

# OH Radicals as Oxidizing Agent for the Abatement of Organic Pollutants in Gas Flows by Dielectric Barrier Discharges<sup>1</sup>

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OH radicals play an essential role in various plasma-chemical processes aimed at the abatement of organic and inorganic pollutants from off-air flows. We report about the oxidation of carbon monoxide in nonthermal air and nitrogen plasmas in dependence on CO inlet concentration and flow humidity. Thereby the reaction  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$  served as a diagnostic tool for OH radical determination in the dielectric barrier discharge at atmospheric pressure. The results were numerically fitted to the equations of a kinetic model allowing the determination of the average OH production efficiency ( $G_{\text{OH}}$ -value) and OH lifetime ( $T_{\text{OH}}$ ) in dependence on flow humidity. Finally, results on ethyl acetate abatement obtained under similar experimental conditions were modeled by OH radical decomposition.

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**KEY WORDS:** VOC abatement; hydroxyl radicals; CO oxidation, nonthermal plasma.

## 1. INTRODUCTION

In the past ten years nonthermal plasmas have been more and more accepted as an efficient tool for the abatement of inorganic as well as organic gas-phase pollutants. Such plasmas are generally produced by e-beams, dielectric barrier and corona discharges or in electrified packed-beds. The main plasma-chemical effect is based on free-radical-initiated decomposition of pollutant molecules.<sup>(1)</sup>

In the case of organic pollution in air streams, complete oxidation is the most desirable method of treatment, leading to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and easily collectable acids. Among the various active plasma species, OH radicals with their high oxidizing potential, are of great importance. They initiate the removal of most volatile organic

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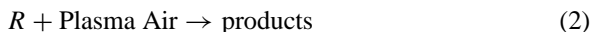
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compounds in atmospheric off-air flows like acetates, aromates or ketones as well as chlorinated hydrocarbons like trichloroethylene. So, the effectiveness of OH generation is one of the key characteristics of a nonthermal plasma source for pollution control. In electric-discharge driven reactors these radicals are mainly created by dissociation of water molecules by direct electron impact, as well as by excited atomic oxygen ( $O(^1D)$ ) and nitrogen ( $N_2^*$ ,  $N^*$ ) collisions. At atmospheric pressure their lifetime is low, usually in the order of some 100  $\mu s$ .

In a previous paper<sup>(2)</sup> the concentration dependence of the removal of volatile organic compounds in dry and humid air flows was studied in two reactors of different scale. The organic pollutant removal rates could be interpreted in terms of an exponential function

$$S(E) = S_o \exp(-E/\beta), \quad \beta = (k_s T_R G_R)^{-1} + S_o/G_R \quad (1)$$

where  $S_o$  and  $S$  denote the initial and final hydrocarbon concentrations,  $G_R$  is the average production efficiency (G-value) of the attacking radical  $R$ ,  $T_R$  is its lifetime with respect to the radical scavenging reaction

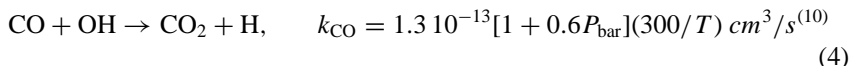


and  $k_s$  is the rate constant of the radical-pollutant interaction

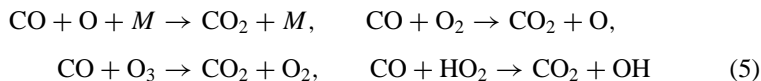


Finally the treatment of ethyl acetate, toluene and acetone in laboratory air was suggested to be controlled by OH radicals with  $G_{OH} \sim 2-5$  ppm/(Wh/Nm<sup>3</sup>) and  $T_{OH}$  in the order of some 100  $\mu s$ .

