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Linear Free Energy Relationships for Polyhalogenated Alkane Transformation by Electron-Transfer Mediators in Model Aqueous Systems

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Linear free energy relationships (LFERs) based on Marcus theory were generated for transformation of C_1- and C_2-polyhalogenated alkanes (PHAs or R−X, where X = H, F, Cl, Br) in model aqueous systems containing bulk reductants and the electron-transfer mediators iron porphyrin or mercaptojuglone (5-hydroxy-2-mercapto-1,4-naphthoquinone). The model systems are representative of common natural environments where iron species and natural organic matter serve as electron shuttles from bulk reductants to pollutants such as PHAs. Seven *ab initio* computational theories were tested for their ability to generate rapid, accurate, and precise estimates of the R−X bond dissociation energy, the largest energetic term in the Marcus equation. The descriptors for the LFERs were computed using B3LYP/6-311++g(d, p) theory/basis set. The LFERs that had the highest correlation coefficients for the two model systems were $\log(k_{\mathrm{FeP}}) = -0.0777(\pm 0.0105)D_{(\mathrm{R-X})}' - 0.00804(\pm 0.00961)\Delta G^{\circ\prime} + 21.7(\pm 2.82)$ (adj $r^2 = 0.946$; $n = 16$) and $\log(k_{\mathrm{Jug}}) = -0.103(\pm 0.0308)D_{(\mathrm{R-X})}' - 0.00958(\pm 0.00513)\mathrm{LUMO} + 22.7(\pm 9.72)$ (adj $r^2 = 0.955$; $n = 12$). $D_{(\mathrm{R-X})}'$ is the bond dissociation energy of the R−X bond that dissociates the transition state, $\Delta G^{\circ\prime}$ is the standard free energy of one-electron reduction, LUMO is the energy of the lowest unoccupied molecular orbital of the PHA, and the numbers in parentheses are 95% confidence limits of the regression coefficient estimates. All coefficients were significant at 90% confidence. These results support earlier hypotheses based on PHA kinetic results, reaction intermediates, and products in the model systems that the initial, rate-limiting step in the reaction in both model systems is a dissociative one-electron transfer. The study supports previous studies that showed, for electron-transfer reactions involving homolytic bond dissociation, the overall reorganization energy term in the Marcus equation is composed primarily of the bond dissociation energy. Correlation of rate constants of polyhalogenated aliphatic compounds measured in related aqueous systems with $D_{(\mathrm{R-X})}'$ and $\Delta G^{\circ\prime}$ suggests one-electron transfer may, at least partially, limit disappearance rates in those systems.

Introduction

Dehalogenation of xenobiotic organic compounds such as C_1- and C_2-polyhalogenated alkanes (PHAs) results in a decrease in molecular size, which subsequently alters the air−water, water−solid, and water−organic (lipid) phase partitioning behavior of these compounds, and thus affects their ultimate fate in the environment. In addition, the products of PHA dehalogenations may be either less or more toxic than the parent compound. Under reducing conditions typical of contamination sites containing PHAs such as groundwater aquifers, landfills, lake sediments, and *in vivo*, various bulk reductants and electron-transfer mediators are present to carry out dehalogenation reactions. The mediators shuttle electrons from the bulk electron donors, which themselves may react with xenobiotic compounds at relatively slow rates (e.g., aqueous species such as inorganic S−II, proteins in microorganisms, or reduced substances excreted by microorganisms), to the PHAs, thereby increasing the rate of transformation and/or altering the reaction pathway.[16,49] Where contamination has been documented, polyhalogenated aliphatic compounds are the most commonly-occurring contaminants in reducing environments.[36,34,53,27] This widespread occurrence and current high production volumes for these chemicals, coupled with the increasingly common use of natural attenuation in groundwater contaminant mitigation,[12] underscore the importance of developing accurate methods to predict transformation rates of these chemicals in such environments.

