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A novel model to predict gas–phase hydroxyl radical oxidation kinetics of polychlorinated compounds

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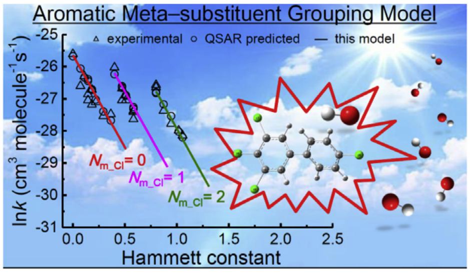
HIGHLIGHTS

- A novel aromatic meta–substituent grouping model for *k* of •OH oxidation of PCBs.
- Polarizability is highly correlated to Hammett constant based on meta–substituents.
- This model features a combination of good predictability and simplicity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel model based on aromatic meta–substituent grouping was presented to predict the second–order rate constants (k) for •OH oxidation of PCBs in gas–phase. Since the oxidation kinetics are dependent on the chlorination degree and position, we hypothesized that it may be more accurate for k value prediction if we group PCB congeners based on substitution positions (*i.e.*, ortho (*o*), meta (*m*), and para (*p*)). To test this hypothesis, we examined the correlation of polarizability (α), a quantum chemical based descriptor for k values, with an empirical Hammett constant (σ^+) on each substitution position. Our result shows that α is highly linearly correlated to $\sum\sigma^+_{\text{o,m,p}}$ based on aromatic meta–substituents leading to the grouping based predictive model. With the new model, the calculated k values exhibited an excellent agreement with experimental measurements, and greater predictive power than the quantum chemical based quantitative structure activity relationship (QSAR) model. Further, the relationship of α and $\sum\sigma^+_{\text{o,m,p}}$ for PCDDs congeners, together with highest occupied molecular orbital (HOMO) distribution, were used to validate the aromatic meta–substituent grouping method. This newly developed model features a combination of good predictability of quantum chemical based QSAR model and simplicity of Hammett relationship, showing a great potential for fast and computational tractable prediction of k values for gas–phase •OH oxidation of polychlorinated compounds.

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1. Introduction

Presence of polychlorinated organic compounds, such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs), in the atmosphere poses adverse effects to both humans and other organisms (Jia et al., 2014; Kampa and Castanas, 2008; Long et al., 2013; Ross, 2004; Xiao et al., 2015a). It is known that in the atmospheric hydroxyl radical (•OH) oxidation is the dominant pathway for attenuating PCBs and PCDDs with half–lives varying from days to month (Atkinson and Arey, 2003; Axelman and Gustafsson, 2002; Beyer and Biziuk, 2009; Carpenter, 2006). Therefore, the second–order rate constants (k, in the unit of cm^3 $molecule^{-1}$ s^{-1}) of •OH oxidation of polychlorinated organic compounds are a key factor to estimate their atmospheric fate and global distribution for better understanding their atmospheric chemistry and regulatory decision making (Beyer and Biziuk, 2009; Totten et al., 2002; Xiao et al., 2015c; Zhuang et al., 2017; Zhuang et al., 2016; Zou, 2010). However, very limited number of experimental k values for these contaminants were measured and reported due to the time–consuming and costly procedures under laboratory conditions (Anderson and Hites, 1996; Atkinson, 1987; Atkinson and Arey, 2003; Yang et al., 2016).

To support the environmental fate estimation and risk assessment, efforts have been exerted to develop models for predicting the gas–phase k values. As the simplest approach, empirical model based on the degree of chlorination was developed first (Anderson and Hites, 1996; Mandalakis et al., 2003). For example, Mandalakis et al. (2003) derived the formula $k = -0.25 \times N_{Cl} + 2.12$, where N_{Cl} is the total number of Cl atoms, for quick estimation of •OH oxidation kinetics of PCBs. This simple model only applies up to 5 Cl atoms and neglects the position of Cl atoms and structural isomers. A different empirical model based on Hammett substituent constants was then developed and explored (Atkinson, 1996; Salter-Blanc et al., 2016; Zetzsch, 1982). Atkinson (1996) and Zetzsch (1982) developed comparable Hammett type models for •OH oxidation kinetics of PCBs: $\log k = -11.71{-}1.34 \times \sum\sigma^+_{\mathrm{o,\ m,\ p}}$ and $\log k = -11.6{-}1.39 \times \sum\sigma^+_{\mathrm{o,\ m,\ p}}$, where $\sum\sigma^+_{\mathrm{o,\ m,\ p}}$ is the sum of electrophilic substituent constants at ortho, meta, and para positions, respectively. Although this type of model is reckoned to be accurate and low computational cost with consideration of substitution positions and degree of chlorination, it still neglects the isomers and the steric effects that exert a great influence on oxidation kinetics (Gross et al., 2001; Hansch et al., 1995). For instance, there is slight difference between the structures of 2,2′–dichlorobiphenyl (*i.e.,* PCB4) and 2,6–dichlorobiphenyl (*i.e.,* PCB10), but their $\sum\sigma^+_{\mathrm{o,\ m,\ p}}$ values are identical, thus resulting in propagation of error in predicting k values.

