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Linear Free Energy Relationship Analysis of Chlorinated Hydrocarbons in Cement Slurries

Jung, B. M.[1*], Batchelor, B.[2], Park, J.Y.[3], and Abdel-Wahab, A.[1]

[1]Chemical Engineering Program, Texas A&M University at Qatar, Doha, Qatar

[2]Department of Civil Engineering, Texas A&M University, College Station, Texas 77843-3136, USA

[3]Department of Civil Engineering, Hanyang University, 17 Haengdang-Dong, Seongdong-Gu,
Seoul, 133-791, Republic of Korea

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ABSTRACT: The present study is to study linear free energy relationships (LFERs) for dechlorination rates in cement/Fe(II) slurries of eight chlorinated hydrocarbons including carbon tetrachloride, chloroform produced from carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene produced from 1,1,2,2-tetrachloroethane, tetrachloroethylene, trichloroethylene, 1,1-dichloroethylene, and vinyl chloride, with six descriptor variables in pursuit of finding a reasonable descriptor showing the highest coefficient of determination (R^2). Seventeen descriptors by various computational methods were screened into six descriptors. In addition, this study correlated logarithms of rate constants (log k) with multiple descriptors. The results have shown that the bond dissociation energy, overall free energy change of the one-electron transfer step, and lowest unoccupied molecular orbital energies calculated by ab initio methods with 6-31G* parameters were strongly correlated with the log k values of eight compounds by Fe(II) in cement slurries. The combinations of descriptors that had the highest correlation coefficient in multiple regression were one-electron reduction potential and gas-phase homolytic-dissociation energy (E_1 and D_{R-X}), which two variables are commonly based on that a dissociative one-electron transfer is the initial and rate-limiting step in the reaction.

Key words: Reductive Dechlorination, Linear Free-Energy, Chlorinated Aliphatic Hydrocarbons, Degradative Solidification/Stabilization

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INTRODUCTION

Recent studies have demonstrated that iron-based degradative solidification/stabilization (DS/S-Fe(II)) can reductively dechlorinate carbon tetrachloride, 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA),1,1,1-trichloroethane (1,1,1-TCA), tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), vinyl chloride (VC), and polychlorinated biphenyls (PCBs) (Hwang and Batchelor, 2000; Hwang and Batchelor, 2002; Son, 2002; Hwang *et al.,* 2005; Jung and Batchelor, 2008; Jung and Batchelor, 2009). These studies have characterized the kinetics of an individual chlorinated compound dependent on Fe(II) dose, pH, and initial target chemical concentrations in cement slurries with Fe(II). Another study related to this work identified active reagents formed in Portland cement containing Fe(II) to reduce chlorinated hydrocarbons, which will be AFm (aluminate-ferrite-monosubstituted) phases of layered double hydroxides (Ko and Batchelor, 2007). Very recently, Jung et al. have developed linear free energy relationships (LFERs) with the kinetic data of six chlorinated aliphatic hydrocarbons (CAHs) investigated in DS/S-Fe(II) process (Jung and Batchelor, 2008). It was the first study to investigate the effect of molecular properties on the rates at which those chlorinated hydrocarbons are dechlorinated by a reductant formed from reaction between Fe(II) and cement hydration products.

LFERs analysis on the fate of chlorinated aliphatic hydrocarbons has been widely conducted to predict the dechlorination rates and to explain the mechanisms of dechlorination in the environment. Pejinenburg et al. correlated the degradation rate constants of chlorinated aromatic hydrocarbons in anoxic sediment with molecular structural descriptors (e.g. the carbon-halogen bond strength) (Pejinenburg *et al.,* 1992). Zhao et al. correlated the reductive dechlorination rate constants of 13 chlorinated aliphatic hydrocarbons in sediment slurry under anaerobic conditions with 26 quantum chemical descriptors computed by PM3 Hamiltonian (Parametric method 3), which is a semi-

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*Corresponding author E-mail: bahngmi.jung@qatar.tamu.edu empirical method for the quantum calculation of molecular electronic structure (Zhao *et al.,* 2001). Perlinger et al. conducted LFERs for transformation of polyhalogenated alkanes using electron-transfer mediators in model aqueous system and reported that the bond-dissociation energy and standard free energy of one-electron reduction were good and accurate descriptors for the transformation rates (Perlinger and Venkatapathy, 2000). Cervini-Silva used LFERs analysis to explain kinetic data for adsorption and dechlorination of RCl in redox-manipulated smectite clay minerals (Cervini-Silva, 2003). In that analysis, bond dissociation energies for RCl heterolysis ($RCl \rightarrow R^+ + Cl^-$) showed the highest coefficient of determination (R^2) of 0.93 with logarithms of the pseudo-first order rate constants (log k) obtained in reduced ferruginous smectite. Also, many studies have developed LFERs for dechlorination by (nano-sized) zero-valent iron (Scherer *et al.,* 1998; Butler and Hayes, 2000; O′ Loughlin and Burris, 2004; Song and Carraway, 2005).

In an earlier work, a simple regression was conducted between log k and only four different descriptor variables (one-electron reduction potential (E_1), two-electrons reduction potential (E_2), gas-phase homolytic bond dissociation enthalpy (D_{R-X}), and lowest unoccupied orbital energy (E_{LUMO}6-31G*) (Jung and Batchelor, 2008), which were selected without any screening tests since those descriptors had been widely used. In that work, the E_{LUMO} values calculated using the ab initio methods (6-31G*) by Scherer et al. were found to be strongly correlated ($R^2 = 0.874$) with logarithm of pseudo-first-order rate constants (log k) for dechlorination in cement slurries with Fe(II) (Jung and Batchelor, 2008). The scope of the present work is to expand the previous work with more sufficient kinetic data and descriptor variables and to discuss the correlation between physicochemical or molecular properties and log k in more detail. Investigated descriptor variables were as follows: one-electron reduction potential (E_1), two-electrons reduction potential (E_2), the homolytic bond dissociation energy (D_{R-X}), vertical attachment energy (VAE), overall free energy change of the one-electron transfer step ($\Delta G^{\circ\prime}$), and lowest unoccupied orbital energy (E_{LUMO}). Different values for the same descriptor variable were collected based on the computational calculation methods (e.g. D_{R-X}, E_{LUMO}). The representative descriptor showing the highest R^2 or considering data accessibility was selected and used for a linear regression with log k. In addition, this study correlated log k with multiple regressors, as well as a linear regressor of a single descriptor used in the earlier work. All descriptor variables and dechlorination rate constants were not calculated in this study, but collected from the literature. The objective of this study is to conduct the LFERs between dechlorination rate constants of all CAHs (CT, CF*, 1,1,2,2-TeCA, 1,1,1-TCA, PCE, TCE, 1,1-DCE, and VC) investigated in cement/Fe(II) slurries and six descriptor variables. Finding reliable descriptors through this study will demonstrate that the molecular structures are important to predict the dechlorination rates of CAHs in those systems or at similar conditions. Furthermore, this study summarized reaction pathways of CAHs that have individually reported regarding DS/S-Fe(II) process. It will provide a valuable information to understand for the relation between molecular or physicochemical properties and reaction rates, and a favorable reaction pathway of CAHs in cement slurries containing Fe(II).

