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Correlation Analysis of Rate Constants for Dechlorination by Zero-Valent Iron

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Dehalogenation is among the most important processes involved in contaminant fate, but despite all the work that has been done on the kinetics of dehalogenation, there are few linear free energy relationships (LFERs) that can be used to explain or predict rates of dehalogenation by environmental reductants. Previously, we summarized kinetic data for dehalogenation of chlorinated alkanes and alkenes by zero-valent iron (Fe^0) and showed that correlation analysis of these data with published two-electron reduction potentials did not give a simple relationship. In this study, we report successful LFERs based on estimated lowest unoccupied molecular orbital (LUMO) energies calculated from semiempirical (AM1 and PM3) and ab initio methods (6-31G*) and one-electron reduction potentials. Solvation effects can be modeled with COSMO and incorporated into semiempirical estimates of E_{LUMO}, but this did not improve the correlation with *k*. The best LFER ($\log k = -5.7 - 1.5\, E_{LUMO}$) explains 83% of the variability in surface area-normalized rate constants (*k*) with ab initio LUMO energies. The LFER is improved by correcting for statistical bias introduced by back transformation from log-linear regression models. New kinetic data for six compounds are compared with rate constants predicted using the unbiased LFER.

Introduction

Correlation analysis in the chemical sciences typically involves regression of substrate property or reactivity data (defined as the response variable) for a series of related compounds with one or several convenient descriptor variables. The resulting linear free energy relationship (LFER) can then be used to estimate values of reactivity for compounds that were not included in the original data set. The predictive power of LFERs makes them enormously important in regulatory decision-making regarding new chemicals in the environment (*1*). In addition, correlation analysis is also an important tool for data validation and mechanistic investigations.

In practice, the major impediment to LFER development for environmental applications is the lack of reliable data from which they can be derived. For example, most quantitative kinetic data for contaminant redox reactions is not derived from a well-defined kinetic model (*2*), making it difficult to compare rate constants among different studies. When reliable kinetic data are reported, there are often not enough compounds studied under equivalent conditions to provide adequate statistical power. Additional problems arise in finding values of each descriptor variable for each substrate included in the correlation. The lack of data for descriptor variables is particularly difficult in correlation analysis of kinetic data, because the descriptor variables for which data are most scarce are often those that are most fundamental (i.e., have the most unambiguous relationship to the process measured by the response variable *k*).

The lack of completely successful LFERs for dehalogenation kinetics is particularly notable because dehalogenation is one of the most important and widely studied of all contaminant degradation pathways. The abundance of dehalogenation studies is due, in part, to the variety of general reaction types available for cleaving carbon−halogen bonds. While the rates of these processes are often fast enough to affect the environmental fate of halogenated hydrocarbons, they tend to vary with substrate and chemical and microbiological conditions. As a basis for remediation technologies, dehalogenation mediated by microorganisms has received a great deal of attention, and there is growing interest in several processes that produce dehalogenation under abiotic conditions, such as reactions involving cyanocobalamin or zero-valent iron (Fe^0). Recently, kinetic data on dechlorination by Fe^0 have become quite abundant (*3*), and they now make up one of the most extensive data sets available for pursuing correlation analysis of contaminant dehalogenation rates.

We have performed correlation analysis using this Fe^0 data set in order to (i) explore the reliability of the available data, (ii) develop LFERs for predicting dechlorination rates by Fe^0, and (iii) improve our understanding of the factors controlling reduction kinetics by Fe^0 and dehalogenation kinetics in general. The goal was to develop a LFER that offers a statistically robust predictive tool and is consistent with the combination of statistical and mechanistic criteria that reflect the mixed purposes of environmental scientists and engineers (*4*). Satisfactory correlations were obtained with a variety of measures of electron affinity as the descriptor variable, and LFERs derived from the best correlations may be suitable for use as predictive models. The analysis also has implications regarding the reduction of solutes by Fe^0 and the degradation of chlorinated aliphatics by competing reduction pathways.

Methods

Training Set Data. The data set of surface area-normalized rate constants (*k*) reported by Johnson et al. (*3*) was used to derive the correlations described in this study. The scope of the data set is limited to chlorinated aliphatic compounds reacting with granular zero-valent iron and does not include halogenated aromatic compounds, zero-valent metals other than Fe^0, bimetallic reductants, or nonaqueous systems. Other experimental variables, such as mixing efficiency, iron type, and adsorption to nonreactive sites are known to affect the rate of dehalogenation (*5, 6*), but quantitative corrections for these factors are not yet practical (*3, 7*). Therefore, the original rate data reported by Johnson et al. (*3*) were used for correlation analysis, and the effects of uncorrected

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TABLE 1. Data for Training Set Compounds

