{O}(^3\text{P})$ (4b)	
Absorption cross section of NO_2 at 172 nm	$\sigma_9 = 1.45 \times 10^{-17}$ [cm ² /molecule]
Absorption cross section of C_6H_6 at 172 nm	$\sigma_{26} = 6.48 \times 10^{-21}$ [cm ² /molecule]
Absorption cross section of H_2O at 172 nm	$\sigma_{22} = 8.16 \times 10^{-19}$ [cm ² /molecule]
Initial reaction temperature	297.6 [K]
Initial concentration of N_2	80 [%]
Initial concentration of O_2	20 [%]
Initial concentration of C_6H_6	200 [ppm]
Initial concentration of NO_2	200 [ppm]
Initial concentration of H_2O	300 [ppm]
The number of repetitions per sec	1000 [times/s]