Novel Prediction Methods for Electrochemical Reduction Characteristics of Chlorinated Aromatics Based on Their Molecular Structures

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A significant quantitative model for predicting reduction characteristic based on the molecular structure, and an empirical estimation method as well, were investigated by using structure-property relationship technique for 87 chlorinated aromatics. These would throw more light on the nature of reduction process, and provide valuable data for designing and choosing a possible (electro-) chemical oxidation/reduction treatment process of chlorinated aromatics.

More and more attention has been paid on the pollution abatement of harmful chemicals in environment. Recently, some of effective techniques such as advanced oxidation processes (AOP), advanced reduction processes (ARP) were introduced into treatment of wastes. It is necessary to grasp correctly the redox characteristics of these pollutants, and to evaluate their possibility of degradation or removal in theory.[1–4] However, it is impossible to measure all of their properties one-by-one because of so many pollutants. Fortunately, the quantitative structure–property relationship technique can be used to predict properties of compounds on the basis of their molecular structures.[5]

Chlorinated aromatics are harmful pollutants, which exist widely and hard to dispose. As for these compounds, ARP is efficient which includes dechlorination reduction mechanism, so the electrochemical reduction potential (E_{RE}) is selected as indicator in this study to evaluate the possibility in ARP treatment. Among all of the reduction potentials of 87 studied chlorinated aromatics (38 naphthalenes, 32 biphenyls, 12 benzenes and 5 phenols), some of them were determined with interrupted-sweep voltammetry in previous reports,[1,6] the others were determined with cyclic voltammetry by ourselves, which the working electrode was a glass-carbon electrode, the counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode, the supporting electrolyte was acetate acid-acetate sodium buffer solution (pH = 4.5), the temperature was $25.0 \pm 0.1\,^{\circ}C$. All solutions were deaerated with high-purity nitrogen. Besides, the quantum chemical parameters of tested compounds were calculated with semi-empirical molecular orbital MOPAC97 procedure[7] by using PM3 Hamiltonian method. All of the statistics analyses were conducted with STATGRAPHICS software.[8]

Quantum chemical parameters can describe the molecular structure accurately and have clear physico-chemical sense. Among them, the energy of the lowest unoccupied molecular orbital E_{LUMO} is one of sensitive parameters in describing the reduction characteristics of organic compounds. The regression results indicated that the E_{RE} of chlorinated benzenes was significantly correlated with parameter E_{LUMO} (shown in Figure 1a). It could be seen from Figure 1a that the chemicals were separated into several groups with the different number of chlorine atoms in molecules n_{Cl}. Another information could be extracted that the reduction potentials possibly correlated with the number of chlorine atom in molecules, and the high correlativity between E_{RE} and n_{Cl}, plotted in Figure 1b, held up this point. Otherwise, the similar conclusion could also be drawn from the results of phenols and naphthalenes as well (the result of naphthalenes was shown in Figures 2a and b). It seemed that, as for chlorinated aromatics, there was certain correlativity between reduction potentials and the number of chlorine atoms in molecules. So, a test was conducted with the data of 32 polychlorinated biphenyls, but the correlativity between E_{RE} and n_{Cl} was not so good as expected, and the correlation coefficient R^2 was 0.616. Considering the specific molecular structure of PCBs, both of the two benzene rings have very similar characteristics due to the conjugate effect and the chlorine atom(s) on different rings would not effect the characteristic each other very seriously. Therefore, the parameter n_{Cl} was corrected with following method: the number of chlorine atoms n'_{Cl} on one

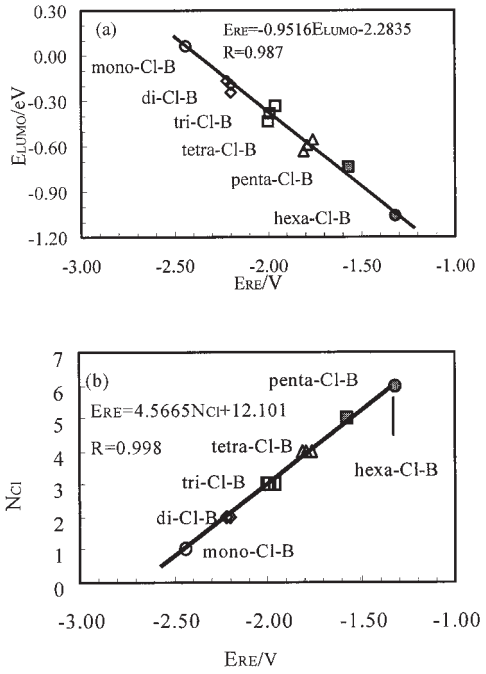

Figure 1. The relationship between E_{RE} and E_{LUMO}, E_{RE} and n_{Cl} for chlorinated benzenes, respectively.