chlorinated aliphatic	abbrev	label	$\bar{k}^a$ (L m^{-2} h^{-1})	N	$E_{LUMO}{}^b$ (eV)	$\hat{k}$ (L m^{-2} h^{-1})	% dev $e_i/\hat{k}$	E_1 (V)	$\hat{k}$ (L m^{-2} h^{-1})	% dev $e_i/\hat{k}$
tetrachloromethane	PCM	a	$(1.2 \pm 1.5) \times 10^{-1}$	11	−3.054	8.9×10^{-2}	36	0.13	5.0×10^{-2}	139
trichloromethane	TCM	b	$(9.2 \pm 7.3) \times 10^{-4}$	3	−2.277	6.2×10^{-3}	−85	−0.23	4.9×10^{-3}	−81
hexachloroethane	HCA	c	$(3.1 \pm 3.3) \times 10^{-2}$	2	−2.555	1.6×10^{-2}	94	0.33	1.8×10^{-1}	−83
1,1,1,2-tetrachloroethane	1112TeCA	d	1.4×10^{-2}	1	−2.390	9.1×10^{-3}	54	−0.22	5.2×10^{-3}	169
1,1,2,2-tetrachloroethane	1122TeCA	e	1.3×10^{-2}	1	−1.982	2.2×10^{-3}	621	−0.34	2.4×10^{-3}	442
1,1,1-trichloroethane	111TCA	f	1.1×10^{-2}	1	−2.160	4.1×10^{-3}	167	−0.23	4.9×10^{-3}	125
tetrachloroethene	PCE	g	$(2.1 \pm 2.7) \times 10^{-3}$	4	−1.689	8.2×10^{-4}	156	−0.36	2.1×10^{-3}	0
trichloroethene	TCE	h	$(3.9 \pm 3.6) \times 10^{-4}$	12	−1.435	3.4×10^{-4}	14	−0.62	3.9×10^{-4}	0
cis-1,2-dichloroethene	c12DCE	i	$(4.1 \pm 1.7) \times 10^{-5}$	3	−1.200	1.5×10^{-4}	−73	−0.89	6.8×10^{-5}	−40
trans-1,2-dichloroethene	t12DCE	j	$(1.2 \pm 0.4) \times 10^{-4}$	4	−1.200	1.5×10^{-4}	−22	−0.85	8.8×10^{-5}	36
1,1-dichloroethene	11DCE	k	$(6.4 \pm 5.5) \times 10^{-5}$	3	−1.140	1.2×10^{-4}	−49	−0.72	2.1×10^{-4}	−69
vinyl chloride	VC	l	$(5.0 \pm 1.5) \times 10^{-5}$	3	−0.761	3.4×10^{-4}	47	−0.95	4.6×10^{-5}	8

[a] Arithmetic averages ± 1 SD from kinetic data previously compiled in refs *3* and *7*. [b] From ab initio calculations with the 6-31G* basis set.

experimental variables were evaluated statistically as possible sources of variance in dehalogenation rates.

Three types of descriptor variables were used for LFER development: (i) LUMO energies calculated by molecular modeling with semiempirical and ab initio methods, (ii) thermodynamic estimates of one- and two-electron reduction potentials compiled from the literature (*8*−*10*), and (iii) diffusion coefficients estimated using the method of Hayduk and Minhas (*11*, *12*). Additional descriptor variables (solubility, sediment−water partitioning coefficient, and vapor pressure) were investigated but gave poor correlations ($r^2 <$ 0.5).

Molecular descriptor variables were calculated using the CAChe WorkSystem software (Oxford Molecular Group Inc., Beaverton, OR). Energies of the LUMO were obtained with the semiempirical method MOPAC (*13*, *14*) and Mulliken II (*15*, *16*) using version 3.9 of CAChe's Macintosh Project Leader interface (running on an IBM RS6000). For comparison, MOPAC was run using the AM1 and PM3 parameter sets (*13*, *14*) for gas-phase calculations and the Conductor-like Screening Model (COSMO) for incorporating solvent effects (*17*). The minimum energy conformation for compounds with more than one plausible geometry was found by comparing heats of formation calculated with the PM3 parameter set. The calculated values of E_{LUMO} for all chlorinated methanes, ethanes, ethenes, and propanes are provided as Supporting Information.

Validation Set Data. New data for disappearance kinetics came from batch tests performed in a manner similar to methods described previously (*18*, *19*) and rate constants published in the literature after November 1995. The two chlorinated ethanes tested in this study were 1,1,1-trichloroethane (Aldrich, 99.5%, anhydrous) and 1,1-dichloroethane (Chem Service). Kinetic experiments were conducted with 10 g of 18−32 mesh (0.5−1.0 mm size fraction) iron turnings (Fluka, puriss grade) in vials containing 12 mL of deionized water. The iron, used without treatment to clean or activate the metal surface, had a specific surface area of 0.019 m^2 g^{-1} (*3*). Mixing was achieved by rotation at room temperature (23 ± 1 °C). Substrate disappearance kinetics were determined by periodically extracting the aqueous phase of bottles with hexane and analyzing the extract by gas chromatography with direct aqueous injection and ECD detection (*19*). Volatilization losses were determined by running a series of control bottles with no iron metal.

Results and Discussion

Definition of the Response Variable. For degradation of chlorinated aliphatic compounds by zero-valent metals, a surface area-normalized, first-order kinetic model has proven to be practical and appropriate (*3*). Thus, the rate of disappearance for a compound P is described by

$$\frac{d[P]}{dt} = -k\rho_a[P] \tag{1}$$

where k is the surface area-normalized rate constant (L h^{-1} m^{-2}) and ρ_a is the surface area concentration of Fe^0 [m^2 (L of solution)$^{-1}$]. By averaging all values of k available as of November 1995, Johnson et al. (*3*) defined a set of representative rates constants ($\bar{k}$) for 13 chlorinated aliphatic compounds. The values of $\bar{k}$ were used in this study for exploratory correlation analysis and are summarized in Table 1. The original data set was used for calculating LFERs, and it can be found in the Supporting Information to Johnson et al. (*3*). New values of k, from this study and others, were used only for LFER validation.

Descriptor Variables from Thermodynamics. There are many descriptor variables that might correlate with k, including one- and two-electron reduction potentials, half-wave potentials, molecular orbital energies, and electron affinities. Correlations between four descriptor variables and $\bar{k}$ are summarized as a matrix of scatterplots in Figure 1. The descriptor variables include two-electron reduction potentials (E_2), one-electron reduction potentials (E_1), and lowest unoccupied molecular orbital energies (E_{LUMO}) calculated by semiempirical methods with solvation (AM1/H$_2$O) and ab initio methods without solvation (CAChe's Mulliken and the 6-31G* basis set).

