



# Uncovering the intrinsic relationship of electrocatalysis and molecular electrochemistry for dissociative electron transfer to polychloroethanes at silver cathode



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## ABSTRACT

The relationship between electrocatalysis and molecular electrochemistry for the reductive dechlorination of organic chlorides has been a central topic for decades. Herein, we try to reveal the catalytic property of silver electrode by investigating the thermodynamics of dissociative electron transfer (DET) to C–Cl bonds of polychloroethanes (PCAs) on both inert (GC) and catalytic (Ag) electrodes. By extending the “sticky” DET model reported by Savéant, we show that the catalyzed DET model can well describe the activation-driving force relationships for the electrocatalytic dechlorination on Ag, where in addition to the possible ion-dipole interactions, the adsorption of chlorinated species onto Ag surface, which is found to play a fundamental role in the electrocatalysis process in this study, is introduced in the new developed DET model. In this work, we firstly report that the catalytic property of Ag electrode characterizing with drastically positive shift of reduction potential is ascribed to the lower of intrinsic barrier free energy, rather than the activation free energy, for the reductive dechlorination. Moreover, the intrinsic relationship of electrocatalysis and molecular electrochemistry is clearly indicated and quantitatively developed. These results may provide new insights in uncovering both the nature of catalytic property of Ag and the relationship of electrocatalysis and molecular electrochemistry for PCAs and other halocarbons.

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## 1. Introduction

Organic chlorides, including alkyl and aryl chlorides, belong to a group of main environment pollutants, which are widely found in the contaminated soils, air and any kind of fluvial mediums such as underground water, lakes and rivers [1,2]. These compounds are particularly dangerous by considering their toxicity or even carcinogenic characters [1,3,4]. Various abatement techniques such as adsorption [5], photocatalytic oxidation [6], zero-valent metal/bimetallic reductive dechlorination [7–9], biodegradation [10], electrochemical oxidation and reduction [11–18] are thus developed for these recalcitrant pollutants. Among these methods, electro-reductive dechlorination is regarded as one of the most promising approaches, which has attracted increasing attention

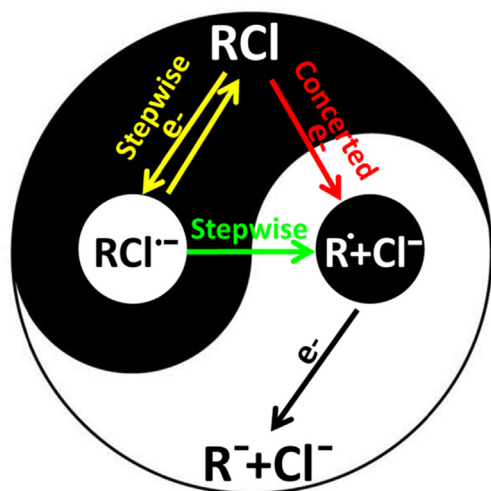
towards reductive cleavage of C–Cl bonds for organic chlorides both from environmental and mechanistic point of views for decades [13–24].

The electro-reductive cleavage of C–Cl bonds of organic chlorides has been extensively investigated for mechanistic studies on dissociative electron transfer (DET) [18–29]. The electro-reductive dechlorination reaction may proceed via two distinct electron transfer mechanisms, namely the concerted and the stepwise DET mechanisms (Scheme 1). In the first case, the electron transfer and the rupture of C–Cl bond take place in a single step, whereas in the latter one, before the bond breaking it involves an intermediate of radical anion formation. Much effort has been devoted to distinguish the DET mechanisms for a large number of organic chlorides by experimentally and theoretically [18–29]. It is found that the molecular structure plays a key role in determining the dissociative electron transfer to C–Cl bonds: aliphatic chlorides normally follow a concerted DET mechanism [18,23,30], whereas the stepwise DET mechanism is generally preferred by the

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**Scheme 1.** DET mechanisms of organic chlorides.

aromatic chlorides [26,31–33]. These could be explained by considering the fact that the foreign electron can be accommodated by the  $\pi^*$  orbitals of aromatic compounds, while the aliphatic chlorides with saturated C–C bonds possess redox accessible (or low lying)  $\sigma^*$  orbitals that cannot hold the incoming electron, leading to their distinct DET mechanism. One efficient diagnostic criterion to identify the concerted and the stepwise DET mechanisms is to measure the value of electron transfer coefficient ( $\alpha$ ) [21,32]. According to the expression of transfer coefficient resulted from the quadratic activation-driving force relationship and from the definition of intrinsic barrier [21]:

$$\alpha = \frac{\partial \Delta G^\ddagger}{\partial \Delta G_0} = \frac{1}{2} \left( 1 + \frac{\Delta G_0^\ddagger}{D_{\text{RCI}} + \lambda_0} \right) = \sqrt{\frac{\Delta G^\ddagger}{D_{\text{RCI}} + \lambda_0}} \quad (1)$$

$$\alpha_{\text{concerted}} = \sqrt{\frac{\Delta G^\ddagger}{D_{\text{RCI}} + \lambda_0}} \ll \alpha_{\text{stepwise}} = \sqrt{\frac{\Delta G^\ddagger}{\lambda_i + \lambda_0}} \quad (2)$$

