九州大学大学院総合理工学報告
第30巻　第2号　294-298頁　平成20年9月

Engineering Sciences Reports, Kyushu University
Vol. 30, No. 2, pp. 294-298, SEP. 2008

Photochemical Removal of NO by Using 172-nm Excimer Lamp without Using Any Catalysts

Masaharu TSUJI, *1,2,† Masashi KAWAHARA,*3 Makoto SENDA*3
Naohiro KAMO,*3 Takashi KAWAHARA,*3 Nobuyuki HISHINUMA*4
†E-mail of corresponding author: *tsuji@cm.kyushu-u.ac.jp*

(Received July 31, 2008)

Photochemical removal of NO by 172-nm Xe_2 excimer lamps (50 or 300 mW/cm^2) was studied at 1 atm. In a batch system, NO could completely be converted to N_2 and O_2 in N_2, and N_2O_5 and HNO_3 in air after about 30 min irradiation using a 300 mW/cm^2 high-power lamp. NO could also be decomposed in a flow system using the high-power lamp. The conversion of NO in N_2 and air (10–20% O_2) was 50% and 30-33%, respectively. The present results provide a new simple photochemical aftertreatment technique of NO in air without using any catalysts.

Key words: *deNOx; VUV photolysis; excimer lamp; environmental technology*

1. Introduction

We have recently initiated development of a photochemical method as a new promising removal method of NO*x* at atmospheric pressure without using expensive catalysts.[1-7] An advantage of photochemical method is that more selective decomposition of NO*x* is possible than NO*x* removal by using conventional electric discharge methods. We have recently studied decomposition of N_2O and NO_2 into N_2 and O_2 by using a 193-nm ArF excimer laser in N_2 at atmospheric pressure.[1-4]

When ArF excimer laser photolysis was applied to practical NO*x* removal process, there are a lot of severe problems.[1-4] They are that excimer laser apparatus is expensive, running cost is high, and the apparatus is big and heavy including high power sources. Another disadvantage is that NO, which is generally emitted in exhausted gases, can not be removed. This is because the dissociation energy of NO(6.496 eV eV) is higher than that of photon energy of ArF laser (6.43 eV).[8,9]

In order to overcome these problems, we used here low cost and compact Xe_2 lamps as a new VUV right source. Since the photon energy of 172 nm Xe_2 excimer lamp (7.21) is higher than the dissociation of NO, decomposition of NO is energetically possible. In the present study, we have attempted NO removal by using 172-nm Xe_2 excimer lamps. For the practical application of the photochemical process, not only a closed batch system but also a flow system was applied to NO removal in N_2 and air.

2. Apparatus

Fig. 1 shows a photolysis chamber having an inside volume of 185 cm^3 used in this study. Light from an unfocused 172-nm Xe_2 lamp (USHIO, UER20H172: 50 or 300 mW/cm^2, 155–200 nm range) was used to remove NO at a room temperature. The low-power Xe_2 lamp was a commercial product, whereas the high-power one was a trial product of USHIO

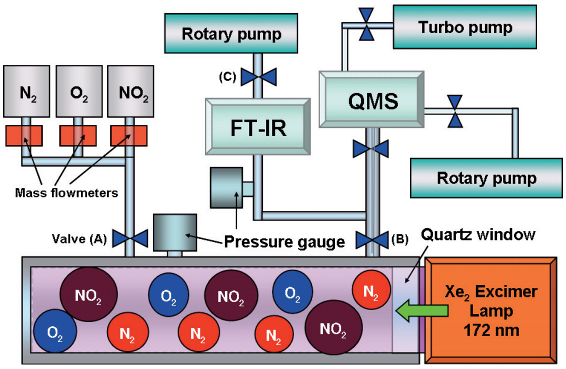


Fig. 1. DeNO chamber by using 172-nm Xe_2 excimer lamp.

---

*1 Institute for Material Chemistry and Engineering
*2 Department of Applied Science for Electronics and Materials
*3 Department of Applied Science for Electronics and Materials, Graduate student
*4 Ushio Inc., Himeji, Hyogo

Inc. The size of a low-power Xe_2 lamp was $\phi = 30$ mm and length = 200 mm, whereas that of a high-power Xe_2 lamp was $\phi = 70$ mm and length = 240 mm.