E_2 corresponds to the overall reduction potential for dehalogenation, from nonradical reactants to nonradical products by hydrogenolysis ($RX + H^+ + 2\,e^- \rightarrow RH + X^-$) or vicinal dehalogenation (e.g., 1,2-dihaloalkanes $+\ 2\ e^- \rightarrow$ alkenes $+\ 2X^-$). The E_2 values used here correspond to reduction by hydrogenolysis (as discussed in greater detail below). Since these half-reactions are not reversible, E_2 is not amenable to direct measurement. There are, however, several methods by which E_2 can be estimated (*10*, *20*). For many years, the set of E_2 values estimated by Vogel et al. (*10*) was the only published set of descriptor data that included all chlorinated aliphatic compounds of environmental importance. Various researchers have attempted to use these data in correlation analysis of dechlorination kinetics (e.g., ref *21*), including our preliminary effort at correlation analysis of k data for reaction with Fe^0 (*3*), but the results have never led to the successful derivation of LFERs. The perspective provided by Figure 1 shows that E_2 is moderately correlated with $\bar{k}$, E_1, and E_{LUMO}. The E_2 for vinyl chloride (labeled l in Figure 1) is the only value that appears to be an outlier in all three correlations. Presumably, the major reason that E_2 does not give robust LFERs for dechlorination kinetics is that the rate-limiting step generally does not involve con-

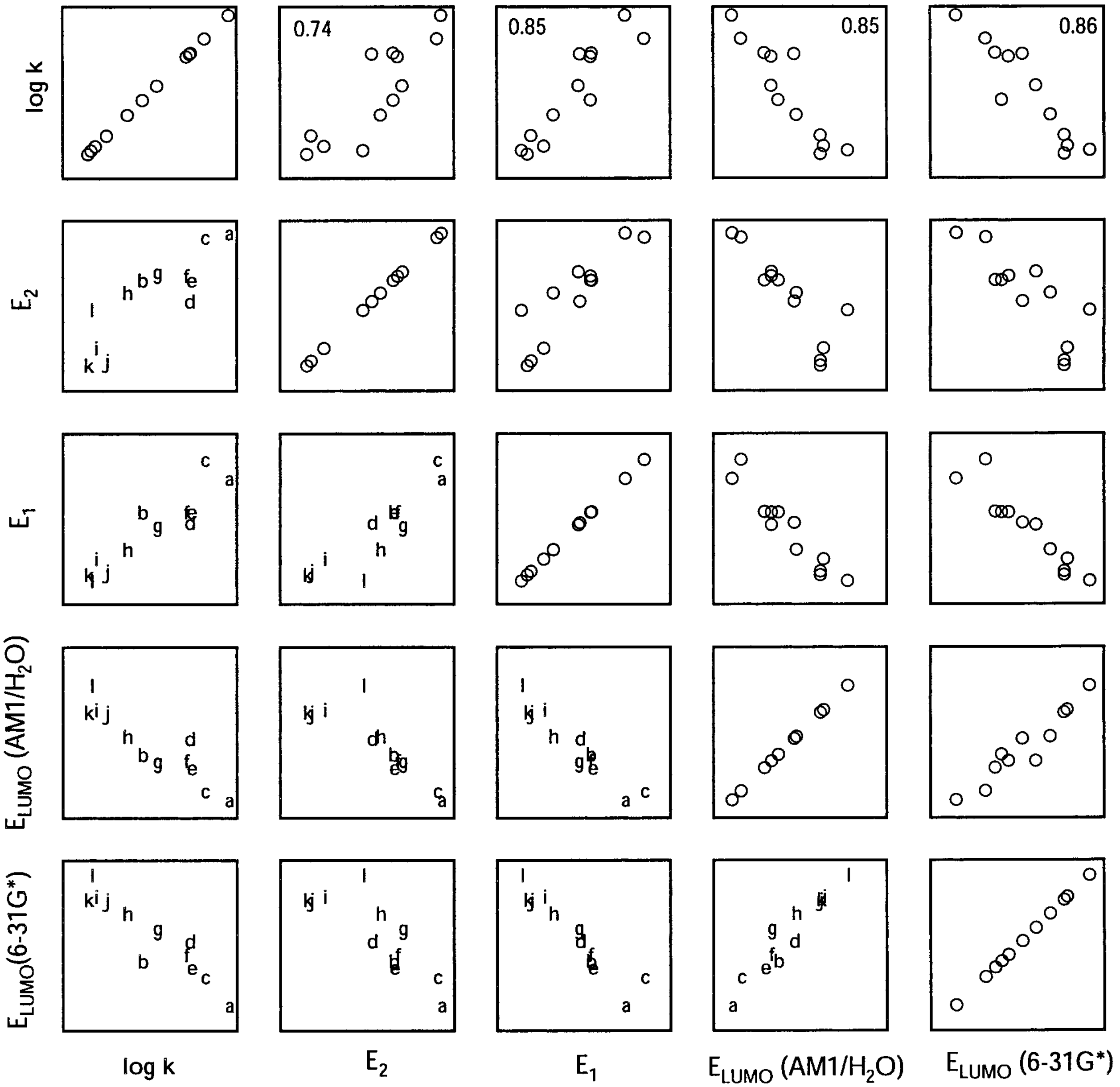

FIGURE 1. Scatter plot matrix of log *k* versus selected electronic descriptor variables. E_2 values are from ref *10*, and E_1 values are from refs 9 and 8. E_{LUMO} AM$_1$/H$_2$O and E_{LUMO} 6-31G* were calculated using molecular modeling software (CAChe). Correlation coefficients, r^2, are given for the top row. The compound labels are defined in Table 1.

certed transfer of two electrons, as implied by the use of E_2, but instead involves initial transfer of a single electron (*22, 23*).

E_1 is a more promising descriptor for dechlorination kinetics, insofar as it represents the potential of the rate-limiting initial electron-transfer step. For hydrogenolysis of simple aliphatics, dechlorination is initiated by dissociative electron transfer (i.e., $RX + e^- \rightarrow R^\bullet + X^-$) not simple electron transfer ($RX + e^- \rightarrow RX^{\bullet-}$), so it is E_1 for the former half-reaction that is of greatest interest (*22, 23*). Again, these reactions are not reversible, so measured potentials are generally not available, and estimation methods offer the only possibility of obtaining a complete and consistent set of data for use in correlation analysis. Estimates of E_1 for all of the chlorinated methanes, ethanes, and ethenes have now been published (*8, 9*), and these data are included in Figure 1. The resulting correlations involving E_1 are sufficiently improved over those involving E_2 that we have chosen to present a LFER for *k* versus E_1 in the following section.