MATERIALS & METHODS

The kinetic data for CT, CF* (CF produced from CT), PCE, TCE* (produced from 1,1,2,2-TeCA), 1,1-DCE, and VC were reported by Hwang et al. (Hwang and Batchelor, 2000; Hwang and Batchelor, 2002; Hwang *et al.,* 2005), and those for 1,1,1-TCA, and TCE* were reported by Jung et al. (Jung and Batchelor, 2008; Jung and Batchelor, 2009). The pseudo-first-order rate constants (k_{obs}) for dechlorination of the CAHs that are subjected to analyses in this study were based on the measured data in the 10% cement slurries with Fe(II) showing the pH ranged from 12.0 to 12.6. CF* and TCE*, which were not chemicals spiked into a reactor initially, but produced from parent compounds, CT and 1,1,2,2-TeCA, respectively. In LFERs analysis of present and previous works, pseudo-first-order rate constants corrected by a partitioning factor ($k = p \times k_{obs}$, where p is a dimensionless partitioning factor of each target organic compound: p = mass in all phases/mass in aqueous phase, and k_{obs} is the observed value of k in the multi-phase reactor) were used instead of k_{obs}. Previous studies commonly published the rate constant as k, which were explained in detail in the references (Hwang and Batchelor, 2000; Hwang and Batchelor, 2002; Hwang *et al.,* 2005; Jung and Batchelor, 2008). The rate constants compiled from the literature were shown in the second column in Table 1. Here, the rate constants for 1,1-DCE and VC were obtained in Fe(II) dose of 100 mM, unlike others were obtained in Fe(II) dose of 40 mM, but other experimental conditions were remained identical. Two regression results with and without rate constants of 1,1,-DCE and VC were compared in Fig. 1. Predicted log k showed the same magnitude of measured log k, regardless of the presence of 1,1,-DCE and VC kinetic data so the rate constants of 1,1-DCE and VC were included in linear regressions to report later.

Seventeen descriptor variables were collected from literatures (Table S1), and screened into six descriptors

Table 1. Published data of pseudo-first-order rate constant and descriptors used in correlation analysis

Compound	k^c (h)*	Radical Product	$^dE_1^o$ (V)	$^eE_2^o$(h) (V)	$^fD_{R-X}$ (kJ/mol)	^{g}VAE (eV)	$^hE_{LUMO}$ 6-31G* (eV)	$^i\Delta G^{o'}$ (kJ/mol)
CT	132^a	CCl_3•	0.085	0.673	270	-0.34	-3.054	19.6
CF*	0.15^a (±27%)	$CHCl_2$•	-0.145	0.560	296	0.35	-2.277	50.7
1,1,2,2-TeCA*	0.0003^a (±42%)	$CHCl_2CHCl$•	-0.257	0.537*	289	0.51	-1.982	54.0
1,1,1-TCA	2.063^a (±2.0%)	CH_3CCl_2•	-0.02	0.555	291	0.64	-2.160	47.8
PCE	0.0042^a (±5.4%)	CCl_2=CCl•	-0.598	0.598	348	0.3	-1.689	99.0
TCE	0.012^a (±5.4%)	Cl•C=CHCl	-0.998	0.505	385	0.59	-1.435	104.6
1,1-DCE	0.008^b (±11.1%)	CH_2=CCl•	-0.802	0.497	361	0.76	-1.140	113.0
VC	0.003^b (±23.8%)	CH_2=CH•	-1.141	0.386	396	1.28	-0.761	142.2

Data are derived from the sources indicated. ^{a}is the rate constant obtained at Fe(II) 40 mM, and ^{b}is the rate constant at Fe(II) 100 mM. ^{c}corrected pseudo-first-order rate constant by partitioning factor ($k=p\times k_{obs}$, where p is a dimensionless partitioning factor of each target organic compound) E_1 is one-electron reduction potential and E_2 is two-electrons reduction potential. ^{d}The ref. is [1]. ^{e}The ref. is [1], E_2^o(h) is two-electrons reduction potential in hydrogenolysis. ^{f}homolytic dissociation energy for the carbon-halogen bond of the reactant in the gas phase which results in the product in the gas phase. Values were derived from computational estimates using density functional theory (pBP method, DN** basis set) [1]. ^{g}Vertical attachment energy [2], ^{h}lowest unoccupied molecular energy, which was calculated from ab initio methods (6-31 G*) [3], ^{i}It was calculated using the Gaussian software package and B3LYP/6-311++(g,p) theory/basis set [4].