The disappearance of a PHA in a reducing environment is governed by the rate-limiting step in its initial reaction. It is often difficult to determine with certainty the mechanism of this rate-limiting step. Frequently, there is only limited knowledge of the type and abundance of reactants present in a given environment, and there is often a mixture of electron donors present, complicating efforts to predict the mechanism of the transformation reaction. In addition, PHAs can react with electron donors that are commonly found in reducing environments by at least four different initial reactions: outer-sphere

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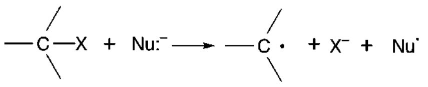
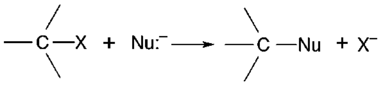
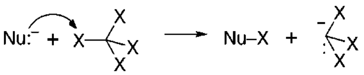
or inner-sphere one-electron transfer in which the R−X bond is broken:


(1)

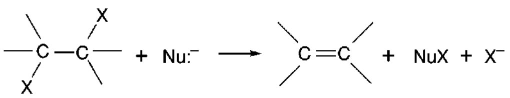
attack by a nucleophilic species at carbon resulting in substitution of the nucleophile,


(2)

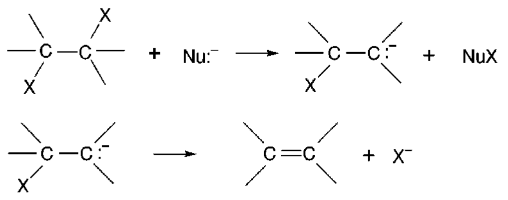
attack by a nucleophile at the halogen resulting in formation of a carbanion (known as an X-philic reaction),


(3a)

and, for C_2-compounds reacting with a nucleophile, E2 reactions:


(4)

For the C_2-alkanes, the E1cb reaction is the two-step reaction to form the alkene and has an initial reaction identical to reaction 3a, followed by halide expulsion to form the same products as the E2 mechanism:


(3a)

(3b)

The various electron donors present and the reaction conditions determine which reaction mechanism occurs and, consequently, which properties of the PHAs are needed to describe their disappearance rate.

The objective of this study was to determine, for two systems designed to model natural aqueous systems capable of dehalogenation transformations of PHAs, whether linear free energy relationships (LFERs) for the one-electron-transfer reaction shown in eq 1 can give accurate and precise predictions of observed reaction rate constants. Such relationships, although not proof of a reaction mechanism, provide support for the proposed mechanism, and are extremely useful in assessing the time required for a given PHA to disappear from the system under a given set of conditions. These LFERs can then be used along with other information to determine the relative rates of reaction of PHAs in similar systems, and to make estimates of absolute rates of reaction.

The two model systems were designed and studied extensively by Schwarzenbach and co-workers[2,3,40−43,49] because of their ability to simulate homogeneous, heterogeneous, and biotic systems containing bulk reductants and electron-transfer mediators.[7,18−20] One system consisted of aqueous solutions containing an iron porphyrin (*meso*-tetrakis(*N*-methylpyridyl)-iron porphin) as electron-transfer mediator and cysteine as bulk reductant, and the other system consisted of juglone (5-hydroxy-1,4-naphthoquinone) as electron-transfer mediator and hydrogen sulfide as bulk reductant. The electron-transfer mediators were selected to model electron-transfer mediators that are commonly found in natural, reducing environments.

