



# Linear free energy relationships of electrochemical and thermodynamic parameters for the electrochemical reductive dechlorination of chlorinated volatile organic compounds (Cl-VOCs)

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## ABSTRACT

Chlorinated volatile organic compounds (Cl-VOCs) belong to a group of the most ubiquitous contaminants in the environment that can be widely found in all kinds of polluted media. Electrochemical reductive dehalogenation is regarded as one of the most promising remediation methods toward these pollutants, but despite all the works that have been done on the kinetics or the dehalogenation mechanisms, few studies on the linear free energy relationships (LFERs) for explaining or predicting the electrochemical dehalogenation reactivity and dehalogenation mechanisms of Cl-VOCs have been conducted. In this study, we successfully developed several LFERs based on the electrochemical parameter (electrochemical reduction potential,  $E_p$ ) with the four thermodynamic parameters associated with molecular structure (lowest un-occupied molecular orbital (LUMO) energy, C-Cl bond dissociation energy (BDE), one- ( $E_1$ ) and two- ( $E_2$ ) electron reduction potentials) to describe the dehalogenation reactivity and dehalogenation mechanisms of Cl-VOCs. Results clearly demonstrate that a good linear correlation of  $E_p$  with LUMO energy is obtained regardless the classes of Cl-VOCs, while separate correlations of  $E_p$  against BDE or  $E_2$  can give rise to three satisfactory linear relationships according to the dehalogenation mechanisms. Hence, the developed LFERs in this study may provide a new insight in predicting the dehalogenation reactivity and dehalogenation mechanisms for Cl-VOCs and other halocarbons.

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## 1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs), including polychloromethanes (PCMs), polychloroethanes (PCAs) and polychloroethylenes (PCEs), have been widely used as solvents for processes such as metal degreasing and dry cleaning, and for the production of pharmaceuticals, pesticides, adhesives and refrigerants. However, these compounds become a group of ubiquitous contaminants that are often detected in environment media in

recent years [1–3]. On another side, these compounds exhibit strong risk to human health and other organisms, some of them are suspected or even identified as carcinogenic property [2]. It is widely recognized that the toxicity of chlorinated substrates is principally aroused by the chlorine atom(s) in the molecular structure [4]. In this context, the detoxification operation appears to become, to some extent, a dechlorination process. Albeit oxidation methods behave remarkable performances for the removal of Cl-VOCs [5,6], the electronegative character of chlorine makes these processes energy intensive. Moreover, the dehalogenation products like, hydrocarbons and chloride ion, are environment benign, it thus makes reductive dehalogenation as promising approaches for the abatement of chlorinated organic contaminants [7–21].

Whereas various of reductive dehalogenation approaches, including biodegradation [7], zero valent metal or bimetallic

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catalysis [8,9], catalytic dechlorination and electrochemical reduction etc. [10–21], have been developed that display distinct dechlorination capacities for chlorinated compounds, some common properties such as dehalogenation pathways, are normally shared. For example, reductive transformation of Cl-VOCs is found to mainly involve two different dehalogenation mechanisms: sequential hydrodehalogenation or reductive  $\beta$ -elimination, regardless of the applied reduction approaches but, dependent on the molecular structure [15,22,23]. It should be noted that both of these processes contain a net of two-electron transfer from the electron donor to organo-chlorides [15,16]. Therefore, it appears that the deduced mechanistic conclusions from one reduction method can provide some useful hints for the others. In fact, the detailed reductive dehalogenation of Cl-VOCs by electrochemical approach has been carefully discussed in the previous publications [12–16,18], and results show that the molecular structure is a key determinant factor for the dehalogenation reactivity and the reduction mechanism. But despite extensive works that have been conducted on the reactivity (kinetics) or the dehalogenation mechanisms by considering the influence of molecular structure [11–21], efforts at developing such quantitative molecular structure-reactivity relationships for reductive dehalogenation reactions have rarely been done. Furthermore, there are too many of chlorinated substances to be experimental investigated in the viewpoint of both energy and finance. Therefore, the primary objective of the present study is to quantitatively relate dehalogenation reactivity in electrochemical reduction of Cl-VOCs to thermodynamic parameters associated with molecular structure in attempts to develop linear free energy relationships (LFERs) or quantitative structure-activity relationships (QSARs) that can be used to predict the reactivity and reduction mechanisms for Cl-VOCs.