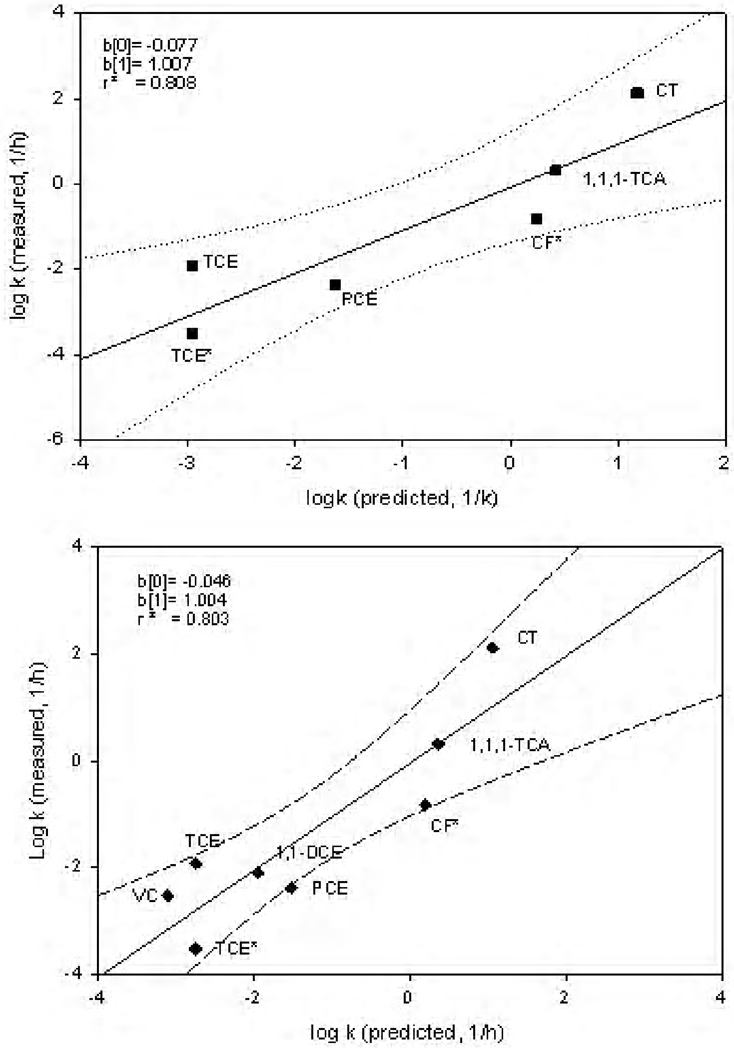

Fig. 1. Measured versus predicted log (k) values for (a) six chlorinated compounds and (b) eight chlorinated compounds investigated in cement/Fe(II) slurries. Figure 1a included the kinetic data of six compounds obtained in the same experimental conditions, whereas in Figure 1b it included two more compounds 1,1,-DCE and VC tested at different Fe(II)

presented from the 4th to 9th column in Table 1: 1) one-electron reduction potential (E_1 V) (Totten and Roberts, 2001), 2) two-electron reduction potential (E_2 V) (Totten and Roberts, 2001), 3) homolytic bond dissociation energy (D_{R-X}, kJmol^{-1}) (Totten and Roberts, 2001), 4) vertical attachment energy (VAE, eV) (Burrow *et al.,* 2000), 5) lowest unoccupied molecular orbital energy (E_{LUMO}, eV) (Scherer *et al.,* 1998), and 6) overall free energy change of the one-electron transfer step ($\Delta G°'$, kJmol^{-1}) (Perlinger *et al.,* 2000). The values of some descriptors were varied dependent on the different computational calculation methods for thermodynamic properties. First, all descriptors were attempted to be regressed with log k, as shown in Fig. S1 and the descriptor having the highest R^2 in regression with log k was generally selected within the same category of descriptors, which were presented in Table 1. The linear regression between log k and a single descriptor variable was expressed by eq. (1). For highly correlated descriptors, the multiple linear regression of two variables as shown in eq. (2) was used.

$$\log k = b_0 + b_1(descriptor_1) \qquad (1)$$

$$\log k = b_0 + b_1(descriptor_1) + b_2(descriptor_2) \qquad (2)$$

It is known that the important transformation mechanism of CAHs in anaerobic conditions is reductive dechlorination. Hydrogenolysis or reductive

β-elimination requires transfer of two electrons in overall. But the first step of the two electron transfer process is assumed to be formation of the radical with a transfer of a single electron (e.g. $RX(aq) + e^- \rightarrow R\bullet(aq) + X^-(aq)$) (Curtis and Reinhard, 1994). In LFERs, many researchers have related the dechlorination rate constants of CAHs with one-electron reduction potential (E_1) (Vogel *et al.,* 1987; Curtis, 1991; Curtis and Reinhard, 1994; Roberts *et al.,* 1996; Scherer *et al.,* 1998; Butler and Hayes, 2000). The values of one-electron reduction potential (E_1) can be calculated by the Nernst relationship using standard gibbs free energy calculated by eqs. (3 and 4) (Curtis, 1991).

$$E_1 = E_1^\circ + \frac{RT}{nF} \ln \frac{\{RX\}}{\{R\bullet\}\{X^-\}} \qquad (3)$$

$$E_1^\circ = -\frac{\Delta G_{rxn}^{\circ}}{nF} = -\Big(\Delta H_f(R\bullet)_{(g)} - T\Delta S_f(R\bullet)_{(g)} \qquad (4)$$

$$+\Delta G_f(X^-)_{(aq)} - \Delta G_f(RX)_{(g)} + RT\ln\frac{H_{RH}}{H_{RX}}\Big)/nF$$

Where E_1 is one-electron reduction potential, E_1° is the standard state one-electron reduction potential, n is the number of electrons transferred, F is Faraday's constant, T is the temperature in Kelvin, R is the gas constant, ΔG_{rxn}° is the gibbs free energy change of the reaction at standard state, ΔH_f (R•) is the enthalpy of formation of radical, ΔS_f (R•) is the entropy of formation of radical, ΔG_f is the free energy of formation, and H is Henry's Law constant. The one-electron reduction potential was calculated from the Nernst equation at 1 mM halide ion activity and unity activity of {RX} and {R•}. Computationally predicted reduction potentials have been widely used for many radicals because experimentally derived ΔH_f° is very limited (Totten and Roberts, 2001). The E_1 values (the 4th column in Table 1) was calculated using bond-additivity corrected MP4 (BAC-MP4, one of ab initio methods) computation predictions (Totten and Roberts, 2001). Ab initio methods are entirely based on theory and used to determine the molecular interaction energies from hydrogen bond and van der Waals interactions (Sum and Sandler, 1999).