Previous work suggested that the initial reaction of PHAs with the iron porphyrin is an outer-sphere, one-electron-transfer process, while that of the reaction with juglone is an outer-sphere, one-electron transfer *and* an X-philic reaction. The reactive species in the system containing juglone appears to be the addition product of juglone and hydrogen sulfide, 5-hydroxy-2-mercapto-1,4-naphthoquinone, hereafter referred to as mercaptojuglone.[41,43] Limited analyses of PHA transformation products in the iron porphyrin system (see also refs 3 and 40, pp 81−83) were consistent with these mechanisms. Logarithmic rate constants for disappearance of PHAs in the iron porphyrin system spanned 4 orders of magnitude, and varied linearly with logarithmic rate constants for polyhalogenated methane transformation by $Co^{II}W_{12}O_{40}^{7-}$ reported by Eberson and Ekström.[10,42] $Co^{II}W_{12}O_{40}^{7-}$ is a strict outer-sphere, one-electron reductant. The slope of the regression of $\log(k_{FeP})$ vs $\log(k_{CoW^{7-}})$ was nearly 1, indicating that the reaction with the iron porphyrin was an outer-sphere, one-electron transfer. The slope of such a regression for rate constants measured for disappearance of PHAs in the system containing juglone, on the other hand, was much greater than 1 (~1.6), indicating a reaction other than outer-sphere, one-electron transfer. Logarithmic rate constants measured in the juglone system spanned a much wider range (7 orders of magnitude) than those measured in the iron porphyrin system, but were parallel to them, suggesting a one-electron-transfer process. Radical products of CCl_4 reaction with iron porphyrin were trapped by adding d_7-isopropyl alcohol to solutions,[3] giving additional evidence that one-electron transfer was operative in the iron porphyrin system. In the juglone system, radical intermediates were not sought. However, a two-electron transfer in addition to an outer-sphere one-electron transfer was indicated by detection of carbenes.[2,42] Carbenes are decay products of the X-philic reaction shown in eq 3a. In contrast, in the iron porphyrin system, carbene decay products were detected only when fluorine was present as a substituent on the methane, and are presumably the result of two sequential one-electron-transfer steps.[3]

In this work, the rate constants measured in these two model systems are subjected to a correlation analysis using descriptors that are indicative of reactions 1−4. The final, recommended LFERs are those employing Marcus theory for outer-sphere, one-electron transfer,[29] which has been extended to describe dissociative electron-transfer (DET) reactions,[1,9,44] as well as to describe inner-sphere, one-electron-transfer reactions.[9,28,45] The number and variety of PHAs in the training set and the ensuing LFER analysis demonstrate the need to include both the free energy of one-electron transfer as well as the bond dissociation energy of the weakest R−X bond in the LFERs to predict PHA transformation rates. Recommendations are given as to the best approach to compute the descriptors.

Methods

Determination of Reaction Rate Constants. The rate constants for disappearance of the polyhalogenated methanes and ethanes that are subjected to analysis in this study were measured in two systems consisting of pH 7.0 buffered, $N_{2(g)}$-purged, aqueous−methanolic solutions containing bulk reductants (5 mM cysteine or 1 mM hydrogen sulfide) and electron-transfer mediators (2−50 μM *meso*-tetrakis(*N*-methylpyridyl)iron porphin or 200 μM 5-hydroxy-1,4-naphthoquinone (estimated mercaptojuglone concentration 4 μM), respectively) at 25 °C. Most of the second-order rate constants for reaction of PHAs with the electron-transfer mediators were reported by Perlinger *et al.*[42] Rate constants of three additional compounds, 1,1,2,2-tetrabromoethane, 1,2-dibromotetrachloroethane, and 1,1-dibromoethane, were measured as checks of the predictability of the LFERs generated from the training set. The first two chemicals were purchased from Aldrich Chemical Co., while the last was purchased from Acros Chemical Co. The purities were 98%, 97%, and 99%, respectively. A detailed description of the methods used to prepare the solutions and measure the rate constants is presented by Perlinger *et al.*[42]