E_1 and E_2, however, are defined for specific reactions with particular products, which makes them inconvenient descriptors for compounds that can dechlorinate by more than one pathway. The dependence on reaction products applies to branching among hydrogenolysis pathways as well as branching between hydrogenolysis and reductive elimination. The former is illustrated by the hydrogenolysis of 1,1,1,2-TeCA, which can yield 1,1,1-TCA or 1,1,2-TCA. In this case, correlations based on the assumption that reduction at the perhalogenated carbon is favored resulted in a better correlation coefficient (for both E_1 and E_2). A more difficult case involves hydrogenolysis of TCE, which can yield *cis*-1,2-DCE, *trans*-1,2-DCE, or 1,1-DCE. In principle, this complication can be accommodated with a descriptor for TCE disappearance that is the weighted sum of the reduction potentials for the three contributing reduction pathways. However, this refinement is not yet practical because we do not have estimates of the reduction potentials of TCE to *cis*-1,2-DCE or data on the branching ratios for formation of *trans*-1,2-DCE and 1,1-DCE. For the present, we have used the values of E_1 and E_2 that correspond to formation of *trans*-1,2-DCE because they give a slightly better correlation with $\bar{k}$ data for TCE.

A quantitative accounting of the effect of branching between hydrogenolysis and reductive elimination would require a more fundamental correction because the two pathways involve different mechanisms. Ideally, the correction should be applied before correlation analysis by extracting separate rate constants for each pathway, but there is not yet enough data to make these calculations. As an alternative, we have selected values of E_1 and E_2 for hydrogenolysis, so that the resulting correlations can be used to test for significant deviations that might be attributable to reductive elimination. The results in Figure 1 show that compounds susceptible to reductive elimination (those with vicinal halogen substituents, compounds labeled c−e, g−j) do not correlate differently than those that can be reduced only by hydrogenolysis (compound labels are listed in Table 1). It is not known how experimental conditions effect branching ratios however, so the effect of branching ratios on descriptor variables such as E_1 and E_2 is still a potential source of difficulty in future applications of LFERs for reduction of halogenated aliphatic compounds.

Descriptor Variables from Molecular Modeling. Molecular descriptors calculated by computer have the advantage that large, consistent sets of calculations can be performed with commercially available software, and they include some quantum-chemical descriptors that are not directly accessible by experimentation. Of the quantum-chemical descriptors that have been used in LFER analysis (*24*), E_{LUMO} is the most easily justified for reduction of chlorinated aliphatics. This is because the LUMO is the frontier molecular orbital into which electron transfer takes place, and the energy of this orbital helps determine the driving force for reaction (*25*). An additional advantage of molecular orbital energies as descriptor variables in correlation analysis is that there is only one value per reactant, so the complications arising from branching pathways may be circumvented.

We have correlated $\bar{k}$ and E_{LUMO} values calculated by a variety of methods and found that all combinations exhibit a high degree of covariance. Semiempirical calculations with AM1 and PM3 parameters are highly correlated ($r^2 = 0.98$) and result in similar correlations (not shown) with $\bar{k}$ ($r^2 =$ 0.81 and 0.76, respectively). The incorporation of solvation effects and the use of ab initio methods improved the correlation with $\bar{k}$ slightly. Figure 1 includes two of the best correlations: $\bar{k}$ versus E_{LUMO} from MOPAC with AM1 parameters and solvation by COSMO (AM1/H_2O), and $\bar{k}$ versus E_{LUMO} by ab initio methods with 6-31G* parameters but no solvation. The scatter plots for both these combinations reveal strong linear correlations, despite important differences in the way the two sets of E_{LUMO} values were calculated.

The effect of solvation on E_{LUMO} values calculated from the semiempirical method is illustrated in Figure 2. Regression on E_{LUMO} values calculated with and without solvation gives slopes slightly less than 1 and slightly negative intercepts for both AM1 and PM3 parameter sets. Thus, the solvation correction results in values of E_{LUMO} that are systematically more negative and span a narrower range. These effects do not favor an improved correlation between E_{LUMO} and $\bar{k}$, and the lack of scatter about the regression lines in Figure 2 suggests that there is little compound-specific variation that is accounted for by the solvation correction. Although the correlation between $\bar{k}$ and E_{LUMO} does improve slightly when the solvation-corrected values are used (r^2 increases from 0.81 to 0.85 for AM1 and from 0.76 to 0.79 for PM3), the regression lines are not statistically different. Therefore, incorporating solvation *does not* make E_{LUMO} a significantly improved descriptor of dehalogenation rates for simple chlorinated aliphatic compounds. This result is consistent with commonly proposed mechanisms for dechlorination (e.g., refs *8* and *19*), which do not involve charged species.

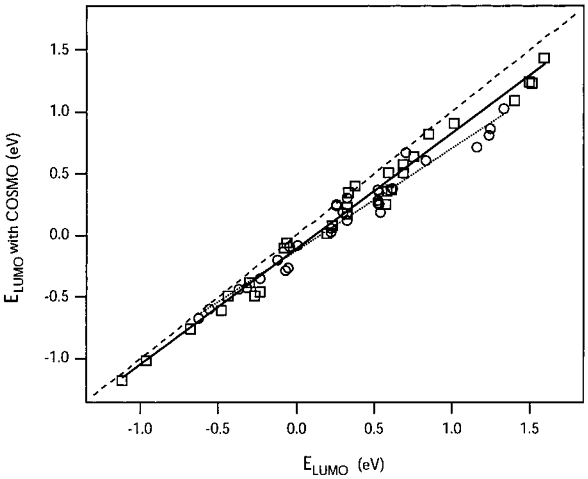

FIGURE 2. Effect of solvation on E_{LUMO} values calculated from semiempirical methods. (□) E_{LUMO} values calculated using AM1 parameter set; (○) E_{LUMO} values calculated using PM3 parameter set. Lines represent regression between E_{LUMO} values calculated with COSMO to account for solvation and E_{LUMO} values calculated without COSMO. Regression on AM1 (solid line) gives $(0.94 \pm 0.02)x - 0.11 \pm 0.02$ with $r^2 = 0.98$. Regression on PM3 (dotted line) gives $(0.83 \pm 0.03)x - 0.12 \pm 0.02$ with $r^2 = 0.96$. The dashed line is included to show perfect agreement (i.e., slope = 1.0).