OH radicals in ac or pulsed discharges have been measured by laser-induced fluorescence<sup>(3-5)</sup> and resonant absorption spectroscopy.<sup>(6)</sup> Campell *et al.*<sup>(7)</sup> used <sup>14</sup>CO as a tracer for the measurement of atmospheric hydroxyl radical concentrations. Su *et al.*<sup>(8)</sup> have applied the nonradioactive version of this method to a nonthermal argon-water plasma. Based hereon we could make a direct proof of the OH radical hypothesis<sup>(2)</sup> by studying CO oxidation in a humid air flow with 2% of water vapor in dependence on plasma energy density at various inlet concentrations.<sup>(9)</sup> The main oxidation pathway



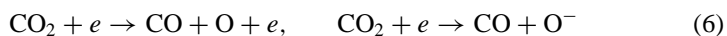
was shown not to be influenced by minor side reactions like



An average  $G_{OH}$ -value of 3.4 ppm/(Wh/Nm<sup>3</sup>) ( $G = 0.41$ ) could be deduced, together with a lifetime of the OH radicals of  $\sim 200$   $\mu s$ .

The advantage of using CO (4) instead of an organic tracer (3) as a probe for studying OH radicals is the absence of any reaction chain with intermediate products, where further OH radicals could be consumed not considered in the overall removal function (1).

In this paper we present further results of the CO oxidation study in dielectric barrier discharges. In these measurements the plasma energy density was more or less fixed and both the carbon monoxide inlet concentration  $\text{CO}_0$  and the flow humidity were varied. The oxidation process itself was quantified by monitoring the amount of synthesized  $\text{CO}_2$ . This is based on the experimental result, that synthesized  $\text{CO}_2$  was not dissociated by electron impact within the experimental error of  $\pm 1$  ppm.<sup>(9)</sup>



The OH production and lifetime parameters were deduced by a nonlinear fitting procedure. Finally, ethyl acetate removal, studied under the same experimental conditions, was modeled on the basis of OH radical attack.

## 2. EXPERIMENTAL SET-UP

The laboratory scale dielectric barrier discharge reactor consisted of a cylindrical glass barrier of 400 mm length with an inner diameter of 23 mm. An outer metallic mesh served as ground electrode and a stainless steel tube of 21.3 mm diameter as hv electrode, leaving a gap of approximately 1 mm (23.7 cm<sup>3</sup> of plasma volume). The reactor was excited by positive pulses of 19 kV amplitude and 45  $\mu\text{s}$  rise time. The pulse repetition rate could be varied between 1 and 107 s<sup>-1</sup>.

The plasma pulse energy was determined using the voltage-charge method (Fig. 1). The discharge voltage  $U$  and the voltage at the integrating capacitor  $U_c$  were recorded by hv probes (Tektronix P6015A, P6009) and a digital storage oscilloscope (Tektronix TDS 520C). The area of the Lissajous figure, representing the energy deposited during one pulse, was typically obtained in the range of 50–60 mJ. At maximum repetition rate, around 90 Wh/Nm<sup>3</sup> of plasma power per unit volume flow could be applied.

Gas flows of 1 and 2 NL/min (STP) were prepared by means of mass flow controllers (MKS) from dry synthetic air (20.5 % O<sub>2</sub> in N<sub>2</sub>) or pure nitrogen (Messer Griesheim). Given the plasma volume of 23.7 cm<sup>3</sup>, a gas flow of 1 NL/min corresponds to a residence time of 1.4 s. Gas humidity was adjusted by bubbling the main part of the flow through distilled water, followed by a temperature stabilized cooling trap. The smaller part was mixed with the “pollutants” under study (CO, CO<sub>2</sub>, ethyl acetate) from lecture bottles (Messer Griesheim) and added to the main flow upstream to the plasma reactor.

CO and CO<sub>2</sub> concentrations were measured by means of a nondispersive infrared absorption detector (Rosemount NGA 2000) downstream to the plasma

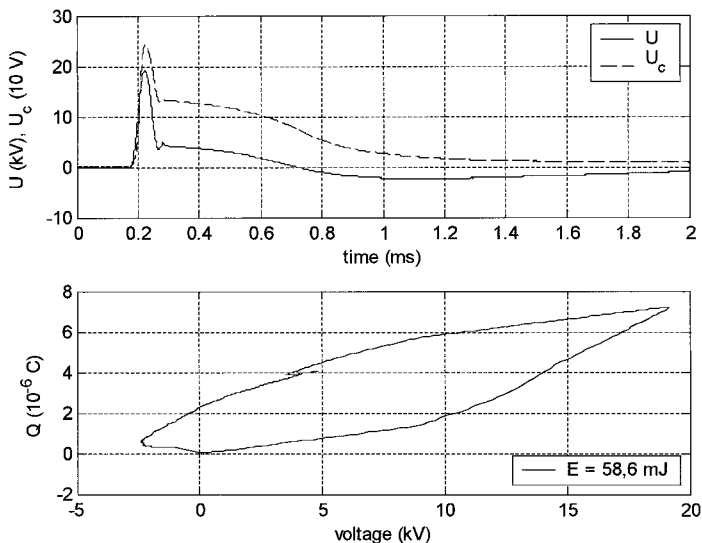


Fig. 1. Voltage and charge traces versus time (upper figure) and Lissajous figure of the dielectric barrier discharge.