To improve predictive performance and reduce modelling uncertainty, quantum mechanics, using density functional theory (DFT) as a non–empirical approach, was developed to calculate the k values (Dang et al., 2015; Sun et al., 2015; Yang et al., 2016) on the basis of transition state theory. The rate constants calculated for •OH oxidation of PCBs are in good agreement with measured values (Yang et al., 2016). However, the DFT based approach is computationally expensive, especially with high level theory and a complete basis set, thus limiting its wide application. Instead, the quantum chemical descriptor based quantitative structure activity relationship (QSAR) model comes into place. The QSAR model mathematically relates structure parameters and chemical reactivities, and exhibits advantages for estimating k values over empirical models (Sudhakaran and Amy, 2013; Xiao et al., 2015b; Yang et al., 2016). For example, Yang et al. (2016) developed a QSAR model with quantum chemical descriptor polarizability (α): $\ln k = -0.054 \times \alpha - 19.49$. The quantum chemical descriptor α is able to distinguish the subtle differences between PCBs congeners even for the structural isomers, thereby significantly enhancing the predictive performance (Yang et al., 2016). Although with accurate feature, quantum chemical descriptor based QSAR model at a higher level of theory is still not computational tractable.

Considering the simplicity of Hammett relationship model and the accuracy of quantum chemical descriptor based QSAR model in predicting k values for •OH oxidation of PCBs are complementary, we hypothesized that a new method can be developed for quick and accurate k prediction by combining these two types of models. To test this claim, the relationship of empirical Hammett constants and non–empirical quantum–chemical descriptors (*i.e.,* α) was explored using explicit grouping method based on the substitution positions of Cl atoms (*i.e.,* ortho, meta and para). The methodology is based on the knowledge that chlorination positions play an essential role in determining the kinetics for •OH oxidation of polychlorinated organic compounds (Santiago et al., 2016; Yak et al., 2000; Zeng et al., 2007). The aromatic meta–substituent grouping method potentially distributes the Hammett constants with same values into different groups and reduces the probability of repetition, thereby improving the accuracy for k prediction. More importantly, the grouping method provides an opportunity to better understand the fundamental chemistry between Hammett constant(s) and quantum–chemical descriptor(s).

2. Computation methods

2.1. Data collection

The experimental k values of •OH oxidation of PCBs measured at 294–300 K were collected from literature (Table A1). The temperature range is of atmospheric relevance. It comprises a total of 70 individual measurements for 26 discrete PCB congeners. PCDDs, containing 75 structural isomers, are used for verification. Although diphenyl and dibenzo–1,4–dioxin did not have the substituted Cl atoms, they were still investigated in this study due to the structural similarities to PCBs and PCDDs (Fig. 1). Note, these k values have been heavily used in classic environmental textbooks and handbooks, such as Multimedia environmental models: The fugacity approach (Mackay, 2001), and Handbook of property estimation methods for chemicals: Environmental and health sciences (Mackay and Boethling, 2000).

2.2. Hammett constants

Hammett constant, σ, is a reflection of the electronic nature and position of substituent, as indicated below:

$$\log\left(\frac{k_{X-Ar}}{k_{H-Ar}}\right) = \sigma\rho \tag{1}$$

where X is the functional group substituted on aromatic compounds (Ar), k_X and k_H are the rate constants for substituted and unsubstituted benzene derivatives, respectively, and ρ is the reaction constant which depends on the type of reaction (Hansch et al., 1991). Both σ and ρ are obtained from a reference reaction, and can quantitatively describe chemical reactivities of substituents (Hammett, 1935; Hansch et al., 1973, 1991).

Previous studies have shown that $\sum\sigma^+_{\mathrm{o,\ m,\ p}}$ can be used to accurately predict the k values for •OH oxidation of PCBs (Atkinson, 1996; Zetzsch, 1982).$\sum\sigma^+_{\mathrm{o,m,p}}$ value is the sum of all substituent constants (σ^+_o, σ^+_m and σ^+_p values) of the Cl atoms attached to the aromatic ring on the ortho, meta, and para positions, respectively (Hansch et al., 1991; Lee and Von Gunten, 2012). The σ^+ value is one for groups that stabilized positive charges via resonance, and the σ^+ scale differs from the σ scale for the electron–donating