where the C–Cl bond breaking energy,  $D_{\text{R-Cl}}$ , in most cases is much larger than the reorganization bond lengths and angles,  $\lambda_i$ ;  $\lambda_0$  represents the solvent reorganization free energy. Therefore, the transfer coefficient in the first case is much smaller than the second one, which is significantly smaller than 0.5 for the concerted DET, whereas  $\alpha > 0.5$  is achieved for the stepwise DET mechanism. This strategy has been proved to be very effective in determining the DET mechanism for many organic chlorides [18,20,21,23,32]. It is noteworthy that caution should always be exercised, as sometimes using transfer coefficient solely is not sufficient to decide whether reductive cleavage of C–Cl bond is a concerted or stepwise mechanism [34,35].

A series of electrochemical experiments have also been conducted for the investigations of various determinant factors on the reductive dechlorination of organic chlorides over the past years, in order to better understanding the dechlorination mechanisms and obtaining high efficient abatement process for these recalcitrant compounds [36–53]. The electro-reductive dechlorination process is found to be influenced by different factors, such as the solvent conditions (e.g. supporting electrolyte [36,37], solvent proticity [38,39] and oxidation-reduction potential [40], imposed current density/potential [41–43], molecular structure [18,44] and electrode materials [45,46], etc. All of these factors in principle contribute to affecting the dechlorination performances. For instances, the increase of bulkier

tetraalkylammonium cations ( $\text{TAA}^+$ , as supporting electrolyte) can result in a negative shift of reduction potential for aryl halides mainly due to the increases of both double layer thickness and the hindered electron tunneling [37]; the solvent proticity deeply affects both reaction mechanisms and catalytic activity of electrodes for the dehalogenation of organic halides, where the extent of catalytic activity is enhanced with the increase of solvent proticity [39]; low solvent ORPs, regulated by using iron anode, were found to favor the reductive dechlorination of trichloroethylene (TCE) in the previous work [40]; sequential hydrodechlorination of chlorinated volatile organic compounds (Cl-VOCs) was clearly observed by stepwise shifting the applied potentials, where the products selectivity could be easily regulated [18,39,40]; the dechlorination mechanisms of Cl-VOCs were found to depend on the molecular structures: geminal Cl-VOCs mainly follow the sequential hydrodechlorination path by eliminating one chlorine ion at each step, while reductive  $\beta$ -elimination is the preferred dechlorination route for the vicinal Cl-VOCs by removal of two chlorine ions simultaneously at one single step [18,23]. It should be noted that the electro-reductive dechlorination has been greatly concentrated on the investigation of catalytic metals over the last decades, where remarkable catalytic cathode is required in order to reduce the overpotential associated with the dissociative electron transfer to C–Cl bonds and avoid the hydrogen evolution reaction in aqueous media [15–18,45,46]. Very often, the activation of C–Cl bonds by electrocatalysis has been achieved with significant positive shift of reduction potential for organic chlorides over catalytic electrodes with respect to the inert one, for instance GC [15–18,22,23,45–47], Pd [48–50], Au [18,45], Ag [14–18,22–24], Ni [44,45] and Cu [42,43,45,46] all are found to possess remarkable catalytic activities for the electro-reductive dechlorination of organic chlorides. In particular, Ag is recognized as the most powerful catalytic electrode in organic solvent over the other metals [14–18,22–24]. The catalytic property of cathodic materials was presumed to ascribe to the adsorption between metal surface and chlorinated substrate as well as its reduction intermediates and products [24,33,47,51,54]. Recently the combined results of density functional theory (DFT) calculation and surface-enhanced Raman spectroscopy (SERS) investigation confirm the assumption that benzyl chloride weakly adsorbs onto the Ag surface [24,47,54]. Whereas the catalytic activity of Ag for reductive cleavage of C–Cl bonds has been clearly indicated by both experimentally and theoretically, neither the nature of the electrocatalytic property of Ag nor the thermodynamics of DET to C–Cl bonds over catalytic metals have been truly unraveled yet. Furthermore, the relationship between electrocatalysis for the reductive dechlorination process and molecular electrochemistry has been a central topic for years. It is known that the electrocatalysis involves a surface catalysis process, in which the activation of substrates exclusively occurs through their adsorption onto electrode surface, whereas for the molecular electrochemistry, the electron transfer from electrode to molecule that is dependent on many factors mainly takes place through simple electronic coupling between the orbitals of substrate and electrode with no or negligible interactions occurrence [21,47]. However, despite that the plausible connection has been established and some interesting outcomes have been achieved [24,32,33,47,51,54], no effort to quantitatively correlate the catalytic activity of Ag with the molecular electrochemistry has been made by far.

In this study, polychloroethanes (PCAs), which belong to a typical group of aliphatic chlorides widely investigated, were chosen as model compounds. Whereas the electron transfer mechanisms, catalytic properties of different cathodic materials, and the reduction routes for PCAs were clearly declared in the previous works [18,42,43], the thermodynamics of electron transfer to C–Cl bonds have not yet been demonstrated. It is

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