Experiments were carried out not only in a closed batch system but also a flow system. The total pressure was kept at atmospheric pressure and the NO concentration diluted in pure N_2 or air (5–20% O_2) was 100 or 200 ppm (v/v). In the batch system, desired gas mixtures were introduced through mass flow controllers and valves (A) and (B) in Fig. 1 were closed. Then, the lamp was irradiated from the right side. In the flow system, stop valves (A), (B), and (C) were open during experiments and the flow rates of each gas were controlled by mass flow controllers. It was kept at 1 *l*/min in the present experiments. The total pressure was controlled by using valve (B).

In the batch experiments, before and after photo-irradiation, outlet gases were analyzed by using HORIBA gas analysis system (FG122-LS) equipped with an FTIR spectrometer and ANELVA gas analysis system (M-200GA-DTS) equipped with a quadrupole mass spectrometer. On the other hand, outlet gases were analyzed on line by using the FTIR spectrometer in the flow experiments. The low sensitive mass spectrometer was used for the determination of N_2/O_2 ratios of buffer gases, whereas the high sensitive FTIR system was used for the detection of NO_x and O_3. The light path length and volume of analyzing chamber in FTIR was 2.4 m and 300 cm^3, respectively. The spectra were measured in the 900-5000 cm^{-1} region with an optical resolution of 4 cm^{-1}. The reliable calibration curves of NO_x (NO, NO_2, and N_2O) in FTIR measurements were supplied by HORIBA Inc. The detection limits of NO, NO_2, and N_2O were, 1, 1, and ~0.5 ppm in our FTIR spectrometers, respectively. The concentration of O_3 was evaluated by reference to its standard spectral data supplied by HORIBA Inc. We determined the residual amount of NO, $[NO]/[NO]_0$, and the formation ratios of NO_2, N_2O, N_2, and O_2 defined as $[NO_2]/[NO]_0$, $[N_2O]/[NO]_0$, $[N_2]/[NO]_0$, and $[O_2]/[NO]_0$, respectively, from gas analyses. Here, $[NO]_0$ is an initial concentration of NO. N_2 and O_2 cannot be detected by FTIR, because these diatomic molecules are inactive for IR light. If other NO_x such as NO, NO_2, and N_2O and O_3 are produced in the photolysis, all of them can be detected. Thus, the formation ratios of N_2 and O_2 in N_2 were determined from N and O balance before and after photolysis.

The following gases were used without further purification: N_2(Taiyo Nissan Inc.: purity >99.9998 %), O_2(Nippon Sanso Inc.: purity >99.99995 %), and NO(Taiyo Nissan Inc.: 2.02 % in N_2). NO was diluted in N_2 or N_2/O_2 mixtures before use.

3. Results and discussion

3.1 NO removal in a batch system

Fig. 2 shows the dependence of residual amount of NO and the formation ratios of products in N_2 on the irradiation time of lamp (50 mW/cm^2). NO can be decomposed into N_2 and O_2 without emissions of high concentrations of NO_2 and N_2O. When 193-nm ArF excimer laser was irradiated to NO, it could not be decomposed because photon energy (6.43 eV) is lower than the dissociation energy of NO (6.496 eV).[8,9]

$$NO + h\nu\ (193\ nm) \rightarrow N(^4S) + O(^3P) - 0.08\ eV \qquad (1)$$

However, the photon energy of 172-nm excimer lamp (7.21 eV) is higher than that of the dissociation energy of NO, it can be decomposed via process (2) and finally converted to N_2 and O_2.[6,8,9]

$$NO + h\nu\ (172\ nm) \rightarrow N(^4S) + O(^3P) + 0.71\ eV \qquad (2)$$

Fig. 3 shows the dependence of residual amount of NO and the formation ratios of products in N_2 on the concentration of NO from 94 to 1065 ppm after 10 min photo-irradiation (50 mW/cm^2 lamp). The residual amount of NO