In fact, some researchers have tried to correlate dehalogenation reactivity with thermodynamic parameters of Cl-VOCs such as one-electron reduction potential ( $E_1$ ), two-electron reduction potential ( $E_2$ ), the lowest unoccupied molecule orbital (LUMO) energy and bond dissociation energy (BDE) over the past years [23–28]. Scherer et al. [24] developed excellent LFERs based on the estimated LUMO energies, in order to predict the reaction rate of chlorinated solvents with zero valent iron. The logarithm of transformed rate constant ( $\log k$ ) was also found to correlate well with  $E_1$  for the same series of compounds. Arnold et al. [23] found that the surface area-normalized rate constant ( $k_{SA}$ ) of chlorinated ethylenes reacting with zero valent zinc correlates well with both  $E_1$  and  $E_2$  for the appropriate reactions. Moreover, it was found that the correlation of  $k_{SA}$  with  $E_2$  allows the prediction of different dechlorination routes and rate constants for both chlorinated ethylenes and chlorinated acetylenes. Onanong et al. [27] examined the relevance of four molecular descriptors (LUMO energy, vertical attachment energy, thermal electron attachment rate constant and electron capture detector) for describing the transformation rates of several chloro-alkanes reacting with granular iron and the results indicated good correlations between  $k_{SA}$  and all the four descriptors ( $R^2 = 0.72$ – $1.0$ ). Noteworthy, albeit correlation analysis that is an important tool for the predictions of dehalogenation reactivity and dehalogenation mechanism, few studies on the correlation analysis of electrochemical dehalogenation reactivity with thermodynamic parameters of Cl-VOCs have been conducted. In addition to the reaction rate constant, the electrochemical reduction potential ( $E_p$ ) is a significant parameter in electrochemical reactions, which not only provides indication for dehalogenation mechanisms, but also reflects the dehalogenation reactivity for different chlorinated compounds. Here we used GC as electrode to determine the  $E_p$  values of Cl-VOCs, by both considering that GC is widely recognized as an inert electrode and cathodic materials do not alter the orders of dechlorination

reactivity and the dechlorination mechanisms for Cl-VOCs [13–16,29,30]. The obtained dechlorination mechanisms may thus conceivably shed some light onto the other catalytic materials and other reductive dehalogenation approaches for reduction of Cl-VOCs. In this study, LUMO energy, BDE,  $E_1$  and  $E_2$  four thermodynamic parameters were used as predictor variables, in order to check whether they can correlate well with the dehalogenation reactivity ( $E_p$ ). The relationships of various alternative descriptors with  $E_p$  were finally examined by using a test compound (pentachloroethane, PCA) through the linear regression analyses. We hope to develop the LFERs that not only enable the predictions of dehalogenation reactivity and dehalogenation mechanisms for Cl-VOCs, notably, to provide a new insight and means for the other halocarbons.

## 2. Experimental

### 2.1. Chemicals

*N,N*-dimethylformamide (DMF) was treated in the presence of anhydrous  $\text{Na}_2\text{CO}_4$  for several days. After double distillations at lower pressure under  $\text{N}_2$ , DMF was then stored in a brown bottle under the protection of Argon. Tetrapropylammonium tetrafluoroborate ( $\text{C}_{12}\text{H}_{28}\text{BF}_4\text{N}$ , TPABF<sub>4</sub>, Fluka) was recrystallized twice in ethanol and dried in a vacuum oven at 70 °C for at least two days. Chloromethane (CM), dichloromethane (DCM), chloroform (CF), carbon tetrachloride (CT), 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), pentachloroethane (PCA), hexachloroethane (HCA), chloroethylene (MCE), 1,1-dichloroethylene (1,1-DCE), 1,2-dichloroethylene (1,2-DCE), trichloroethylene (TCE) and tetrachloroethylene (PCE) were purchased from Sigma-Aldrich and used directly as received.

### 2.2. Experiment setting

Electrochemical measurements were performed on a computer controlled EG&G PARC Model 273 potentiostat/galvanostat. All experiments except specified were conducted at 25 °C in a three electrodes system with GC rod (Tokai, GC-20) as working electrode, a Pt wire as counter electrode and Ag/AgCl/Me<sub>4</sub>NCl(sat) in DMF+acetonitrile (3:1,V/V) solution as reference electrode, respectively. The reference electrode was calibrated at the end of each experiment against the ferricenium/ferrocene couple ( $E_{\text{Fc}^+/\text{Fc}}^0 = 0.475$  V vs. SCE in DMF), which allowed conversion of all potentials to saturated calomel electrode (SCE) scales. It is noteworthy that all the potential values in this paper were calibrated to SCE unless stated otherwise. The electrode was prepared and polished as previously described [15].

### 2.3. Cyclic voltammetry experiment

Voltammetric experiments were performed in a thermostatic undivided cell, with 0.1 M TPABF<sub>4</sub> as supporting electrolyte and 2 mmol L<sup>-1</sup> of determined chlorinated substrate dissolved in DMF solvent each time. The system was operated under Argon flow conditions throughout the experiment. Cyclic voltammograms were recorded on GC electrode at 0.2 V s<sup>-1</sup>. For the electrochemical reduction of each Cl-VOCs, three parallel experiments were conducted to ensure the repeatability of experiment. It should be noted that the voltammetric measurement of PCA was performed on a computer controlled Autolab workstation (AUT85812), where saturated calomel electrode was used as the reference electrode directly, while the other conditions were kept unaltered. It should be noted that except those of PCA and PCEs, all

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