Two-electron reduction potential (E_2) used in this work corresponded to hydrogenolysis reaction ($RX + H^+ + 2e^- \rightarrow RH + X^-$). For several compounds (e.g. PCE, TCE) in cement/Fe(II) system, the predominant transformation pathway was known to be reductive beta-elimination (Hwang and Batchelor, 2000; Jung and Batchelor, 2008), not hydrogenolysis. However, E_2 values corresponding to hydrogenolysis pathway were applied to all regression regardless of the reaction pathway with the type of chemicals, which were cited from Totten et al. (Totten and Roberts, 2001). Calculated reduction potentials (E_1 and E_2) were different with reference sources because it is due to different values of enthalpy or entropy for radical or species formation (Totten and Roberts, 2001). Totten et al. (2001) described that ΔH_f° values were varied by 10 to 20 kJ/mole and were more dependent on the methods (experimentally, empirically or computationally determined), which led to an error of about 0.1 V in calculated E_1 and E_2 values.

D_{R-X} is the enthalpy energy required to break the bond for R-Cl to dissociate into R• and Cl• (Totten and Roberts, 2001). The bond dissociation energy is a measure of its strength. Four different D_{R-X} values were extracted from the literature and one of them (the 9th column in Table S1) was calculated by eq. (5) using experimentally obtained thermodynamic parameters.

$$D_{R-X} = \Delta H_f(R\bullet)_{(g)} + \Delta H_f(X\bullet)_{(g)} - \Delta H_f(RX)_{(g)} \qquad (5)$$

Where $\Delta H_f(RX)_{(g)}$, $H_f(R\bullet)_{(g)}$, and $\Delta H_f(X\bullet)_{(g)}$ are the enthalpies of formation of alkyl halide, alkyl radical, and halide, respectively, in gas phase. Other D_{R-X} values were estimated with various computational methods. The D_{R-X} values in the 7th column in Table S1 was calculated using the Gaussian software package and B3LYP/6-311++g(d, p) theory/basis set according to Perlinger et al (Perlinger and Venkatapathy, 2000), those in the 8th column in Table S1 were derived from computational estimates using density function theory (pBP method, DN** basis set) according to Totten et al (Totten and Roberts, 2001), and those in the 10th column in Table S1 were calculated at G2MP2 level using Gaussian 94 according to Liu et al (Liu *et al.,* 2000). In computational chemistry (e.g. calculating the structures and properties of molecules) computer programs are used to implement the quantum chemistry methods such as ab initio methods, density functional theory, and semi-empirical quantum chemistry methods. The software packages used in computational chemistry include COSMOS, MOPAC, and Gaussian etc. The B3LYP and pBP method are density functional theory methods, which is the modeling method used to investigate the electronic structure (Pattanayak *et al.,* 2000). DN**, 6-311++g(d,p), and G2MP2 is a basis set, a set of functions used to create the molecular orbitals (Scherer *et al.,* 1998; Perlinger and Venkatapathy, 2000; Totten and Roberts, 2001). The ab initio calculation consists of the method and the basis, expressed as method/basis (e.g. B3LYP/6-311++g(d, p)).

The electron affinity is the energy released when an electron is attached to an atom or a molecule to become an anion (Loyaux-Lawniczak *et al.,* 2000). The vertical electron affinity (VEA) is equal to the energy difference between anion and neutral molecule at the equilibrium geometry of neutral molecule. The vertical attachment energy is simply negative of VEA. The values of vertical attachment energy (VAE, eV) in the 7th column in Table 1 were cited from the reference by Burrow et al (Burrow *et al.,* 2000).

The lowest unoccupied molecular orbital (LUMO) is the frontier molecular orbital where electron transfer takes place and E_{LUMO} is related to the susceptibility for a molecule to be attacked by nucleophiles (Karelson and Lobanov, 1996). Scherer et al. have described that E_{LUMO} has an advantage as a descriptor variable in LFER analysis because there is only one value per reactant so the complications with branching pathways (e.g. hydrogenolysis and elimination reaction) may be avoided (Scherer *et al.,* 1998). Scherer et al. have suggested five different lowest unoccupied molecular energies using different molecular modeling programs: ab initio methods (6-31G*), AM1, AM1 with COSMO, PM3, and PM3 with COSMO (Scherer *et al.,* 1998). AM1 (Austin model 1) and PM3 (Parametric method number 3) are one of semi-empirical methods in quantum chemistry. COSMO (conductor-like screening model) is the model to determine the electrostatic interaction of a molecule with a solvent. The E_{LUMO} values calculated from ab initio methods with 6-31G* basis set were presented in the 8th column in Table 1. The E_{LUMO} ($kJmol^{-1}$) values from the B3LYP/6-311++g(d,p) theory/basis set according to Perlinger et al. (Perlinger and Venkatapathy, 2000) were also regressed with log k. Another descriptor $\Delta G°'$, the standard free energy of one-electron reduction, were estimated by Perlinger et al. (Perlinger and Venkatapathy, 2000), which is given in the 9th column in Table 1.

RESULTS & DISCUSSIONS

Descriptor values computed using different theories and different basis sets that were cited from the literature were compared to select the best available values, which was not attempted in an earlier LFERs study in cement/Fe(II) system. Six descriptors determined in screening tests were shown in Table 1. Fig. 2 shows a scatter plot of log k versus selected six descriptors (E_1, E_2, D_{R-X}, VAE, E_{LUMO} 6-31G*, $\Delta G°'$) and among descriptor variables. It demonstrates which parameters are correlated. Both one-electron reduction potential (E_1) and two-electrons reduction potential (E_2) have been used for reductive dechlorination reactions so that these two parameters are expected to correlate with other descriptors. Fig. 2 shows that each of E_1 and E_2 was well correlated with alternative descriptors (D_{R-X}, VAE, E_{LUMO} 6-31G*, and G°′), and especially E_1 was better correlated with D_{R-X} (R^2=0.994) and $\Delta G°'$ (R^2=0.916). The high correlation between E_1 and $D_{R-X,}$ or E_1 and $\Delta G°'$ would be due to that those variables commonly involve cleavage of the carbon-halogen bond. E_2 was better correlated with VAE (R^2=0.932) and E_{LUMO} (R^2=0.818) than other variables (E_1, $D_{R-X,}$ and $\Delta G°'$). The E_{LUMO} and VAE was also highly correlated (R^2=0.800) with each other because both are common measures of the energy related to the addition of an electron to an atom.