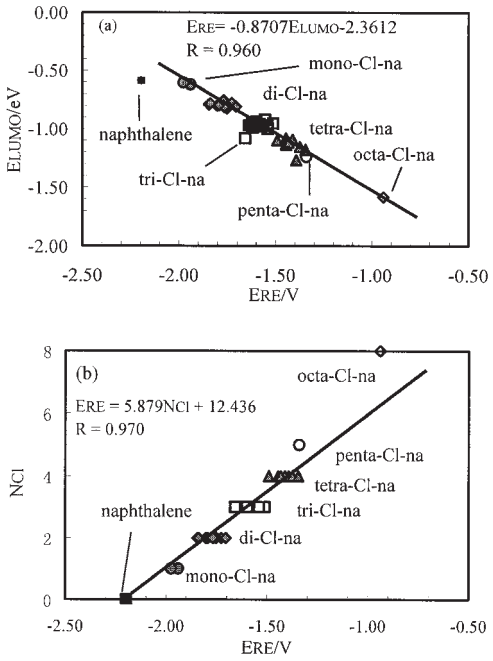

Figure 2. The relationship between E_{RE} and E_{LUMO}, E_{RE} and n_{Cl} for chlorinated naphthalenes, respectively.

of the two benzene rings containing more chlorine atom replaced the total number of chlorine atoms in chemical molecule n_{Cl}. The regression result proved that the correlativity was highly improved (R^2 was 0.726). However, the aim of quantitative structure property relationship was to develop a universal, accurate and reliable model for predicting property of compounds as more as possible. On the basis of this point, it was tried to investigate the relationship between E_{RE} and n'_{Cl} of all the 87 studied chlorinated aromatics, but the R^2 was 0.594.

In order to obtain a high quality prediction equation, the calculated quantum chemical parameters were introduced into candidate descriptors along with indicator variable n'_{Cl}, and the quantitative relationship was developed through stepwise multiple regression analysis:

$$E_{RE} = -2.451 - 0.631E_{LUMO} + 0.075n'_{Cl} \quad (1)$$

$$N = 87, R^2_{adj.} = 0.916, SE = 0.082, F = 470.04, p < 0.0001$$

Where, N is the number of sample in regression analysis, R^2_{adj} is multiple correlation coefficient adjusted with freedom, SE is standard error, F is F-test value, p is the significance level.

It could be extracted from above eq (1) that, E_{RE} of organic compound was negatively related to E_{LUMO}, and positively related to n'_{Cl}. When the value of E_{LUMO} is low, the unoccupied orbital is readily to accept the electrons during reaction, the reduction potential is high, and the compound is easily to be reduced. In addition, -Cl is electron-accepting substituent, and the density of electron would reduce greatly as more chlorine atoms on benzene ring, so the molecule of target compound is readily to accept more electrons, and easily to be reduced.

Both of the important parameters n'_{Cl} and n'_{Cl} for dechlorination reduction reaction were included in eq (1), and the result of t-test also indicated parameters E_{LUMO} and n'_{Cl} were significant. The frequency distribution of prediction residuals of eq (1) agreed with normal function N (-1.890×10^{-15}, 0.067^2), and the statistical analysis results of residuals indicated that the coefficient of skewness was -0.894, the coefficient of kurtosis was 1.639. Moreover, eq (1) was reliable through robustness test and fit-of-goodness test, the plot of observed values *vs* fitted values of the tested compounds is shown in Figure 3.

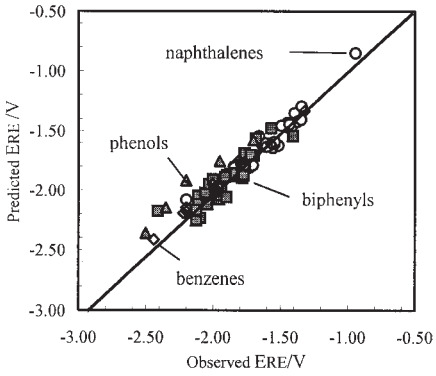

Figure 3. The plot of predicted E_{RE} *vs* observed E_{RE}.

Based on the above analyses, eq (1) is robust enough to predict the reduction characteristics of chlorinated aromatics. Additionally, quantum chemical parameters with clear physico-chemical sense can be easily obtained and comprehensively describe the structural information of chemicals. The more important is that, the obtained model will be benefit to evaluate the possibility of disposal for pollutants, it also provide useful help for designing and choosing a possible (electro-) chemical oxidation/reduction treatment process of chlorinated aromatics.

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References and Notes

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