Journal of Photochemistry and Photobiology A: Chemistry 274 (2014) 13–19

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Effect of humidity on the production of ozone and other radicals by low-pressure mercury lamps

Ryo Ono [a,*], Yusuke Nakagawa [b], Yusuke Tokumitsu [a], Hiroyuki Matsumoto [c], Tetsuji Oda [b]

[a] Department of Advanced Energy, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 227-8568, Japan
[b] Department of Electrical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[c] Corporate Advanced Technology Center, Iwasaki Electric Co. Ltd., 1-20 Fujimicho, Gyoda, Saitama 361-0021, Japan

ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form
16 September 2013
Accepted 27 September 2013
Available online 10 October 2013

Keywords:
Low-pressure mercury lamp
Humidity
Ozone density
Radicals
Reaction model

ABSTRACT

An ultraviolet (UV) process using a low-pressure mercury lamp is affected by ambient humidity. It is due to strong influence of humidity on the production of ozone and other radicals by the UV light. In this paper, a photochemical reaction model under the irradiation of a low-pressure mercury lamp is developed, and the effect of humidity on the production of ozone and other radicals [O, $O(^1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, OH, HO_2, H, and H_2O_2] by a low-pressure mercury lamp is discussed using the reaction model. The validity of the reaction model is confirmed by comparing the ozone densities calculated using the model with experimentally measured ozone densities, and they showed good agreement. The reaction model shows that the ozone density decreases with increasing humidity for three reasons: (i) attenuation of 185 nm light due to absorption by H_2O, leading to a decreased O atom production by $O_2 + h\nu(185\,\text{nm}) \longrightarrow O + O$ which is required to produce ozone by $O + O_2 + M \longrightarrow O_3 + M$; (ii) ozone destruction by $O_3 + h\nu(254\,\text{nm}) \longrightarrow O(^1D) + O_2(a^1\Delta_g)$, where the resulting $O(^1D)$ partly reacts with H_2O before converting back to O_3 after quenching to O; and (iii) an ozone destruction cycle $OH + O_3 \longrightarrow HO_2 + O_2$ and $HO_2 + O_3 \longrightarrow OH + 2O_2$. The effect of humidity on the densities of other radicals is also discussed using the reaction model.

1. Introduction

An ultraviolet (UV) process using a low-pressure mercury lamp is widely used for surface treatment, sterilization, and water treatment. The UV process often utilizes ozone produced by the UV light. In the "UV/O_3 process", it is empirically known that an increase in humidity reduces the ozone density, which can lower the effect of the UV/O_3 process. This is partially caused by the catalytic ozone destruction cycle involving OH and HO_2 [1,2]:

$$OH + O_3 \longrightarrow HO_2 + O_2,$$

$$HO_2 + O_3 \longrightarrow OH + 2O_2.$$

The production of OH and HO_2 by a low-pressure mercury lamp was experimentally confirmed using light absorption measurements [1,3].

In contrast, some UV processes are enhanced by humidification, such as those that use radicals produced in a humid environment (e.g., OH and HO_2). The decomposition of volatile organic compounds (VOCs) using a low-pressure mercury lamp is enhanced by humidity because OH radicals efficiently decompose VOCs [4,5]. Our group used a low-pressure mercury lamp for the surface treatment of dye-sensitized solar cells and found that the effect of using the lamp is improved by humidification [6]. Furthermore, some UV processes are not significantly influenced by humidity [7,8]. To understand the effects of humidity on the UV processes, the photochemical reactions occurring under the irradiation of a low-pressure mercury lamp should be investigated.

In this paper, a photochemical reaction model under the irradiation of a low-pressure mercury lamp is developed, and the effect of humidity on the densities of ozone and other radicals [O, $O(^1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, OH, HO_2, H, and H_2O_2] produced by the lamp is examined using the reaction model. After the reaction model is described in the next section, the validity of the reaction model is confirmed by comparing the ozone densities calculated using the model with experimentally measured ozone densities. Then, the effect of humidity on the production of ozone and other radicals is discussed using the reaction model. Particularly, the decrease in ozone density with increasing humidity is discussed in detail.

2. Reaction model

The reaction model under the irradiation of a low-pressure mercury lamp is described in this section. The low-pressure mercury

* Corresponding author. Tel.: +81 3 5841 6663; fax: +81 3 5841 6663.
E-mail address: ryo-ono@k.u-tokyo.ac.jp (R. Ono).

