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Photo-dissociation of dimethylamine by KrBr* excilamp

Qiuyi Han [a,b,c], Zhaolian Ye [d], Jie Zhao [d], Graeme Lister [e], Shanduan Zhang [b,c,*]

[a] Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China
[b] Engineering Research Center of Advanced Lighting Technology, Ministry of Education, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China
[c] Institute for Electric Light Sources, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China
[d] College of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, People's Republic of China
[e] Ceravision Limited, Science and Innovation Centre, Bletchley Park, Bletchley MK3 6EB, UK

HIGHLIGHTS

- A KrBr excilamp emitting 207 nm is used for photo-dissociation of dimethylamine.
- Four parameters are adopted for comprehensive evaluation of the degradation.
- The radiant efficiency of 207 nm is accurately measured.
- The optimum conditions are proposed to achieve high efficiency and energy yield.
- Five secondary products are identified for understandings of reaction pathways.

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ABSTRACT

A study of dimethylamine photo-dissociation in the gas phase has been conducted using UV radiation delivered from a KrBr* excilamp, driven by a sinusoidal electronic control gear with maximum emission at wavelength of 207 nm. The electrical input power and radiant power of the lamp were measured to determine their effects on the degradation. The influence of flow velocity and initial concentration of dimethylamine were also examined. In order to evaluate the photo-dissociation process comprehensively, several parameters were investigated, including removal efficiency, energy yield, carbon balance and CO_2 selectivity. It is shown that the removal efficiency increases with enhanced input power and decreased gas flow rate. A high removal efficiency of 68% is achieved for lamp power 102 W and flow velocity 15 $m^3\ h^{-1}$. The optimum dimethylamine initial concentration is around 3520 mg m^{-3}, for which the energy yield reaches up to 442 g $kW\ h^{-1}$ when the input power is 65 W. In addition, two chain compounds (1,3-bis-dimethylamino-2-propanol; 3-penten-2-one, 4-amino) and three ring organic matters (1-azetidinecarboxaldehyde, 2,2,4,4-tetramethyl; N-m-tolyl-succinamic acid; *p*-acetoacetanisidide), were identified by GC–MS as secondary products, in order to demonstrate the pathways of the dimethylamine degradation.

1. Introduction

Excilamps, a class of high power light sources which emit narrow band radiation in the ultraviolet and vacuum ultraviolet region, have attracted much attention recently, not only because of their discharge mechanism and characteristics, but also due to their potential industrial applications (Gellert and Kogelschatz, 1991; Sosnin et al., 2006; Lomaev et al., 2012; Matafanova and Batoev, 2012). The excimer molecules (rare gas Rg_2^*, halogen X_2^*) and exciplex molecules (rare gas halide RgX* and mercury halide HgX*) can be selected to provide narrow band radiation at different wavelengths, according to the requirements for various applications. As a result of their high efficiency and long lifetime, the configurations of dielectric barrier discharge (DBD) are widely used in excilamps, which can be reliably operated at high electrical power.

Recently, a great deal of research has been reported on the degradation of organic pollutants in waste gas and water by excilamps, validating the feasibility of degrading many pollutants such as 4-chlorophenol (Gomez et al., 2010, 2012; Murcia et al., 2012), and 2,4-dichlorophenoxyacetic acid (Matafonova et al., 2008). Matafanova and Batoev (2012) have summarized the major progress on application of excilamps for pollutant degradation, including direct UV photolysis, UV/H_2O_2 and UV/TiO_2, UV/Fenton and UV/ozone as well as UV/biodegradation. However, the research activities described were focused on KrCl*, XeBr* and XeCl* excilamps.

* Corresponding author at: Engineering Research Center of Advanced Lighting Technology, Ministry of Education, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China. Tel.: +86 21 65642319; fax: +86 21 65646818.
E-mail address: sdzhang@fudan.edu.cn (S. Zhang).

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Few applications has been published with regard to KrBr* excilamps, which emit a strong band at 207 nm; this is possibly due to the relatively low efficiency of these lamps, and the presence of three major bands in the UV range. However, it has been found that the absorption rate of 207 nm photons by DNA molecules is nearly twice that for 254 nm photons emitted by mercury lamps (Samuel, 1988). Further, the high energy of the 207 nm photons suggests the possibility of using it to break down certain bonds that are only poorly dissociated by UV at longer wavelength. Feng et al. (2006) studied the photo degradation of organic dyes by a planar KrBr* excilamp, demonstrating the feasibility of 207 nm photons. Fang et al. (2007) successfully removed the CS_2 from gas streams by a reactor that combined a DBD plasma and 207 nm radiation from KrBr* exciplexes, showing that the degradation efficiency reached 80%, compared to 50% when only plasma was used for the same conditions. Several experimental studies have been reported on UV production from KrBr* excilamps (Feng and Zhu, 2006; Shuaibov and Grabovaya, 2006; Avdeev et al., 2008; Erofeev and Tarasenko, 2008; Sosnin et al., 2011), achieving the efficiency of 2–4% under optimum conditions, which improves the competitiveness of these excilamps for industrial applications.