reactor. A  $0.2 \mu\text{m}$  particle filter and a cooling trap at  $0^\circ\text{C}$  were used in order to protect the IR cells of the analyzer. The analyzer was routinely calibrated by means of lecture gases.

In air flows, because of cross interference from synthesized ozone, carbon monoxide could be measured only when the discharge was switched off. So, for the oxidative removal of CO, it was necessary to follow the changes of  $\text{CO}_2$  concentration. During several hours the stability of the  $\text{CO}_2$  detector was better than 1 ppm.

Ethyl acetate was measured on line by means of a fast process gas chromatograph with a photo-ionization detector (IUT).

### 3. NUMERICAL MODELING

The rate equations for CO oxidation in a nonthermal plasmas in air or nitrogen are <sup>(9)</sup>

$$d[\text{CO}]/dt = -k_{\text{CO}}[\text{CO}] [\text{OH}] \quad (7)$$

$$d[\text{OH}]/dt = G_{\text{OH}}E/\tau - [\text{OH}]/T_{\text{OH}} - k_{\text{CO}}[\text{CO}] [\text{OH}] \quad (8)$$

$$d[\text{CO}_2]/dt = -d[\text{CO}]/dt \quad (9)$$

where  $G_{\text{OH}}E/\tau$  is the time averaged OH source term,  $E$  is the plasma energy density,  $\tau$  is the residence time in the plasma reactor ( $\tau = L/v$ ,  $L$  - reactor length,

$v$  - flow velocity) and  $t$  is time ( $0 \leq t \leq \tau$ ).  $G_{OH}$  and  $T_{OH}$  are fitting parameters. Relation (9) is justified since no  $CO_2$  decomposition could be found in plasma activated air.

Equations (7)–(9) can be solved analytically only in case of low removal ( $1 - [CO]/[CO_0] \ll 1$ ) and short-lived radicals ( $T_{OH} \ll \tau$ ). Therefore, in order not to be restricted by these conditions, a numerical algorithm was implemented which finds the optimum parameters  $G_{OH}$  and  $T_{OH}$ , starting from the measured  $CO_2$  concentrations in dependence on  $CO_0$ , and given values of energy density  $E$  and gas flow humidity (nonlinear least square fit).

The results on ethyl acetate abatement were modeled in the same manner. The rate constant ( $k_{ethyl\ acetate} = 1.94 \cdot 10^{-12} \text{ cm}^3/\text{s}$ ) was taken from Atkinson *et al.*<sup>(11)</sup>.

#### 4. RESULTS AND DISCUSSION

Figures 2 and 3 show two examples of the measured  $CO_2$  yields in humid air and nitrogen respectively. Plasma energy density at fixed repetition rate of  $107 \text{ s}^{-1}$  was in the range of  $87\text{--}97 \text{ Wh}/\text{Nm}^3$  in air and  $92\text{--}106 \text{ Wh}/\text{Nm}^3$  in nitrogen. The  $CO$  inlet concentration varied between 200 and 1000 ppm. Water vapor content did not exceed 2.8 % in air and 2.1 % in  $N_2$ . Now, every curve belonging to a certain humidity contains the information about one pair of parameters  $G_{OH}$  and  $T_{OH}$ . The solid lines represent the result of numerical modeling.