In the absence of strong solvation effects, the greater accuracy of ab initio methods offers the best opportunity for improving the correlation between $\bar{k}$ and E_{LUMO}. The results can be seen in Figure 1, which includes the best correlations we obtained to E_{LUMO} values from semiempirical methods (MOPAC with AM1 parameters and COSMO) and ab initio methods (Mulliken with 6-31G* basis set). The distribution of data in the two scatterplots are very similar, but there is slightly less scatter with the ab initio descriptor ($r^2 = 0.85$ for AM1/H_2O versus 0.86 for 6-31G*). Based on these statistical considerations and considering the increased availability of ab initio methods in commercially available molecular modeling software, we conclude that ab initio methods (despite large computational requirements) may offer an improved way to calculate E_{LUMO} values for use as the descriptor variable in LFERs for dehalogenation kinetics.

Regression and Regression Diagnostics. Considering the substantial uncertainties in $\bar{k}$, it is difficult to envision further refinements in descriptor variables that would improve on the correlations in Figure 1. Instead, the next step is to derive LFERs from the best correlations and to explore the application of these as tools for interpreting dehalogenation kinetics by Fe^0. Raw k data, rather than $\bar{k}$, have been used to obtain LFERs that are unbiased due to the large variability in (i) the number of data available for each compound ($N =$ 1−12) and (ii) the magnitude of k for each compound. The scatterplots for k versus two descriptors, E_1 and the ab initio values of E_{LUMO}, are shown in Figure 3.

To obtain LFERs from the two sets of data in Figure 3, we used a mechanistically based semilogarithmic model relating kinetic data to a single descriptor variable (*4*):

$$\log k = \log b_0 + bx + \epsilon \tag{2}$$

where b_0 and b are the adjustable parameters, x is the descriptor variable, and ϵ represents variability in k not explained by x, i.e., indeterminant error. The adjustable parameters b and b_0 were estimated by least squares

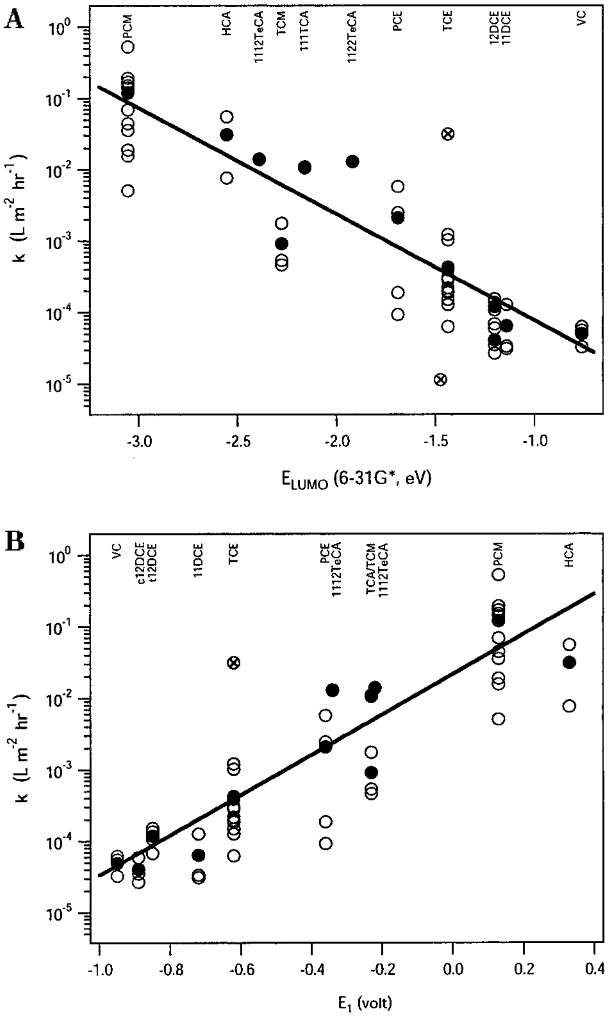

FIGURE 3. (A) Correlation between log *k* and E_{LUMO}. (B) Correlation between log *k* and E_1. Open circles (○) represent individual data, and solid circles (●) indicate the average *k* values ($\bar{k}$) reported in Table 1. Solid lines represent the unbiased prediction using eq 5 and parameters given in Table 2. Point marked with an X was treated as an outlier.

TABLE 2. Parameter Estimates and Statistics on Linear Regression[a]

descriptor	log b_0	b	N	r^2	s[b]	error, ϵ	CF = 10^e
E_{LUMO}	-5.74 ± 0.20	-1.49 ± 0.10	48	0.832	0.52	0.137	1.37
E_1	-1.82 ± 0.11	2.81 ± 0.20	48	0.810	0.56	0.155	1.43

[a] Analysis of variance (ANOVA tables) are provided as Supporting Information. [b] Standard error of the estimate.

regression on all of the original data for *k*. The results are summarized in Table 2, and the regression lines based on eq 2 are plotted as solid lines in Figure 3. A correlation based on E_{LUMO} values from MOPAC with PM3 parameters and COSMO was presented previously (*26*).