Table 2 presents linear regression equations between log k and single descriptor (eqs. 1~6) and multiple linear regression equations for two descriptors that showed higher coefficients of determination (R^2) than 0.8. Pairs of descriptors showing higher correlation were D_{R-X} and E_1, D_{R-X} and E_2, D_{R-X} and VAE, D_{R-X} and E_{LUMO}, D_{R-X} and DG°¢, and VAE and E_{LUMO}. Multiple regression equations with two variables showing the highest correlation (R^2) was log k=33.5-8.43E_1-0.116D_{R-X} (R^2=0.833).The linear regressions between log k of eight chlorinated compounds and six descriptor variables are shown in Fig.S2. The order of the determination coefficients (R^2 value) for six descriptors with log k was D_{R-X} >DG°¢ > E_1 > E_{LUMO} 6-31G* > E_2 > VAE. The bond dissociation energy (D_{R-X}) by pBP/DN** predictions showed the highest correlation (R^2=0.804) with log k for dechlorination of eight CAHs (CT, CF*, 1,1,1-TCA, PCE, TCE, TCE*, 1,1-DCE, and VC) by Fe(II) in cement slurries, whereas the best correlation was found to be E_{LUMO} 6-31G* (R^2=0.874) for six compounds excluding 1,1-DCE and VC in an earlier work (Jung and Batchelor, 2008). Fig. S2a shows the correlation between log k and E_1 with a reasonably high R^2 of 0.777. Many researchers (Scherer *et al.,* 1998; Arnold *et al.,* 1999) have suggested that the reduction of CAHs is likely to proceed with the first electron transfer to form alkyl radical species as a rate-limiting step. The one-electron reduction potential was reported to be well correlated (R^2=0.85) with the log k for CAHs dechlorination by ZVI, regardless of the chemical family (e.g. chlorinated methanes, ethanes and ethenes) (Scherer *et al.,* 1998). Arnold and Roberts (Arnold and Roberts, 1998) investigated the kinetics of dechlorination for a family of chlorinated ethenes by ZVI, and found an excellent correlation (R^2=0.958) of E_1 with the rate constant normalized on the basis of the surface area of ZVI. Totten and Roberts (Totten and Roberts, 2001) described that a greater halogen substitution for the halogenated methanes was expected to result in the higher values of E_1 and the presence of α-chlorines for chlorinated ethanes was expected to have the greater effect on reduction potential than that of β-chlorines. In Fig. S2a, when PCE, TCE and the TCE* including β-chlorines were excluded, the R^2 value increased up to

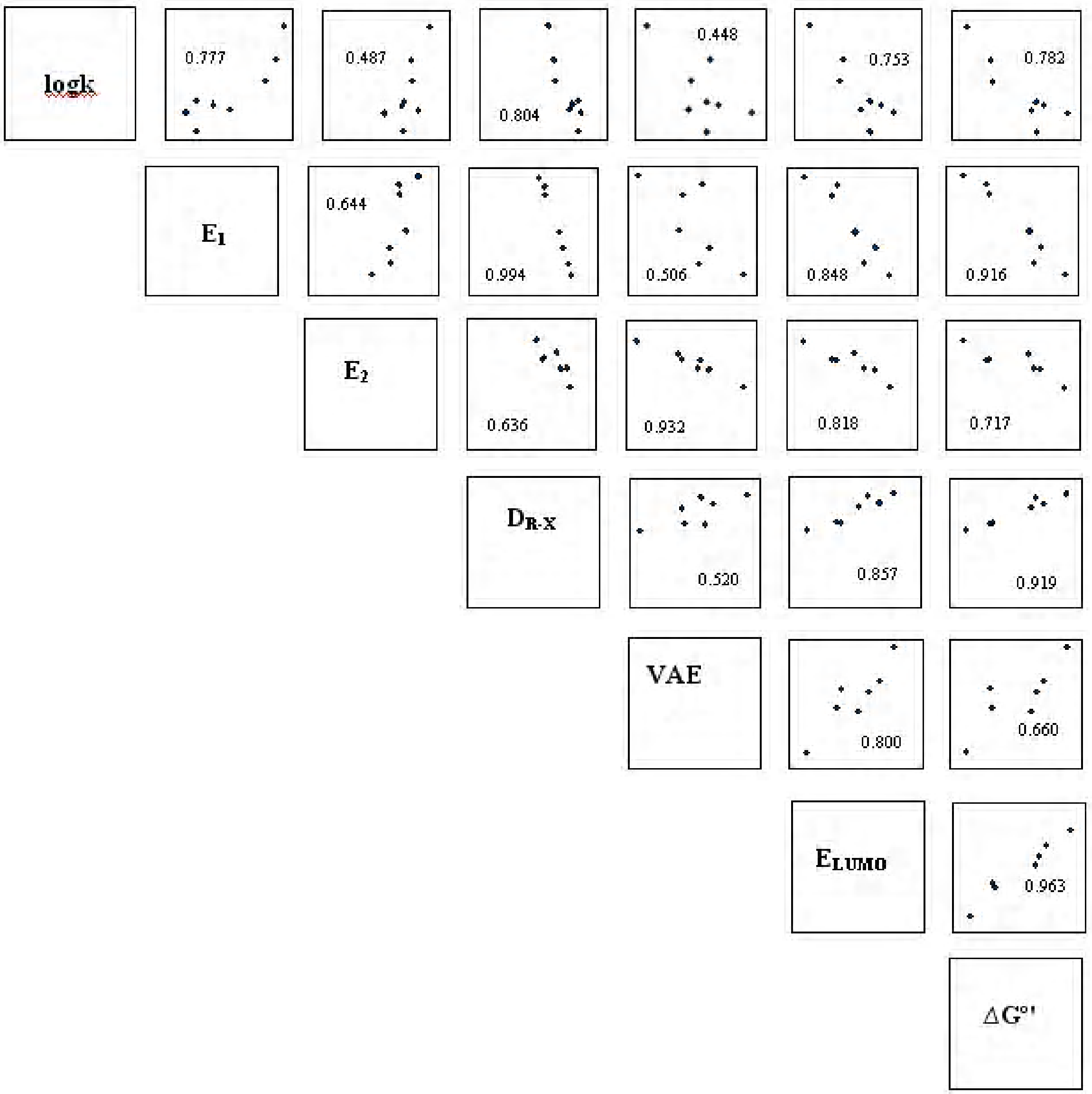

Fig. 2. Scattered plots of the selected six descriptors. Numbers in the panels refer to R2-values

0.805. Although E_1 is a good descriptor, it leaves a limitation because E_1 cannot reflect the distribution of reaction products (Song and Carraway, 2005). The two-electrons reduction potential (E_2) showed a relatively weak correlation (R^2=0.486, Fig.S2b) with log k because this work used the E_2 values based on hydrogenolysis, but actually some CAHs (e.g. PCE and TCE) were dechlorinated following reductive elimination pathway in the cement/Fe(II) system. The better correlation (R^2=0.913) was found in the regression between E_2 and log k when it was applied to the CAHs (CT, CF, 1,1,1-TCA, and VC) that were dechlorinated following hydrogenolysis pathway. The two-electrons reduction potential seems to be a descriptor variable that is sensitive to the pathway of dechlorination.