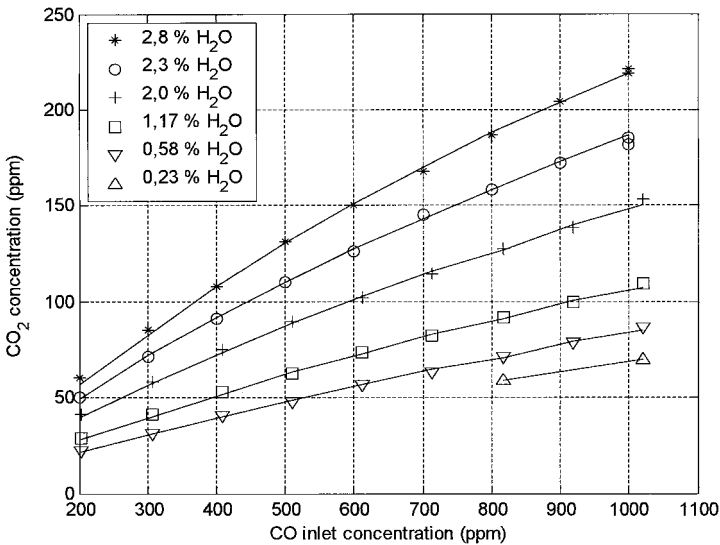


Fig. 2.  $CO_2$  yield in dependence on  $CO$  inlet concentration in humid synthetic air at  $87\text{--}97 \text{ Wh}/\text{Nm}^3$ .

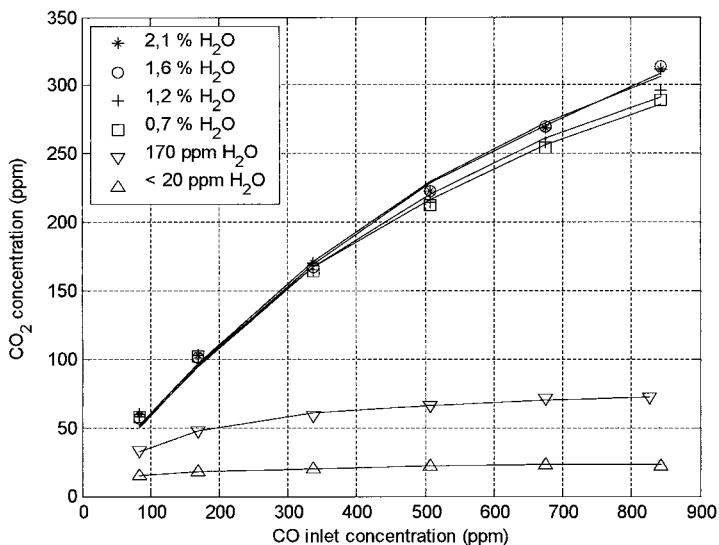
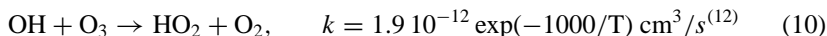


Fig. 3. CO<sub>2</sub> yield in dependence on CO inlet concentration in humid nitrogen at 92–106 Wh/Nm<sup>3</sup>.

The figures show that the CO<sub>2</sub> yields increase with CO inlet concentration in both matrix gases. This is exactly what would be expected if OH radicals not only take part in reaction (3), but are also scavenged by reaction (2). With increasing humidity, the CO<sub>2</sub> yield at fixed CO<sub>0</sub> steadily increases in the air plasma, whereas in nitrogen it displays some kind of saturation. In fact, the overlapping traces in Fig. 3 indicate that both the  $G_{OH}$  and  $T_{OH}$  parameters change only slightly in the range of 1–2 % of water vapor.

In Figs. 4 and 5 the fitted  $G$ -factors and lifetime values are plotted against humidity. In air with 2 % humidity (Fig. 4) the  $G$ -factor of  $\sim 5$  ppm/(Wh/Nm<sup>3</sup>) is somewhat higher in comparison to the “energy density averaged” value of 3.4 ppm/(Wh/Nm<sup>3</sup>) reported previously,<sup>(9)</sup> whereas the lifetime is smaller ( $\sim 100$  compared to 200  $\mu$ s). Of course, a detailed analysis of the data showed that both parameters depend on energy density too. At constant humidity,  $G_{OH}$  increases and  $T_{OH}$  decreases towards higher plasma energy densities.