1010-6030/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochem.2013.09.012

Table 1
Rate coefficients (k [cm^3/s]) at 298 K and cross-sections (σ [cm^2]) of the reactions considered in the reaction model. The ratios written in R7, R10, R13–R16, and R22 are branching ratios.

	Reactions	k and σ	Refs.
(R1)	$O_2 + h\nu(185\,nm) \longrightarrow O + O$	[a] $\sigma_1 = 1.2 \times 10^{-20}$	–
(R2)	$O + O_2 + M \longrightarrow O_3 + M$	$k_2 = 6.0 \times 10^{-34}[O_2]$	[10]
		$= 5.6 \times 10^{-34}[N_2]$	
(R3)	$O_3 + h\nu(254\,nm) \longrightarrow$ products	$\sigma_3 = 1.16 \times 10^{-17}$	[11]
(R4)	$H_2O + h\nu(185\,nm) \longrightarrow H + OH$	$\sigma_4 = 7.14 \times 10^{-20}$	[10]
(R5)	$O + O_3 \longrightarrow O_2 + O_2$	$k_5 = 8.0 \times 10^{-15}$	[10]
(R6)	$O(^1D) + N_2 \longrightarrow O + N_2$	$k_6 = 2.6 \times 10^{-11}$	[12]
(R7)	$O(^1D) + O_2 \longrightarrow O + O_2(X,\ a,\ b)$	$k_7 = 4.0 \times 10^{-11}$ (15:5:80)	[10]
(R8)	$O(^1D) + H_2O \longrightarrow OH + OH$	$k_8 = 2.2 \times 10^{-10}$	[10]
(R9)	$O(^1D) + O_3 \longrightarrow O_2 + O_2,\ O_2 + O + O$	$k_9 = 2.4 \times 10^{-10}$ (1:1)	[10]
(R10)	$O_2(a) + O_2 \longrightarrow O_2 + O_2$	$k_{10} = 1.6 \times 10^{-18}$	[10]
(R11)	$O_2(a) + O_3 \longrightarrow O_2 + O_2 + O$	$k_{11} = 3.8 \times 10^{-15}$	[10]
(R12)	$O_2(a) + H_2O \longrightarrow O_2 + H_2O$	$k_{12} = 5 \times 10^{-18}$	[10]
(R13)	$O_2(a) + O_2(a) \longrightarrow O_2(X, b) + O_2$	$k_{13} = 2.8 \times 10^{-17}$ (1:1)	[13]
(R14)	$O_2(b) + N_2 \longrightarrow O_2(X, a) + O_2$	$k_{14} = 2.1 \times 10^{-15}$ (1:9)	[10,13]
(R15)	$O_2(b) + H_2O \longrightarrow O_2(X, a) + H_2O$	$k_{15} = 4.6 \times 10^{-12}$ (1:9)	[10,13]
(R16)	$O_2(b) + O_3 \longrightarrow O_2(X, a) + O_3,\ O + 2O_2$	$k_{16} = 2.2 \times 10^{-11}$ (3:27:70)	[10,13]
(R17)	$OH + O \longrightarrow O_2 + H$	$k_{17} = 3.5 \times 10^{-11}$	[10]
(R18)	$H + O_2 + M \longrightarrow HO_2 + M$	$k_{18} = 5.5 \times 10^{-32}[N_2]$	[10]
(R19)	$HO_2 + O \longrightarrow OH + O_2$	$k_{19} = 5.8 \times 10^{-11}$	[10]
(R20)	$OH + HO_2 \longrightarrow H_2O + O_2$	$k_{20} = 1.1 \times 10^{-10}$	[10]
(R21)	$H + O_3 \longrightarrow OH + O_2$	$k_{21} = 2.9 \times 10^{-11}$	[14]
(R22)	$H + HO_2 \longrightarrow OH + OH,\ H_2 + O_2,\ H_2O + O$	$k_{22} = 8.0 \times 10^{-11}$ (90:7:3)	[10]
(R23)	$H + OH + M \longrightarrow H_2O + M$	$k_{23} = 6.9 \times 10^{-31}[N_2]$	[15]
		$= 4.4 \times 10^{-30}[H_2O]$	
(R24)	$OH + OH \longrightarrow H_2O + O$	$k_{24} = 1.5 \times 10^{-12}$	[10]
(R25)	$OH + OH + M \longrightarrow H_2O_2 + M$	[b] $k_{25} = 5.2 \times 10^{-12}$	[10]
(R26)	$OH + H_2O_2 \longrightarrow H_2O + HO_2$	$k_{26} = 1.7 \times 10^{-12}$	[10]
(R27)	$OH + O_3 \longrightarrow HO_2 + O_2$	$k_{27} = 7.3 \times 10^{-14}$	[10]
(R28)	$HO_2 + HO_2 + M \longrightarrow H_2O_2 + O_2 + M$	[b,c] $k^0_{28} = 2.9 \times 10^{-12}$	[10]
(R29)	$HO_2 + O_3 \longrightarrow OH + 2O_2$	$k_{29} = 2.0 \times 10^{-15}$	[10]
(R30)	$O + H_2O_2 \longrightarrow OH + HO_2$	$k_{30} = 1.7 \times 10^{-15}$	[10]
(R31)	$H_2O_2 + h\nu(185\,nm) \longrightarrow OH + OH$	$\sigma_{31} = 8 \times 10^{-19}$	[10]
(R32)	$H_2O_2 + h\nu(254\,nm) \longrightarrow OH + OH$	$\sigma_{32} = 7.0 \times 10^{-20}$	[10]