A weak correlation was observed with VAE (R^2=0.448, Fig. S2d), as well as E_2. Burrow et al. (Burrow *et al.,* 2000) found that the rate constants for dehalogenation were satisfactorily correlated with VAE, but only within the same family of chlorinated ethenes. The better correlation within the same family was explained by that two families of chlorinated ethanes and ethenes are different in orbital symmetry or dechlorination mechanisms (Burrow *et al.,* 2000). However, a linear regression between VAE and the rate constants which were limited to chlorinated ethenes (PCE, TCE, 1,1-DCE, and VC) in cement slurry including Fe(II) did not show better correlation, unlike

Table 2. Equations of regression of log (k) versus descriptors and regression statistics

No.	Equation	R^2	SE	p-value
Eq.6	$\text{Logk} = 3.29E_1 + 0.545$	0.777	0.928	0.004
Eq.7	$\text{Logk} = 15.08E_2 - 9.42$	0.486	1.407	0.054
Eq.8	$\text{Logk} = -0.0332D_{R\text{-}X} + 9.97$	0.804	0.870	0.003
Eq.9	$\text{Logk} = -2.65\text{VAE} + 0.0273$	0.448	1.459	0.069
Eq.10	$\text{Logk} = -2.17E_{LUMO} - 5.14$	0.753	0.975	0.005
Eq.11	$\text{Logk} = -0.0391?\,G^{o\prime} + 1.97$	0.782	0.917	0.004
Eq.12	$\text{Logk} = 0.896 + 3.37E_1 - 0.571E_2$	0.777	1.016	0.024
Eq.13*	$\text{Logk} = 33.5 - 8.43E_1 - 0.116D_{R\text{-}X}$	0.833	0.880	0.011
Eq.14	$\text{Logk} = 0.591 + 3.061E_1 - 0.341\text{VAE}$	0.780	1.008	0.023
Eq.15*	$\text{Logk} = -1.81 + 2.012E_1 - 0.930E_{LUMO}$	0.798	0.968	0.018
Eq.16*	$\text{Logk} = 1.37 + 1.55E_1 - 0.022\quad G^{o\prime}$	0.797	0.970	0.019
Eq.17	$\text{Logk} = 11.02 - 1.054E_2 - 0.035D_{R\text{-}X}$	0.805	0.951	0.017
Eq.18*	$\text{Logk} = -10.2 + 16.3E_2 + 0.236\text{VAE}$	0.487	1.541	0.189
Eq.19*	$\text{Logk} = -1.47 - 10.4E_2 - 3.26E_{LUMO}$	0.796	0.972	0.019
Eq.20	$\text{Logk} = 4.64 - 3.91E_2 - 0.046\quad G^{o\prime}$	0.791	0.983	0.02
Eq.21	$\text{Logk} = 9.63 - 0.032D_{R\text{-}X} - 0.189\text{VAE}$	0.805	0.950	0.017
Eq.22*	$\text{Logk} = 5.69 - 0.024D_{R\text{-}X} - 0.665E_{LUMO}$	0.814	0.928	0.015
Eq.23*	$\text{Logk} = 7.41 - 0.022D_{R\text{-}X} - 0.014\quad G^{o\prime}$	0.811	0.934	0.015
Eq.24*	$\text{Logk} = -8.34 + 2.13\text{VAE} - 3.37E_{LUMO}$	0.811	0.935	0.016
Eq.25	$\text{Logk} = 2.12 + 0.569\text{VAE} - 0.044\quad G^{o\prime}$	0.789	0.988	0.02
Eq.26*	$\text{Logk} = 1.89 - 0.027E_{LUMO} - 0.039\quad G^{o\prime}$	0.782	1.004	0.022

For the sake of precision, three significant figures were included in the coefficients in the regression equations. SE stands for the standard error of regression. P-value for regression analysis using Sigma 11.0. Regressions for 17 descriptors were presented in supporting information. Correlation analysis showed that two variables are dependent each other in eqs with * (13, 15, 16, 18, 19, 22, 23, 24, and 26).

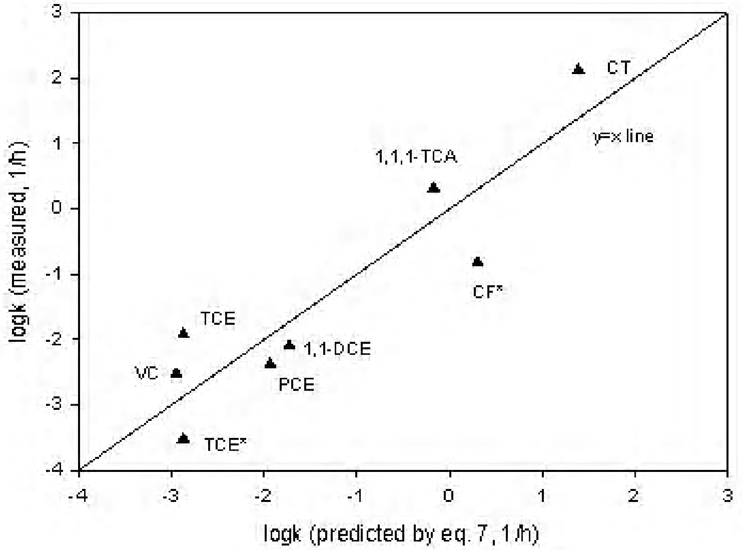

Fig. 3. Measured log k versus predicted log k values for eight chlorinated compounds in cement/Fe(II) system. Predicted log k values were computed using the LFERs in eq. 13 (see Table 2)

the findings by Burrow et al.

