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# Q13 Intrinsic chemiluminescence production from the degradation of haloaromatic pollutants during environmentally-friendly advanced oxidation processes: Mechanism, structure–activity relationship and potential applications

Q15 Q14 *Ben-Zhan Zhu*, Chen Shen, Hui-Ying Gao, Li-Ya Zhu, Jie Shao, Li Mao**

*State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences and University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100085, PR China. E-mail:* bzhu@rcees.ac.cn

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The ubiquitous distribution of halogenated aromatic compounds (XAr) coupled with their carcinogenicity has raised public concerns on their potential risks to both human health and the ecosystem. Recently, advanced oxidation processes (AOPs) have been considered as an “environmentally-friendly” technology for the remediation and destruction of such recalcitrant and highly toxic XAr. During our study on the mechanism of metal-independent production of hydroxyl radicals (•OH) by halogenated quinones and $H_2O_2$, we found, unexpectedly, that an unprecedented •OH-dependent two-step intrinsic chemiluminescene (CL) can be produced by $H_2O_2$ and tetrachloro-*p*-benzoquinone, the major carcinogenic metabolite of the widely used wood preservative pentachlorophenol. Further investigations showed that, in all •OH-generating systems, CL can also be produced not only by pentachlorophenol and all other halogenated phenols, but also by all XAr tested. A systematic structure–activity relationship study for all 19 chlorophenolic congeners showed that the CL increased with an increasing number of Cl-substitution in general. More importantly, a relatively good correlation was observed between the formation of quinoid/semiquinone radical intermediates and CL generation. Based on these results, we propose that •OH-dependent formation of quinoid intermediates and electronically excited carbonyl species is responsible for this unusual CL production; and a rapid, sensitive, simple, and effective CL method was developed not only to detect and quantify trace amount of XAr, but also to provide useful information for predicting the toxicity or monitoring real-time degradation kinetics of XAr. These findings may have broad chemical, environmental and biological implications for future studies on halogenated aromatic persistent organic pollutants.


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Q16 * *Corresponding author. E-mail:* starmarry@163.com (Li Mao).

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## Introduction

Halogenated aromatic compounds (XAr) have been widely used as pesticides, herbicides, wood preservatives, personal care agents, pharmaceuticals, flame retardants, and many other industrial products (Zhu and Shan, 2009; Zhu et al., 2011a; Dann and Hontela, 2010; De Wit, 2002). Most of these compounds are poorly biodegradable both in water and soil, which makes them persistent and widely distributed in the environment, and have earned them the name persistent organic pollutants (POPs) from UNEP (United Nations Environment Program) (Zhu and Shan, 2009; Zhu et al., 2011a; Dann and Hontela, 2010; De Wit, 2002). The ubiquitous distribution of these recalcitrant and highly toxic XAr coupled with their carcinogenicity has raised public concerns on their potential risks to both human health and the ecosystem (Dann and Hontela, 2010; De Wit, 2002; Ramamoorthy, 1997; Fang et al., 2000; Zimbron and Reardon, 2009; Lan et al., 2008; Gupta et al., 2002; Sorokin et al., 1995; Zhang and Huang, 2003; Zhong et al., 2012; Peller et al., 2003). Polyhalogenated phenols are an important class of XAr, and some of them, such as the widely used wood preservative pentachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP), have been listed by the U.S. Environmental Protection Agency (EPA) as priority pollutants. Recently, PCP has been classified as a group I human carcinogen by the International Agency for Research on Cancer (IARC Working Group, 2016).

Among all the techniques used or tested so far, advanced oxidation processes (AOPs) have been increasingly favored as an “environmentally-friendly” technology for treating recalcitrant chlorinated phenols (CPs) and other XAr in the remediation of contaminated water or soil (Von Sonntag, 2008; Wang and Xu, 2012; Pera-Titus et al., 2004). Several alternative techniques have been well established for the oxidation and degradation of CPs and XAr, such as Fenton and Fenton-like oxidation (Zimbron and Reardon, 2009; Liou et al., 2004; Liao et al., 2007), UV-photolysis (Lente and Espenson, 2003; Chu, 1999), and ozonation (Hong and Zeng, 2002), during which the recalcitrant XAr were degraded or even mineralized. In those “environmentally-green” AOP systems, which are based on hydrogen peroxide (Fenton and Fenton-like reactions) and ozone ($O_3$, $O_3/H_2O_2$), the most reactive radical intermediate formed is the hydroxyl radical (Von Sonntag, 2008).

Chemiluminescence (CL) is a phenomenon in which molecules in a chemically generated excited state liberate energy with light emission. CL frequently accompanies organic peroxide decomposition and free radical formation (Schuster, 1979; Matsumoto, 2004; Almeida de Oliveira et al., 2012; Widder, 2010; Adam et al., 2005). Since the CL intensity is governed by the rate of the chemical reaction, it can be used to quantify any analyte whose concentration is rate-determining (Grayeski, 1987). CL intensity-based analytical assays are inherently highly sensitive, rapid, and simple to operate, without requiring pre-treatment of samples. Therefore, they are being increasingly used as a sensitive analytical method in various research fields (Grayeski, 1987; McCapra, 2000). For example, the reactive oxygen species (ROS) generated during UV-irradiation of nano-$TiO_2$ were selectively and sensitively detected by CL method (Wang et al., 2014); trace amount of transition metal ions such as ferrous(II) and cobalt(II) in estuarine and coastal waters could be quantitatively determined by a pyrogallol–$H_2O_2$ CL system (Cannizzaro et al., 2000); and a good molecular imprinting CL sensor could be designed to recognize and separate target molecules when combining the molecular imprinting with high-sensitivity CL method (Lin and Yamada, 2000).

The hydroxyl radical (•OH) is an extremely reactive ROS which is important in chemistry, biology, toxicology, medicine,



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