[a] See text.
[b] Calculated using low- and high-pressure limits and broadening factor.
[c] $k_{28} = k^0_{28}\{1 + 1.4 \times 10^{-21} \exp(2200/T)[H_2O]\}$.

lamp emits radiation at wavelengths of 185 nm and 254 nm. The 185 nm radiation dissociates O_2 into $O(^3P)$:

$$O_2 + h\nu(185\,nm) \longrightarrow O(^3P) + O(^3P). \quad (R1)$$

$O(^3P)$ reacts with O_2 to produce O_3:

$$O(^3P) + O_2 + M \longrightarrow O_3 + M. \quad (R2)$$

O_3 is dissociated by the 254 nm radiation to produce $O(^1D)$, $O(^3P)$, $O_2(a^1\Delta_g)$, and $O_2(v)$:

$$O_3 + h\nu(254\,nm) \xrightarrow{\phi_3} O(^1D) + O_2(a^1\Delta_g), \quad (R3a)$$

$$\xrightarrow{1-\phi_3} O(^3P) + O_2(X^3\Sigma_g^-, v), \quad (R3b)$$

where $\phi_3 = 0.9$ [9].

In addition, the 185 nm radiation dissociates H_2O:

$$H_2O + h\nu(185\,nm) \longrightarrow H + OH. \quad (R4)$$

Thus, the UV radiation from the low-pressure mercury lamp produces $O(^3P)$, $O(^1D)$, $O_2(a)$, O_3, OH, and H. These radicals react as shown in reactions R5–R32, which are listed in Table 1 along with their rate coefficients at 298 K. The absorption cross-sections and the rate coefficients of reactions R1–R4 are also shown in Table 1.

The cross-section of R1, σ_1, is uncertain. It was previously reported that σ_1 of the low-pressure mercury lamp depends on the O_2 column, with values ranging from 0.6×10^{-20} to 1.2×10^{-20} cm^2 [16]. In another study [17], the range of values for σ_1 were reported to be 1.4×10^{-20} to 1.8×10^{-20} cm^2. In our experiment, σ_1 is measured using our lamp, as shown in the next section, and is estimated to be 1.2×10^{-20} cm^2. This σ_1 value is used in our model.

3. Verification of reaction model

For the verification of the reaction model developed in the previous section, the ozone densities calculated using the reaction model are compared with experimentally measured ozone densities. A cylindrical reaction cell equipped with a low-pressure mercury lamp shown in Fig. 1 is used for the verification. The ozone density at the gas outlet of the reaction cell is measured and compared with that calculated using the reaction model. The experiment and simulation are detailed below.

3.1. Experiment

A 36-cm long low-pressure mercury lamp is placed in the cylindrical cell, as shown in Fig. 1. The photo-reaction cell is made from aluminum, and black non-glossy paint is applied to the inner wall of the cell to reduce reflections. The radius of the lamp, r_0, is 0.9 cm

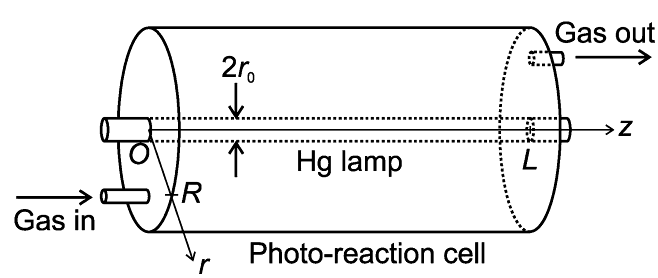

Fig. 1. Photo-reaction cell equipped with a low-pressure mercury lamp.