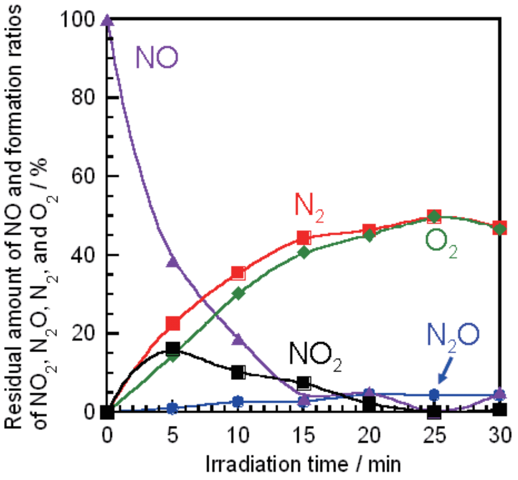


Fig. 2. Dependence of residual amount of NO and the formation ratios of products on the irradiation time of 172-nm excimer lamp (50 mW/cm^2) at a NO concentration of 100 ppm in N_2 at a total pressure of 1 atm.

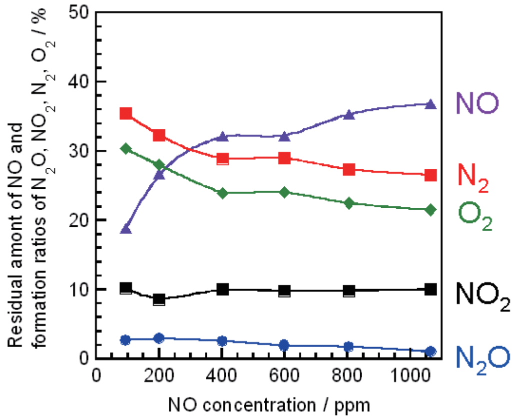


Fig. 3. Dependence of residual amount of NO and the formation ratios of products in N_2 on the concentration after 10 min photo-irradiation of a low-power excmer lamp (50 mW/cm^2).

increases from 19 to 37% with increasing the NO concentration from 94 to 1065 ppm. The formation ratio of NO_2 is nearly constant (~10%) and that of N_2O slightly decreases from 3 to 1% in the same NO concentration range. This result shows that NO conversion decreases only by a factor of two, even though NO concentration increases by a factor of about 10 in the 94-1065 ppm range.

Figs. 4a and 4b show FTIR spectra of NO (200 ppm) in air (10% O_2) before and after 30 min photo-irradiation by using a high-power excimer lamp (300 mW/cm^2). Before, photo-irradiation, weak NO and NO_2 peaks are observed. After 10 min photo-irradiation, the intensity of NO peak decreases, whereas that of NO_2 increases (not shown in Fig. 4). After 30 min photo-irradiation, NO and NO_2 peaks disappear, and besides strong O_3 peaks, N_2O_5 and HNO_3 peaks appear. On the basis of these findings, 172-nm photolysis processes of NO in air can be separated to two stages. Since absorption coefficient of O_2 at 172 nm is larger than that of NO by a factor of 9,[6,7] and concentration of O_2 is higher than that of NO by a factor of 500, direct photolysis of NO (2) will be insignificant for NO removal in the presence of O_2(10%).

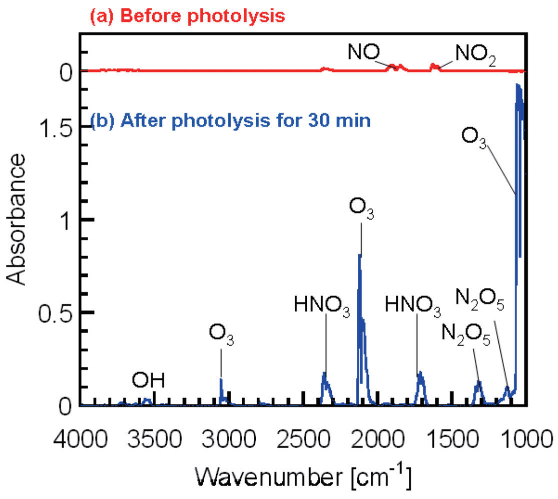


Fig. 4. FTIR spectra of NO (200 ppm) in air (10% O_2) before and after 30 min photo-irradiation by using a high-power excimer lamp (300 mW/cm^2).