OH radical production efficiency in air increases with growing humidity. It ranges from 2–7 ppm/(Wh/Nm<sup>3</sup>) and agrees well with that found in the large scale reactor from the removal of volatile organic compounds. OH radical lifetime also increases with rising humidity. This is probably caused by the strong influence of ozone on OH radicals via the reaction



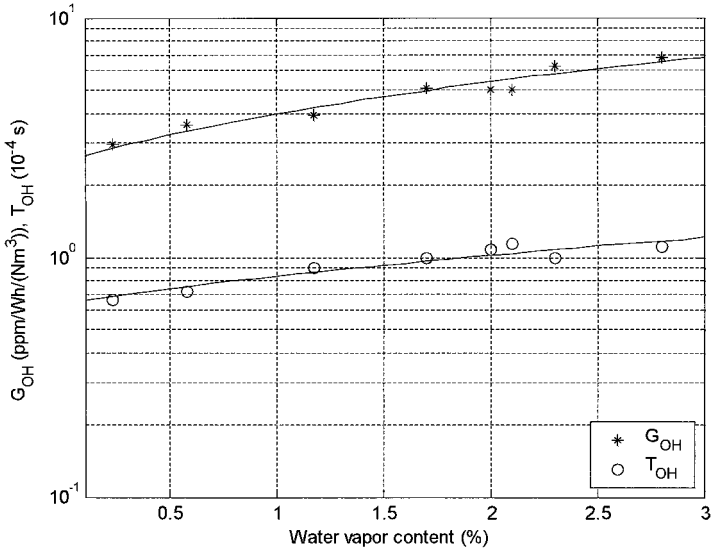


Fig. 4. Average OH production and lifetime in the dielectric barrier discharge in humid synthetic air at 81–97 Wh/Nm<sup>3</sup>.

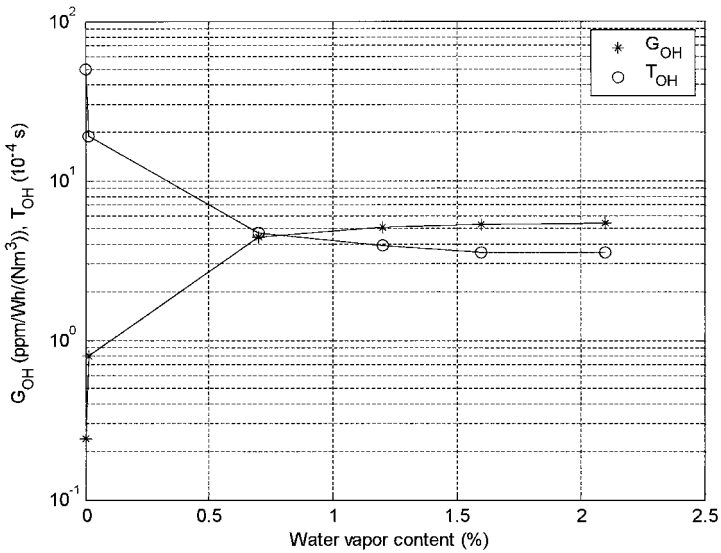
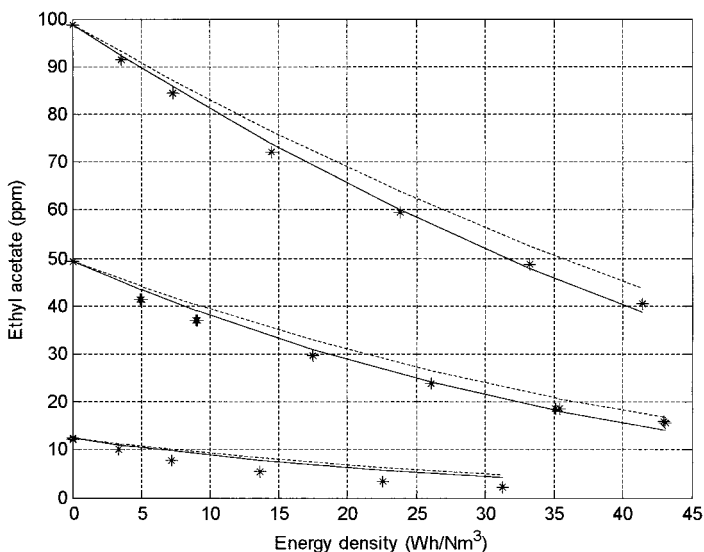


Fig. 5. Average OH production and lifetime in the dielectric barrier discharge in humid nitrogen at 92–106 Wh/Nm<sup>3</sup>.