A coaxial DBD KrBr* excilamp driven by a sinusoidal electronic control gear (ECG) was utilized to degrade the dimethylamine (DMA) gas. As the major raw material used in pesticides, surfactants, photographic chemicals, explosives, dyes and pharmaceuticals, DMA is widely used in the chemical industry and consequently can be detected in most waste water and waste gas from related factories (Mulcahy et al., 2000; Chen et al., 2010). DMA is harmful to human health, inducing allergic reaction, headaches, eye and throat irritation. Therefore, it is important to pay attention to the treatment of this representative organic nitrogen-containing compound. The removal efficiency was studied as a function of lamp power, initial concentration of DMA and gas flow velocity. In order to comprehensively evaluate the performance of photo-dissociation by KrBr* excilamp, energy yield *Ey*, carbon balance *Cb* and CO_2 selectivity were investigated, while the secondary products were analyzed through a GC–MS to determine the principal reaction mechanisms.

2. Experimental setup

2.1. Gaseous DMA preparation

The DMA gas was carried by N_2 which flowed through the DMA solution, kept at 0 ± 1 °C by iced water. The sodium sulphate Na_2SO_4 powder was added to the DMA solution with a concentration of 33%, so that the majority of water was absorbed. As shown in Fig. 1, N_2 flowed through the solution at constant flux controlled by the pressure gauge, transmitting the volatilized DMA gas into the three buffer chambers one by one, in order to produce the gas mixture with a particular constant concentration, which was controlled by N_2 flux.

2.2. UV exposure

A coaxial KrBr* excilamp with the geometry shown inner the photochemistry reactor of Fig. 1, was used as the UV light source to provide UV exposure, principally at 207 nm. The lamp, filled with a gas mixture of Krypton and bromine, consisted of two quartz tubes with wall thickness of 1.5 mm and outer diameter of 40 and 25 mm respectively. Hence the entire discharge vessel has a gap of 6 mm with a length of 100 mm. The stainless steel foils attached to the inner surface of the narrow tube served as the high voltage electrode, while a ring metal mesh covering the outer tube served as the grounded electrode. The untreated gases then flowed around the outer surface of the excilamp and were exposed to UV radiation. The lamp was driven by a sinusoidal ECG at lamp power ranging from 16 to 102 W.

2.3. Sample collection

Fig. 1 illustrates the photo-dissociation process of DMA, which simulates the industrial waste gases, including the sample collection as well as the production of DMA gases and the photochemistry reactor. The prepared gaseous DMA were transmitted to the UV excilamp reactor by the exhaust fan (2X-3, China) after being mixed with air to a predetermined concentration. The mixture gas samples were collected by a six-way-valve autosampler connected with a desiccator before and after the photochemistry reaction, which was analyzed by two on-line GC. The concentration of gas inflow C_{in} was adjusted by a flow-meter to 0–6000 mg m^{-3}, while the flow velocity was controlled by an exhaust fan at 0–30 m^3 h^{-1}. It is important to note that surrounding temperature *T* and relative humidity *Rh* monitored by an electronic temperature-humidity meter (HD-TE03, China) are variable with the weather conditions, due to the open system for the experiment. However they had little effect on the accuracy of the results, owing to the constant condition for the contrast experiment.

2.4. Analysis instruments

The excilamp based on DBD was driven by a sinusoidal ECG, the output voltage, current and power waveforms of which will be shown in Section 3. The lamp input power ranges from 16 to 102 W. Due to power losses in the ECG, it is necessary to measure the electrical power applied to the excilamp itself, in order to make meaningful comparisons of the conversion efficiency of electrical power to 207 nm radiation.

The voltage and the current, measured by a high voltage probe (Tektronix P6015A, 1000:1, rise time 5 ns) and a current probe

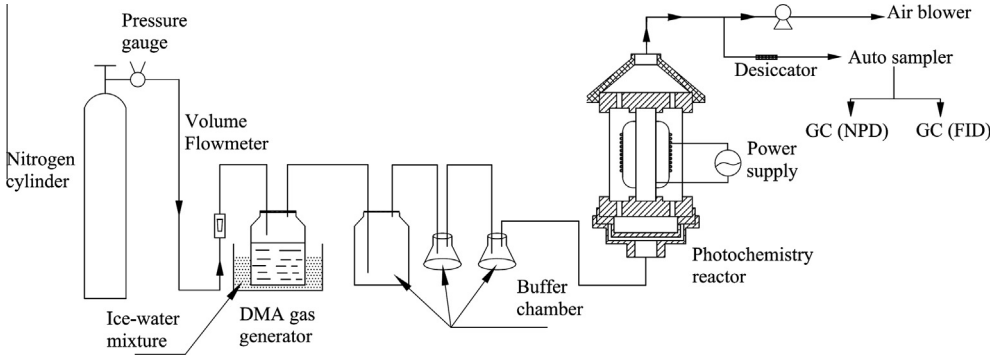

Fig. 1. Simulation process of photo-dissociation of industrial exhaust DMA gas by KrBr* excilamp.