At the first stage of NO photolysis in air, NO is converted to NO_2 through reactions (3) and (4) at thermal energy.[10,11]

$$NO + O + M \rightarrow NO_2 + M$$
$$(1.0 \times 10^{-31}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}\ for\ M{=}N_2}) \qquad (3)$$

$$2NO + O_2 \rightarrow 2NO_2$$
$$(1.93 \times 10^{-38}\ \mathrm{cm^6\ molecule^{-2}}) \qquad (4)$$

Without addition of NO, a high concentration (about 2%) of O_3 is produced in air under 172-nm photo-irradiation. O_3 is produced via famous VUV photolysis of O_2 followed by the three-body reaction.[10,11]

$$O_2 + h\nu\,(172\ \mathrm{nm}) \rightarrow O + O$$
$$(4.6 \times 10^{-19}\ \mathrm{cm^2\ molecule^{-1}}) \qquad (5)$$

$$O + O_2 + M \rightarrow O_3 + M$$
$$(5.6 \times 10^{-34}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}\ for\ M{=}N_2}) \qquad (6)$$

At short irradiation times, the concentrations of NO and NO_2 are high, whereas the concentration of O_3 is low. Under these conditions, O_3 is completely consumed through the following processes.[10,11]

$$NO_2 + h\nu\,(172\ \mathrm{nm}) \rightarrow NO + O(^3P, ^1D, ^1S) \qquad (7)$$

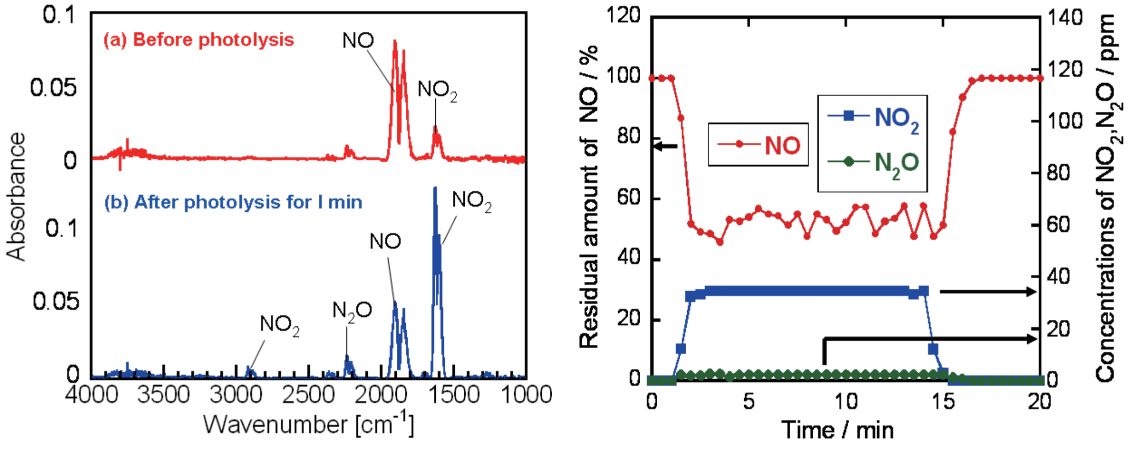
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$(1.8 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \qquad (8)$$

These cyclic reactions, which are famous reactions as destruction of ozone layer in the upper atmosphere,[12] occur significantly. In this case, O_3 can not be observed.

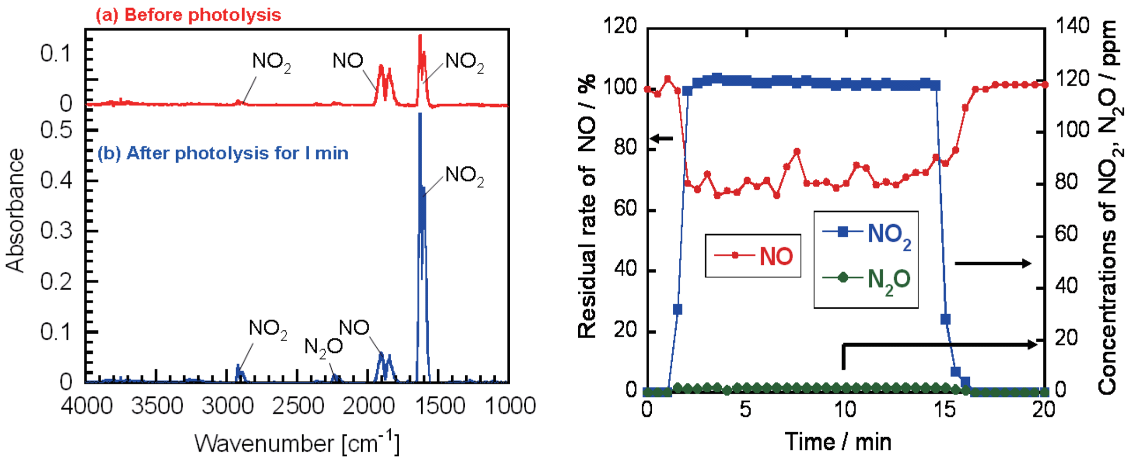
In the second stage, the concentration of O_3 becomes sufficiently high, so that extra O_3 is accumulated in the photolysis chamber. In such a case, O_3 concentration is higher than that required for (8) and the reaction of excess O_3 with NO_2 leading to N_2O_5 via NO_3 takes place.[10,11]

