



Kinetic analysis of the photochemical decomposition of gas-phase chlorobenzene in a UV reactor: Quantum yield and photonic efficiency

Lianfeng Zhang, William A. Anderson *

Department of Chemical Engineering, University of Waterloo, 200 University Ave. W, Waterloo, Ontario, Canada N2L 3G1

HIGHLIGHTS

- ▶ UV photolysis of chlorobenzene in air occurs with a 115% quantum efficiency.
- ▶ The presence of SO₂ and water increases quantum efficiency to 145%.
- ▶ High ozone concentrations increased quantum efficiency to 1541%.
- ▶ The photoreactor photonic efficiency was improved by SO₂ and ozone.

ARTICLE INFO

Article history:

Received 16 August 2012
Received in revised form 1 December 2012
Accepted 4 December 2012
Available online 8 December 2012

Keywords:

UV
Ozone
Photolysis
Chlorobenzene
Air emissions
Advanced oxidation
Sulfur dioxide

ABSTRACT

The destruction of a chlorinated aromatic compound by UV photolysis and advanced oxidation was examined for potential use in air emissions treatment. The fluence rate distribution in a photoreactor was analyzed by a finite model, and this was used to estimate quantum yield and photonic efficiency for the photochemical decomposition of chlorobenzene in air. The analysis indicates that the quantum yield was constant at approximately 115%, but the presence of the common flue gas components sulfur dioxide and water could increase it to approximately 145%. Ozone, which strongly absorbs UV photons and promotes radical chain reactions, enhanced the quantum yield to 1534% when present at 2253 ppm. When SO₂ or ozone are present, “effective” quantum yield may be more informative for analysis, since it includes the number of photons absorbed by all reacting species. In this work, the effective QY ranged from 3.9% to 108.7%, with low values indicating that photons were wasted in processes that did not degrade the target organic. An analysis of photonic efficiency shows that the photo-reactor is more efficient at high concentrations of the target organic pollutant, and when ozone or sulfur dioxide are present.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

With the increasing concern for environmental problems, organic chemicals in the industrial gas discharges are increasingly regulated. Compared with conventional gas treatment methods such as adsorption, absorption, and thermal/catalytic incineration, photochemical methods have been gaining more attention in the last two decades [1–10]. Photolysis technologies have some potential advantages, including: (1) they have the ability to destroy a wide spectrum of organic compounds; (2) the reaction is relatively independent of temperature [1–4]; (3) they can potentially mineralize the pollutants to carbon dioxide and water.

The photon energy of UV light is at the same level as various chemical bonds in the organic pollutants, and so the attack of UV photons on organic chemicals can induce photochemical cleavage

of the bonds, leading to decomposition. In such a photochemical reaction system, the primary products of the direct photon attack are radicals, which then may initiate additional chain reactions. In literature, the concept of quantum yield is often used to express the efficiency of photon-driven reactions, but the definition is sometimes not applied consistently. According to the IUPAC definition [11], quantum yield (QY) is the ratio of the amount of reactant consumed to the amount of absorbed photons (typically for monochromatic radiation absorbed by the reactant). While this is useful for characterizing the photoreactivity of a compound, it is less informative for practical reactor engineering applications, where photons may be absorbed by various other components, and other reactions may influence the consumption rate of the target reactant. Therefore, photonic efficiency (PE) has been defined as the ratio of the amount of reactant consumed to the quantity of photons entering the reactor [12,13]. Thus QY is an intrinsic property of a photolytic reaction, whereas PE characterizes the overall efficiency of a photochemical reactor, which may increase or decrease

* Corresponding author. Tel.: +1 (519) 888 4567; fax: +1 (519) 888 4347.

E-mail address: wanderson@uwaterloo.ca (W.A. Anderson).