Derivation of the Marcus Equation. Marcus theory was applied to develop LFERs for the measured reaction rate constants. The theory assumes that reduction reactions occur in single-electron-transfer steps by relating reaction rate constants to the change in free energy due to the transfer of a single electron from an electron donor (either iron(II) porphyrin or mercaptojuglone hydroquinone mediator in this case) to an acceptor (PHAs in this case). The observed rate constant of such a reaction, k_{obs}, is related to the free energy of the reaction as[29]

$$k = \kappa Z \exp -\left[\frac{\lambda(1 + \Delta G_{\mathrm{o}}{}^{\circ\prime}/\lambda)^2}{4RT}\right] \tag{5}$$

where k = second-order rate constant of one-electron transfer ($\mathrm{M^{-1}\ s^{-1}}$), κ = transmission coefficient = 1.0, Z = frequency factor = 6.0×10^{11}, λ = overall reorganization energy, $\Delta G_{\mathrm{o}}{}^{\circ\prime}$ = overall free energy change of the one-electron-transfer step, = $\Delta G^{\circ}{}_{\mathrm{oxidant}} - \Delta G^{\circ}{}_{\mathrm{reductant}} + (Z_1 - Z_2 - 1)e^2 f/Dr_{12}$ (the prime symbolizes correction for electrostatic effects, accomplished through inclusion of the third term in the equation, Z_1 and Z_2 = charges of the oxidant and reductant, respectively, e = electronic charge = 4.770×10^{-10} esu, f = a factor defining the effect of ionic strength,[17] D = dielectric constant of the solution, r_{12} = the collision distance between the reductant and the oxidant in angstroms), and R and T have their usual meanings.

The overall reorganization energy, λ, is comprised of the inner reorganization energy, λ_{i}, and the outer reorganization energy, λ_{o}. The inner reorganization energy, λ_{i}, is comprised of the bond strength, angle deformation, and torsional movement terms, and the outer reorganization energy, λ_{o}, is comprised of solvent-induced changes in the electrostatic environment of the reactants.

Multiplying the terms in the exponent in eq 5 gives

$$k = Z \exp -\left[\frac{(\lambda + 2\Delta G_{\mathrm{o}}{}^{\circ\prime} + (\Delta G_{\mathrm{o}}{}^{\circ\prime})^2/\lambda)}{4RT}\right] \tag{6}$$

To simplify the presentation of the LFERs, the third term in eq 6 was neglected such that logarithmic transformation in eq 6 gives a linear dependence of k on $\Delta G_{\mathrm{o}}{}^{\circ\prime}$ and λ (eq 7). Calculations using the measured reduction potential of iron porphyrin of +0.065 V (measured by Schoder[47] for the iron porphyrin used in the present study in aqueous solution at pH 7.0 with no axial ligands present) and the estimated reduction potential of mercaptojuglone semiquinone (−0.037 V[40]) indicated that the third term accounts for at most 2% of the total of the three terms over the range of $\Delta G_{\mathrm{o}}{}^{\circ\prime}$ and λ values of the compounds in the data set. This third term can be expected to be negligible over small ranges in $\Delta G_{\mathrm{o}}{}^{\circ\prime}$ for large λ-values as in the present study.[9] Equation 6 was further simplified by substituting bond strength in place of the overall reorganization energy:

$$k = Z \exp -\left(\frac{D_{(\mathrm{R-X})} + 2\Delta G_{\mathrm{o}}{}^{\circ\prime}}{4RT}\right) \tag{7}$$

In dissociative electron-transfer reactions in which a bond is broken in the transition state, the bond strength is the largest factor in the inner reorganization energy, λ_{i}.[1,9,44] The outer reorganization energy, λ_{o}, as calculated by the polarized continuum model (PCM) of Tomasi and co-workers[5,31,32] and using the same theory and basis set as in the calculation of bond strength, ranged between 0.5 and 5 kJ $\mathrm{mol^{-1}}$ for the PHAs in the training set. This amounted to less than 2% of the total reorganization energy (comprised of bond strength alone), and was neglected.