Fig. S2c shows the linear regression between logk and D_{R-X} by pBP/DN** predictions. D_{R-X} estimated by computational methods showed a high correlation with log k: B3LYP/6-311++g(d,p) (R2=0.805), pBP/DN** (R^2=0.804), and G2MP2 ab initio method (R^2=0.807), whereas the D_{R-X} calculated from experimental enthalpies showed a relatively poor correlation with log k (R^2=0.646). The D_{R-X} for removal of chlorine from an unsaturated carbon atom (chlorinated ethenes) is much greater than the D_{R-X} for chlorinated methanes or chlorinated ethanes, as shown in Table 1. For chlorinated ethenes, halogen substituents attract electrons from the carbon-halogen σ bond and the carbon-carbon π bond (Liu *et al.,* 2000), therefore the π-bond of chlorinated ethenes contributes to the relatively high energy of the carbon-halogen bond. It indicates that the kinetic data set for CAHs with double bond may yield high correlation with $D_{R-X.}$ Nevertheless, the result shown in Fig. S2c showed that D_{R-X} was the best descriptor to correlate with log k for reductive dechlorination in cement/Fe(II) system, regardless of the family of chemicals. Butler and Hayes (Butler and Hayes, 2000) reported that D_{R-X} showed the best relationship (R^2=0.82) with the rate constant for dechlorination by iron sulfide.

E_{LUMO} was correlated with log k in Fig. S2d. E_{LUMO} characterizes the tendency of a compound to accept electrons and to be reduced. The greater E_{LUMO} value a compound show, the less tendency to accept electrons and the lower rate constants of the reductive dechlorination it shows. Scherer et al. reported that the best LFERs was shown in the regression between the surface area normalized rate constant (k_{SA}) and the E_{LUMO} calculated from ab initio methods using 6-31G* basis set (R^2=0.83). In this study, the E_{LUMO} calculated according to Scherer et al. showed a high correlation with log k (Fig. S2e), though it was not the best. Linear regression between log k and $\Delta G^{\circ\prime}$ produced the R^2 of 0.8 (Fig. S2f).

Accurate prediction of log k will be influenced by which descriptors are included in the regression, how many variables are included in the regression, and the dependence among variables. Each descriptor was evaluated in single regressions to find a reliable variable then multiple regressions with two variables were performed (see Table 2). Fig. 3 shows plots of the log k measured for eight CAHs versus the log k predicted by eq. 13 in Table 2, showing the highest R^2 in multiple regression. All predicted rate constants were within one order of magnitude of the measured rate constants. The regression line has a slope of one and an intercept of near zero value. The data were scattered around the y=x line. Notable outliers were TCE* and CF* that were commonly transformed from a parent compound, 1,1,2,2-TeCA and CT, respectively. Multicollinearity among the independent variables were evaluated because correlated variables can include similar information so that lead to ovefitting. The multicollinearity for two variables was found in eqs 13, 15, 16, 18, 19, 22, 23, 24, and 26.

The possible products and pathways for dechlorination of an individual chlorinated compound (PCE, TCE*, 1,1-DCE, VC, 1,1,1-TCA, 1,1,2,2-TeCA, CT, and CF*) in cement/Fe(II) system were independently reported in the literatures (Hwang and Batchelor, 2000; Hwang *et al.,* 2005; Jung and Batchelor, 2008; Jung and Batchelor, 2009). However, these pathways were not overallly discussed or characterized dependent on the family of C2 chlorinated hydrocarbons such as chlorinated ethanes, and ethenes. Fig. 4 summarized transformation pathways of C2-chlorinated hydrocarbons investigated in DS/S-Fe(II). It suggests possible or confirmed transformation pathways and observed by-products from target contaminants (PCE, TCE, 1,1-DCE, VC, 1,1,2,2-TeCA, and 1,1,1-TCA). The major pathway of 1,1,1-TCA, CT, CF*, and VC was reported to be hydrogenolysis (Hwang and Batchelor, 2002; Hwang *et al.,* 2005; Jung and Batchelor, 2009), and PCE, TCE, and TCE* produced from 1,1,2,2-TeCA followed the reductive β-elimination (Hwang and Batchelor, 2000; Hwang *et al.,* 2005; Jung and Batchelor, 2008). Similarly, Arnold et al. (Arnold *et al.,* 1999) reported that reductive β-elimination was the only pathway through species containing the α, β pair of chlorine atoms (e.g. PCE, TCE, cis-DCE, and trans-DCE) in zero-valent metal system1. 1,1-DCE followed the reductive α-elimination pathway and yielded ethane as major product in cement/Fe(II) system (Hwang *et al.,* 2005).

In summary, polychlorinated ethenes (e.g. PCE, and TCE, and TCE*) favored the reductive β-elimination pathway producing acetylene as a final predominant product, while polychlorinated ethanes and methanes (e.g. 1,1,1-TCA, CT, CF*) not containing double bond preferred to follow the hydrogenolysis pathway in cement/Fe(II) slurries. 1,1,2,2-TeCA underwent the dehydrochlorination pathway forming TCE* in the cement solution of high pH, which is not a reductive dechlorination pathway.