The validity of the model presented in eq 2 can be assessed by analysis of residuals based on the log-transformed response variable (log *k*). Residual analysis provides a means for testing that ϵ is randomly and normally distributed and that no significant descriptor variable has been omitted from the model (*27*). To do this for the LFERs represented in Figure 3, we calculated the residuals (e_i) of the log-transformed response variable (represented by y_i) from

$$e_i = y_i - (\log b_0 + bx) \tag{3}$$

and plotted the standardized residual (e_i/s) versus the descriptor variable (x). The results are shown in Figure 4 for the two descriptors variables E_{LUMO} and E_1. Inspection of the plots reveals no systematic trends in the residuals indicative of errors in the model (eq 2) or anomalous values (outside two standard deviations) due to individual outliers.

Although the lack of systematic trends in the residuals plots suggests that the errors are randomly distributed, it does not demonstrate that the distribution is normal. This, however, can be seen in the histogram of residuals from the E_{LUMO} correlation, shown in Figure 5, which reveals the distinctive bell-shaped pattern associated with a normal distribution. The sampling increment used to generate Figure 5 was selected to give five or more occurrences in most intervals, resulting in a bin width of 0.35 and a total of 7 bins. Application of the Lillefors (*28, 29*) and Kolmogorov–Smirnov (*30*) tests for normality (at the 95% confidence level) confirm that the distribution shown in Figure 5 is normal. Equivalent results (not shown) were obtained for the residuals from the LFER based on E_1.

Residuals plots can also be useful in assessing whether additional descriptor variables should be included in the model. As discussed earlier, other experimental variables, such as mixing efficiency and iron type, are known to affect *k* (*3, 7*). Although most of these variables do not lend themselves to making quantitative corrections in *k* before correlation analysis, we can test for their effect after correlation analysis by analyzing the relationship of the residuals to other descriptors (*27*). For example, the role of diffusion can be assessed by plotting the standardized residuals versus the diffusion coefficient, as shown in Figure 4. The lack of correlation between these parameters suggests that a multiple regression model that included diffusion coefficients would not improve on the LFERs in Figure 3. The lack of correlation with diffusion coefficients is consistent with electrochemical evidence showing that mass transport has little influence on the reduction rate of carbon tetrachloride by Fe^0 (*31*).

Prediction and Validation. To use LFERs in a predictive mode, it is important to consider that eq 2 is derived by linear transformation of an exponential model represented by eq 4:

$$k = b_0 10^{bx} \tag{4}$$

Because the error term, ϵ, is not included in this equation, using it to predict *k* will give biased results (*32, 33*). To obtain unbiased estimates of *k*, each term, including the error term, should be included in the exponential model, as shown in eq 5:

$$k = b_0 10^{bx} 10^{\epsilon} \tag{5}$$

To use this model, it is necessary to estimate the expected value of 10^{ϵ}. For ϵ that is normally distributed (recall Figure 5), it has been shown (*34*) that 10^{ϵ} will be log-normally distributed with an expected value of

$$E[10^{\epsilon}] = 10 \exp\left(\mu_{\epsilon} + \frac{\sigma_e^2}{2}\right) \tag{6}$$

where μ_{ϵ} is the mean error and σ_{ϵ}^2 is the mean variance. To evaluate eq 6 for a normal distribution, an appropriate procedure (*35*) is to assume that $\mu_{\epsilon} = 0$ and σ_{ϵ}^2 can be estimated from

$$\sigma_{\epsilon}^2 = \frac{\sum_{i=1}^{N} e_i^2}{N - 2} \tag{7}$$

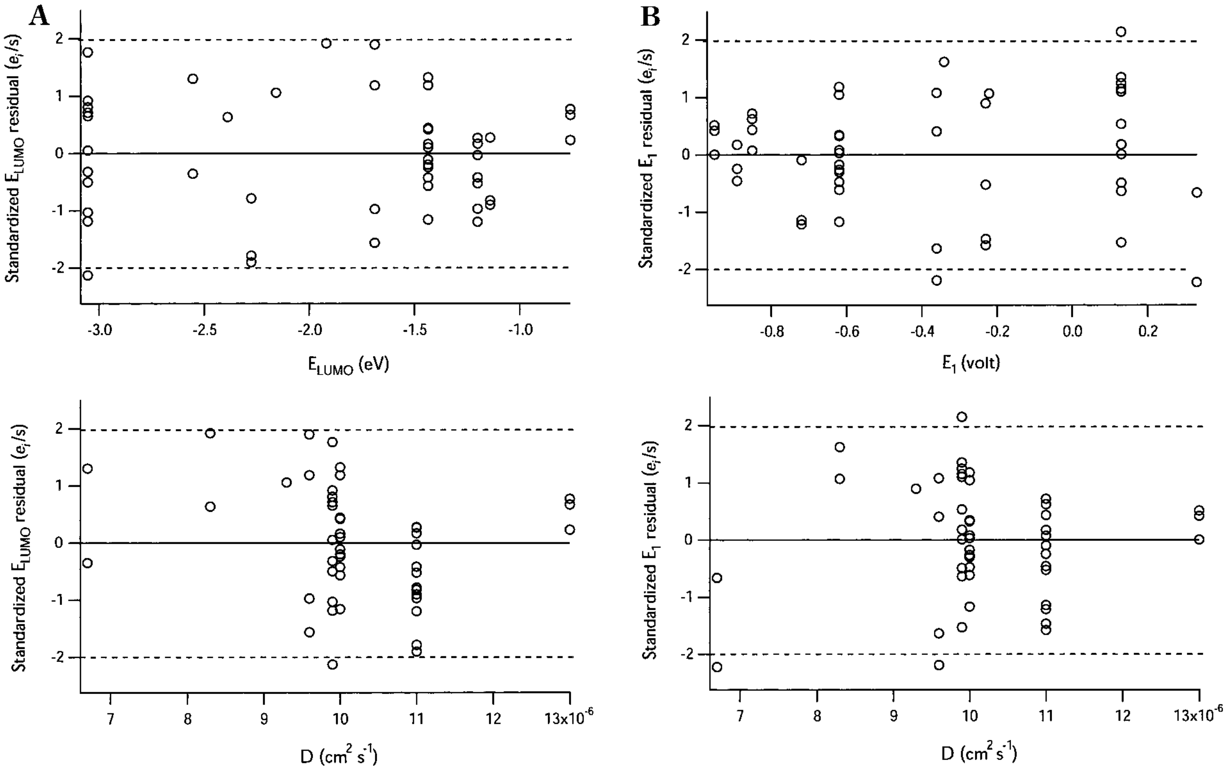

FIGURE 4. (A) Standardized residual plots for log *k* versus E_{LUMO} correlation. (B) Standardized residual plots for log *k* versus E_1 correlation. Dashed lines are included to indicate acceptable spread in the data (± 2 standard deviations). Estimated diffusion coefficients are tabulated in Supporting Information.