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (9)$$
$$(3.5 \times 10^{-17}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}})$$

(a) N_2



(b) Air (10% O_2)



(c) Air (20% O_2)

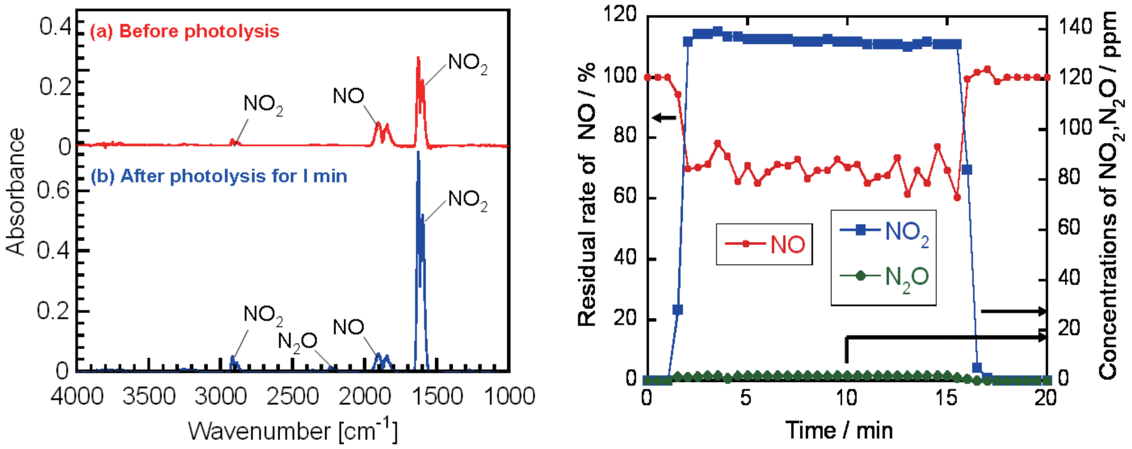


Fig. 5. FTIR spectra and dependence of residual amount of NO and the concentrations of products on the irradiation time of 172-nm excimer lamp (300 mW/cm^2) at a NO concentration of 200 ppm in N_2, and air (10 or 20% O_2) at a total pressure of 1 atm in a flow system.

$$NO_2 + NO_3 + N_2 \rightarrow N_2O_5 + N_2 \quad (10)$$
$$(3.6 \times 10^{-30}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}})$$

Then, N_2O_5 peaks are observed.

In the photolysis chamber, there is a small amount of residual H_2O (~90 ppm), as observed weak OH peaks from residual H_2O in FTIR spectra (e.g. Fig. 4). N_2O_5 has a high reactivity with H_2O leading to HNO_3.[10,11]

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (11)$$
$$(2.5 \times 10^{-22}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}})$$

Therefore, HNO_3 peaks are also observed after 30 min photo-irradiation. The observation of N_2O_5 and HNO_3 is consistent in our recent study on NO_2 under 172-nm photolysis, where the same products were obtained as dominant final products.[6]