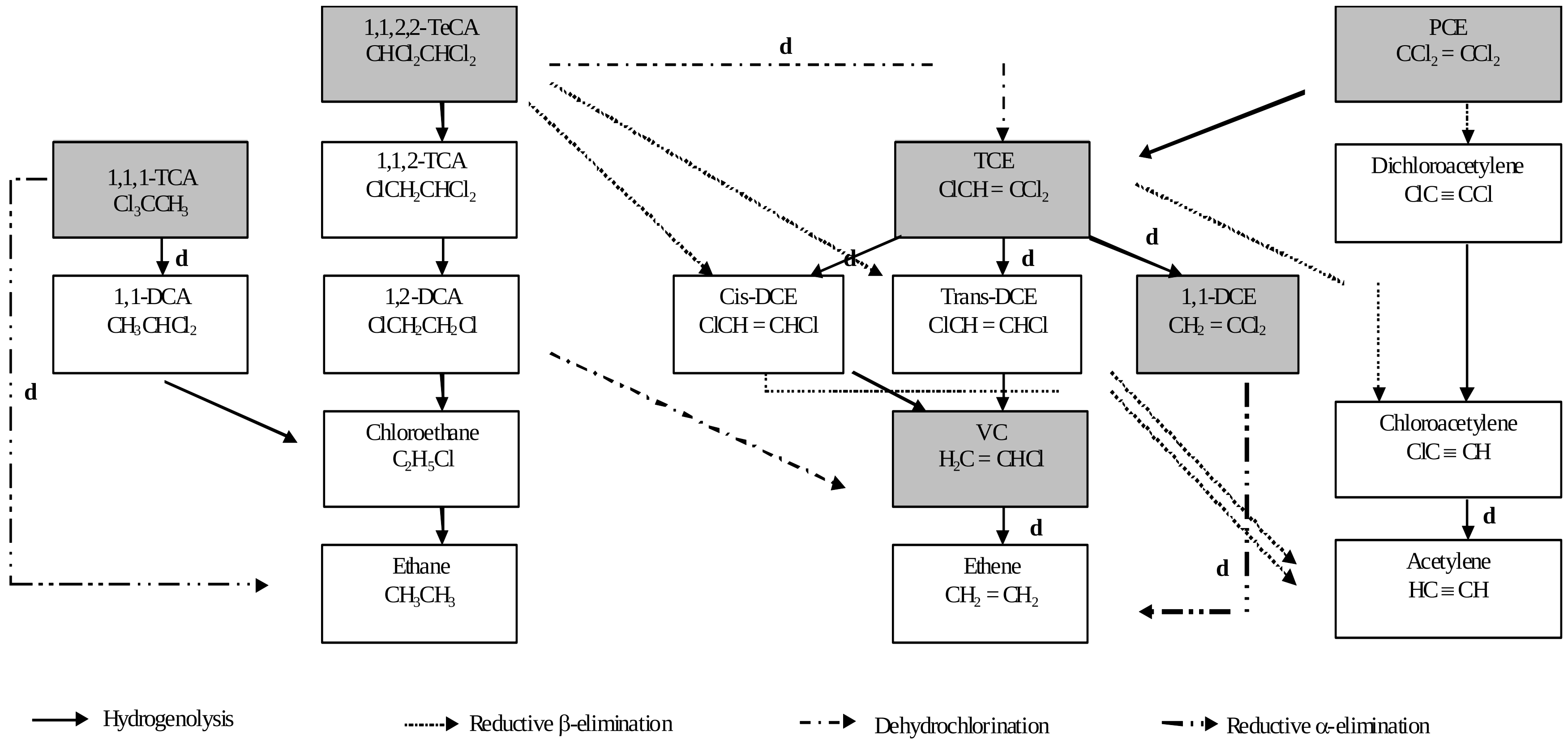

Fig. 4. Transformation pathway of C2-chlorinated aliphatic hydrocarbons in iron-based degradative solidification/stabilization. The chemicals of a shaded box were target compounds used in cement/Fe(II) system [1-4]. The symbol of "d" indicates a pathway yielding by-product detected in cement/Fe(II) slurries

(1)Jung, B. and Batchelor, B., Dechlorination of trichloroethylene formed from 1,1,2,2-tetrachloroethane by dehydrochlorination in Portland cement slurry including Fe(II), Chemosphere 71, 726-734, 2008.
(2)Jung, B. and Batchelor, B., Kinetics of transformation of 1,1,1-trichloroethane by Fe(II) in cement slurries, J. Hazard. Mater. 163, 1315-1321, 2009.
(3)Hwang, I. and Batchelor, B., Reductive dechlorination of tetrachloroethylene by Fe(II) in Cement Slurries, Environ. Sci. Technol. 34 (23), 5017-5022, 2000.
(4)Hwang, I., Park, H., Kang, W., and Park, J., Reactivity of Fe(II)/cement systems in dechlorinating chlorinated ethylenes, Journal of Hazardous Materials 118 (1-3), 103-111, 2005.

CONCLUSION

Our previous studies have investigated the reductive dechlorination of chlorinated compounds including carbon tetrachloride, 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,1,1-trichloroethane (1,1,1-TCA), tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), vinyl chloride (VC), and polychlorinated biphenyls (PCBs) in cement/Fe(II) slurries and reported the rate constants for the reductive transformation. The results showed that chlorinated aliphatic hydrocarbons generally followed pseudo first-order kinetics. And those some kinetic data were correlated with thermodynamic parameters in an earlier study. However, not sufficient kinetic data and widely used descriptors were selected for a linear free energy relationship study as the first attempt in iron-based degradative solidification/stabilization process. In this study, the reductive dechlorination rate constants of eight chlorinated aliphatic hydrocarbons (PCE, TCE, 1,1-DCE, VC, TCE*, 1,1,1-TCA, CT, CF*) were obtained and correlated with 17 descriptors. Seventeen descriptors by various computational methods were screened into six descriptors: one-electron reduction potential (E_1), two-electron reduction potential (E_2), homolytic bond dissociation energy (D_{R-X}), vertical attachment energy (VAE), lowest unoccupied molecular orbital energy (E_{LUMO}), and overall free energy change of the one-electron transfer step ($\Delta G^{\circ\prime}$). As a single regressor, $D_{R-X,}$ derived from computational estimates using pBP method with DN** basis set, showed the highest correlation with logk. E_1, “G^{o}”, and E_{LUMO} were also well correlated with dechlorination rates in cement/Fe(II) slurries. The E_{LUMO} (lowest unoccupied orbital energy) values calculated using 6-31G* method showed better correlation with log k than any other E_{LUMO} values calculated by different methods, which was accorded with the results by Scherer et al. (Scherer *et al.,* 1998). In multi regressions with two variables, combinations of E_1 and D_{R-X} showed the highest correlation coefficients in cement/Fe(II) system. E_1, D_{R-X} and “G^{o}” are commonly based on one-electron transfer step. High correlation of $E_{1,}$ $D_{R-X,}$ and “G^{o}” with log k suggests that a dissociative electron transfer is initial and rate-limiting step in transformation of chlorinated aliphatic hydrocarbons in Fe(II)/cement slurries, as observed in other LFERs.

1.1.

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