TABLE 3. New Data for Validation Set Compounds

chlorinated aliphatic	abbrev	measured *k* (L m^{-2} h^{-1})	ref	E_{LUMO} (eV)	$\hat{k}$ (L m^{-2} h^{-1})	% dev $e_i/\hat{k}$	E_1 (V)	$\hat{k}$ (L m^{-2} h^{-1})	% dev $e_i/\hat{k}$
1,1-dichloroethane	11DCA	1.5×10^{-3} [a]	*b*	−1.267	1.9×10^{-4}	689	−0.40	1.6×10^{-3}	−6
1,1,1-trichloroethane	111TCA	2.2×10^{-3}	*b*	−2.160	4.1×10^{-3}	−46	−0.23	4.9×10^{-3}	−55
1,1,1-trichloroethane	111TCA	4.6×10^{-1}	39	−2.160	4.1×10^{-3}	11 310	−0.23	4.9×10^{-3}	9290
trichloroethene	TCE	3.2×10^{-2} [c]	38	−1.435	3.4×10^{-4}	9 310	−0.62	3.9×10^{-4}	8100
trichloroethene	TCE	1.0×10^{-3}	45	−1.435	3.4×10^{-4}	194	−0.62	3.9×10^{-4}	156
vinyl chloride	VC	7.3×10^{-6}	46	−0.761	3.4×10^{-5}	−78	−0.95	4.6×10^{-5}	−84

[a] Average of two experiments. [b] Measured in this study. [c] Metal surface area/volume of solution = 500 m^{-1}.

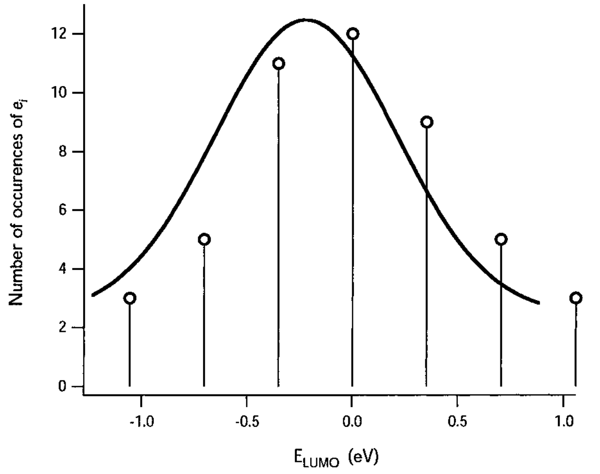

FIGURE 5. Histogram of residuals for the log *k* versus E_{LUMO} correlation. Circles mark the centers of each E_{LUMO} interval. The solid curve is a nonlinear least-squares fit to the Gaussian function.

where e^2_i is the sum of squared residuals from regression. Combining eqs 6 and 7 gives the general form of the correction factor (CF) necessary to use eq 5:

$$10^{\epsilon} = 10 \exp \frac{\frac{1}{2}\sum_{i=1}^{N} e_i^2}{N-2} \tag{8}$$

The values of 10^{ϵ} given in Table 2 indicate that use of eq 4 instead of eq 5 to estimate *k* gives a 37% bias with E_{LUMO} and a 43% bias with E_1. Surprisingly, we have not seen this correction applied in the environmental literature on LFERs involving kinetics, although it has been discussed in other contexts, such as in the estimation of river loads from discharge data (*36*) and metal toxicity from water hardness (*37*). A survey of LFERs for the latter (*37*) showed that the bias ranged from 2 to 57%.

The model represented by eq 5 together with the fitted parameters for each LFER (Table 2) can be used to calculate expected values of the rate constant, $\hat{k}$, for any chlorinated aliphatic compound. The results of these calculations are summarized in the Supporting Information for all chlorinated methanes, ethanes, and ethenes as well as selected chlorinated propanes (those with up to three chlorines). To test these predictions, and thereby to validate our predictive model, new kinetic data were measured for two chlorinated aliphatics with an unbuffered batch system containing granular Fe^0. The compounds studied were chosen to provide

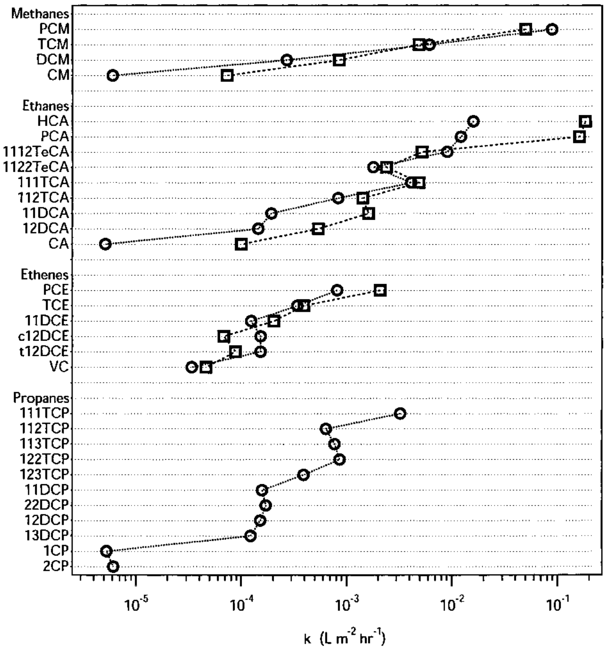

FIGURE 6. (○) Predicted k values based on correlation between log k and E_{LUMO}. (□) Predicted k values based on correlation between log k and E_1. Values were calculated using eq 5 and the coefficients given in Table 2.