**Fig. 6.** Ethyl acetate removal rates in synthetic air (99 and 12 ppm in a flow of 2 NI/min, 49 ppm in 1 NI/min) with 2% of water vapor, in dependence on energy density; solid lines represent optimum values for  $G_{OH}$  and  $T_{OH}$ , dashed lines represent the values obtained from CO oxidation.<sup>(9)</sup>

Indeed, ozone synthesis decreases with increasing humidity, typically from 30 ppm/(Wh/Nm<sup>3</sup>) in dry air down to 15–20 ppm/(Wh/Nm<sup>3</sup>) at 2 % of water vapor. From that, taking into account an energy density of  $\sim 90$  Wh/Nm<sup>3</sup>, ozone scavenges OH radicals within  $\sim 400$   $\mu$ s.

The situation is quite different in nitrogen, where with growing humidity OH lifetime increases. We believe that the higher absolute values are due to the absence of ozone. But the situation is too complex to be explained by only a few processes.

Figure 6 shows the removal rates of 12, 49, and 99 ppm ethyl acetate in humid air. The numerical fitting procedure results in  $G_{OH} = 3.7$  ppm/(Wh/Nm<sup>3</sup>) and  $T_{OH} = 212$   $\mu$ s (solid lines in Fig. 6). These values are in very good agreement with those obtained from CO oxidation as reported previously<sup>(9)</sup> (3.4 ppm/(Wh/Nm<sup>3</sup>) and 200  $\mu$ s, dashed lines in Fig. 6).

## 5. CONCLUSIONS

By measuring the CO<sub>2</sub> yields in CO-containing humid gas flows in a dielectric barrier discharge, a method is proposed to determine the average OH radical production efficiency and their lifetime.

In air flows,  $G_{OH}$  was found to be in the range of 2–7 ppm/(Wh/Nm<sup>3</sup>). Lifetime increases with rising humidity.

In nitrogen plasmas with above 1 % of water vapor,  $G_{\text{OH}}$  and  $T_{\text{OH}}$  saturate at 5–6 ppm/(Wh/Nm<sup>3</sup>) and 300–400  $\mu\text{s}$ . The higher lifetime in comparison to air is attributed to the absence of ozone.

Ethyl acetate abatement in a humid air plasma could be modeled by OH radical decomposition, with  $G_{\text{OH}} = 3.7$  ppm/(Wh/Nm<sup>3</sup>) and  $T_{\text{OH}} = 212$   $\mu\text{s}$ .

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## REFERENCES

1. L. A. Rosocha and R. A. Korzekwa, *J. Adv. Oxid. Technol.* **4**, 247 (1999).
2. R. Rudolph, K.-P. Francke, and H. Miessner, *Plasma Chem. Plasma Process.* **22**, 401 (2002).
3. J. Ershov and J. I. Borysow, *J. Phys. D: Appl. Phys.* **28**, 68 (1995).
4. R. Sankaranarayanan, B. Pashaie, and S. K. Dhali, *Appl. Phys. Letters* **77**, 2970 (2000).
5. J. J. Coogan and A. D. Sappey, *IEEE Trans. Plasma Sci.* **24**, 91 (1996).
6. C. Hibert, I. Gaurand, O. Motret, and J. M. Pouvesle, *J. Appl. Phys.* **85**, 7070 (1999).
7. M. J. Campell, J. C. Farmer, C. A. Fitzner, M. N. Henry, J. C. Sheppard, R. J. Hardy, J. F. Hopper, and V. Muralidhar, *J. Atmospheric Chem.* **4**, 413 (1986).
8. Z. Su, H.-H. Kim, M. Tsutsui, K. Takashima, and A. Mizuno, *Thermal Sci. Engng.* **7**, 23 (1999).
9. R. Rudolph, K.-P. Francke, and H. Miessner, *Proc. Eighth Intl. Symp. High Pressure Low Temperature Plasma Chem.*, Pühajärve (2002), p. 323.
10. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **28**, 191 (1999).
11. R. Atkinson, K. R. Darnall, A. C. Lloyd, A. M. Winer, and J. N. Pitts, *Adv. Photochem.* **11**, 375 (1979).
12. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **26**, 521 (1997).