3.2 NO removal in a flow system

Figs. 5a–5c show FTIR spectra and the dependence of residual amount of NO and concentrations of NO_2 and N_2O on the irradiation time of lamp in a flow system in the O_2 concentration range of 0–20%. In the FTIR spectra, not only NO but also NO_2 was observed due to reaction (4) before photo-irradiation. The relative intensity of NO_2 to that of NO in air (10, 20% O_2) was higher than that in N_2. The Xe_2 lamp was switched on at 1 min and switched off at 15 min. After photo-irradiation NO peaks decrease, whereas NO_2 peaks become strong. A weak N_2O peak is also observed. In N_2, about 50% of NO was converted to NO_2, N_2O, N_2, and O_2. On the other hand, about 33 and 30% of NO were converted to NO_2, N_2O, N_2, and O_2 in air at O_2 concentrations of 10 and 20%, respectively. In both cases, dominant products are NO_2 resulting from reactions (3) and (4). These results show that NO can be converted to NO_2. However, all O_3 is consumed via NO cycle reactions (7) and (8). Therefore, excess O_3, which can produce N_2O_5 and HNO_3 via subsequent reactions (9)–(11), are absent in these experimental conditions. In the flow system, NO is continuously supplied and destroy O_3 efficiently through reaction (8), the conversion of NO to N_2O_5 and HNO_3 are suppressed greatly.

4. Conclusions

In summary, NO removal process by using 172-nm excimer lamp has been studied to develop a new photochemical removal process without using any catalysts. It was found that NO could be converted to N_2 and O_2 in N_2 and N_2O_5 and HNO_3 in air in the batch system after 30 min photo-irradiation using the high-power 300 mW/cm² lamp. In a flow stem, about 50% of NO in N_2 and 30–33% of NO in air could be converted to NO_2. In air, a high concentration of O_3 was produced due to an efficient 172-nm photolysis of O_2. However, NO destroys O_3 very efficiently. Therefore, it was difficult to convert NO_2 to N_2O_5 and HNO_3 in air even the concentration of NO was kept at a low level (200 ppm). N_2O_5 can be easily removed as HNO_3 by the addition of H_2O. There is an efficient catalyst, which can reduce HNO_3 to N_2. Thus, if NO can be converted to N_2O_5 and finally to HNO_3 by using O_3, this technique becomes more useful method for NO removal in air. In order to overcome this problem, further improvement of deNO apparatus, proving rapid conversion of NO to N_2O_5 and HNO_3, will be required.

Acknowledgments

This work was partly supported by Joint Project of Chemical Synthesis Core Research Institutions. The authors thank Ushio Corporation for the use of a high power lamp.

References

1) M. Tsuji, J. Kumagae, T. Tsuji, T. Hamagami, *J. Hazard. Mater.*, 2004, *108*, 189.
2) M. Tsuji, K. Noda, H. Sako, T. Hamagami, T. Tsuji, *Chem. Lett.*, 2005, *34*, 496.
3) M. Tsuji, H. Sako, K. Noda, M. Senda, T. Hamagami, T. Tsuji, 2005, *Chem. Lett.*, *34*, 812.
4) M. Tsuji, H. Sako, M. Senda, K. Noda, T. Hamagami, M. Kawahara, T. Tsuji, *Focus on Hazardous Materials Research*, Edited by Leonora G. Mason, Nova Science Publishers, New York, 2007, Chapter 4, pp. 143-163.
5) M. Tsuji, M. Kawahara, M. Senda, K. Noda*, Chem. Lett.*, 2007, *36*, 376.
6) M. Tsuji, M. Kawahara, M. Senda, K. Noda, H. Sako, N. Kamo, K. S. N. Kamarudin, *J. Hazard. Mater. In press* (2008).
7) M. Tsuji, N. Kamo, M. Senda, M. Kawahara, T. Kawahara, N. Hishimuma *J. Hazard. Mater*, submitted.
8) H. Okabe, *Photochemisty of Small Molecules*. 1978, John Wiley & Sons, New York.
9) NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June 2005 Release (http://webbook.nist.gov/chemistry/).
10) IUPAC Gas *Kinetic Data Evaluation, Summary Table of Kinetic Data,* June 2006 (*http://www.iupac-kinetic.ch.cam.ac.uk*).
11) R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, M. J. Rossi, J. Troe. J. Phys. Chem. Ref. Data 26 (1997) 1329-1499. Updated data were obtained from NIST Chemical Database on the Web, Public Beta Release 1.4, Standard Reference Database 17, Version 7.0 (*http://kinetics.nist.gov/kinetics/* index.jsp).
12) D.J. Jacob, Introduction to Atmospheric Chemistry, Princeton Univ. Press, New Jersey, 1999.