more data on the less reactive (i.e., less chlorinated) members of each family of congeners, because the majority of previously reported rates were for compounds that displayed fast kinetics (i.e., the more highly chlorinated compounds). Table 3 summarizes our two new values of k along with four recently reported literature values for TCE, VC, and 111TCA (note that 111TCA was also part of the training set) and the corresponding values of $\hat{k}$. Four of the new data conform to the same general trend in reactivity predicted by the LFERs, with e_i that are of the same magnitude as the residuals for the original training set data. The new values for TCE (*38*) and 111TCA (*39*), however, show markedly faster reaction rates than those predicted by the LFERs. The 111TCA rate constant may be anomalously high because of the high concentrations of NaCl (0.1 M) used in the experiments. The presence of chloride at concentrations up to 0.1 mM have been shown to increase the rate of carbon tetrachloride reduction by 4-fold, presumably by destabilizing the oxide film (40).

Insights from LFERs. To obtain a better perspective on how molecular structure is related to the kinetics of dechlorination by Fe^0, the values of $\hat{k}$ estimated from LFERs derived in this study are summarized graphically in Figure 6. As expected (*3*), rates decrease systematically with the number of chlorines on the most halogenated carbon(s) within each family of congeners. However, the figure also reveals remarkably little offset between each congener family. As a result, most monohalogenated aliphatics have $k \approx 10^{-5}$ L m^{-2} h^{-1}, dihalogenated aliphatics have $k \approx 10^{-4}$ L m^{-2} h^{-1}, trihalogenated aliphatics have $k \approx 10^{-3}$ L m^{-2} h^{-1}, etc. Superimposed on this general trend are two other revealing patterns: (i) perhalogenation of one or more carbons apparently favors increased reactivity, and (ii) dechlorination rates for the ethenes seem to be slightly less sensitive than the alkanes to degree of chlorination.

The increase in k associated with perhalogenation of alkanes may be due to the differences in the stability of the intermediates that result from the initial electron transfer (3° > 2° > 1°, etc.). The comparative insensitivity of ethenes to the effect of chlorine substituents may reflect the effect of unsaturation. The latter might be due to differences in bond strength ($sp^2 > sp^3$); however, then we would expect $\hat{k}$ to be less for all alkenes relative to the corresponding alkanes, which is not the case. An alternative explanation can be postulated by analogy to an analysis of polarographic reduction potentials by Fukui et al. (*41*). They concluded that electron transfer to halogenated aliphatic compounds occurs into the lowest unoccupied σ level (presumably antibonding) because the wide variation in observed reduction potentials is similar to the wide variation in the calculated energies of these orbitals. In contrast, they found that the lowest energy π levels are almost identical for the chlorinated ethenes. Thus, the comparative insensitivity of $\hat{k}$ to the degree of chlorination on ethenes (seen in Figure 6) may reflect a greater importance of π orbitals in determining the rate of reduction of chlorinated alkenes by Fe^0. Other recent studies have presented arguments for (*42*, *43*) and against (*44*) the involvement of π orbitals in electron transfer to unsaturated halogenated aliphatics.

Two final examples of useful insights that can be derived from this correlation analysis arise from comparisons between the two sets of $\hat{k}$ data in Figure 6. First, note that $\hat{k}$ for HCA and PCA are notably greater when calculated from E_1 than when calculated from E_{LUMO}. Inspection of Figures 1 and 3 shows that HCA only appears to be an outlier in plots that involve E_1. (PCA is not included in either figure because no measured values of k have been reported.) A similar result was obtained by Perlinger (*21*), who found that PCA and HCA behaved as outliers among chlorinated and brominated alkanes in a correlation between E_1 (from Curtis) and E_{LUMO} (calculated independently of the values reported here). Second, Figure 6 reveals a more systematic deviation for mono- and dichlorinated methanes and ethanes in that $\hat{k}$ tends to be higher when estimated from E_1 than when estimated from E_{LUMO}. It is tempting to interpret this difference as evidence for or against dissociative electron transfer, because E_1 values should reflect the energy of C−X bond breaking (*22*, *23*) whereas E_{LUMO} values do not (and bond strength varies with degree of halogenation). Unfortunately, the available measured data (including the new values of k reported in Table 3) are not yet adequate to resolve which LFER is more accurate for the least halogenated alkanes. This issue will likely attract further investigation due to the desirability of complete dechlorination in remediation applications of Fe^0.

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Symbols

ρ_a	surface area concentration (m^2 L^{-1})
[P]	molar concentration of substrate (mol L^{-1})
k	surface area-normalized reaction rate constant (L h^{-1} m^{-2})
$\bar{k}$	averaged representative surface area-normalized rate constant (L h^{-1} m^{-2})
$\hat{k}$	predicted surface area-normalized rate constant (L h^{-1} m^{-2})
E_{LUMO}	energy of the lowest unoccupied molecular orbital (eV)
E_1	one-electron reduction potential (V)
E_2	two-electron reduction potential (V)

r^2	correlation coefficient
b, b_0	adjustable parameters from linear least-squares regression
ϵ	model error
e_i	regression residual ($k_\mathrm{i} - \hat{k}$)
s	standard deviation
μ_ϵ	mean error
σ_ϵ^2	mean variance
N	number of data points

Supporting Information Available

Four tables detailing the summary of molecular-based and product-dependent variables for chlorinated aliphatics and ANOVA for log k vs E_LUMO and E_1 correlation (5 pages). Ordering information is given on any current masthead page.

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