The overall free energy of the reaction in eq 7, $\Delta G_{\mathrm{o}}{}^{\circ}$, is composed of the difference in free energies of formation of the oxidant and the reductant, $\Delta G^{\circ}{}_{\mathrm{oxidant}} - \Delta G^{\circ}{}_{\mathrm{reductant}}$. Because all of the rate constants measured in the two model systems were measured under identical conditions (except for cases in which pH was increased to increase the reaction rate, as indicated in Tables 1 and 2 of ref 42), the free energy of the reductant in a given system was constant. This term was removed from the other two terms in the exponent and multiplied by Z, giving a new constant, $C = Z \exp(+\Delta G^{\circ}{}_{\mathrm{reductant}}/2RT)$. The correction term for electrostatic effects on the overall standard free energy of the reaction presented in eq 5 was included with calculations of $\Delta G^{\circ}{}_{\mathrm{oxidant}}$, but is not explicitly shown in eqs 8−14 below to keep the equations of reasonable length. Also, for the remainder of this paper, the standard free energy of one-electron reduction of a given PHA will be referred to as $\Delta G^{\circ\prime}$ rather than $\Delta G^{\circ\prime}{}_{\mathrm{oxidant}}$. The constant C was incorporated into eq 7, and the equation was transformed to a logarithmic expression to make the dependent variable linearly related to the independent variables. This operation is an acceptable method for regressions in which the values of the dependent variable have systematic error variances (ref 37, pp 126−134):

$$\log(k) = \log(C) - \frac{1}{4 \times 2.303RT}(D_{(\mathrm{R-X})} + 2\Delta G^{\circ\prime}) \tag{8}$$

To compute ΔG° for the half-reaction of eq 1 in aqueous solution, the Born−Haber approach similar to that applied by Curtis *et al.*[6] was employed:

$$\Delta G^{\circ} = \Delta G^{\circ}(\mathrm{R}^{\bullet})_{\mathrm{aq}} + \Delta G^{\circ}(\mathrm{X}^{-})_{\mathrm{aq}} - \Delta G^{\circ}(\mathrm{RX})_{\mathrm{aq}} \tag{9}$$

where $\Delta G^{\circ}(\mathrm{RX})_{\mathrm{aq}}$, $\Delta G^{\circ}(\mathrm{R}^{\bullet})_{\mathrm{aq}}$, and $\Delta G^{\circ}(\mathrm{X}^{-})_{\mathrm{aq}}$ are the standard free energies of formation of the alkyl halide, alkyl radical, and halide anion in the aqueous phase, respectively.

Because the reaction is dissociative in the transition state, measured reduction potentials cannot be used to determine the above standard free energy changes.[22] The aqueous standard free energies of the PHAs and the corresponding radicals formed in the reduction reaction can be estimated from the corresponding energies in the gaseous state and by accounting for the energy of partitioning from the gaseous phase into the aqueous phase according to the ratio of the Henry's law constants of $\mathrm{R}^{\bullet}$ and R−X. Henry's law constants of radicals are generally not available, but were assumed to be equal in value to those for R−H, as treated by other authors.[6,8,22] Substituting the gas−liquid partitioning relationship into eq 9 gives

$$\Delta G^{\circ} = \Delta G^{\circ}(\mathrm{R}^{\bullet})_{\mathrm{g}} + \Delta G^{\circ}(\mathrm{X}^{-})_{\mathrm{aq}} - \Delta G^{\circ}(\mathrm{RX})_{\mathrm{g}} + RT \ln\left[\frac{K_{\mathrm{H}}(\mathrm{R}^{\bullet})}{K_{\mathrm{H}}(\mathrm{RX})}\right] \tag{10}$$

where $\Delta G^{\circ}(\mathrm{R}^{\bullet})_{\mathrm{g}}$ and $\Delta G^{\circ}(\mathrm{RX})_{\mathrm{g}}$ are the standard free energies of the alkyl radical and the alkane in the gas (g) phase, respectively, and $K_H(R^\bullet)$ and $K_H(RX)$ are the Henry's law constants of the alkyl radical and alkane, respectively.

If the bond dissociation energy, $D_{(R-X)}$

$$D_{(R-X)} = \Delta H°(R^\bullet)_g + \Delta H°(X^\bullet)_g - \Delta H°(RX)_g \qquad (11)$$

is substituted for the enthalpy terms in eq 10 and entropy terms are written explicitly,

$$\Delta G° = D_{(R-X)} + T[\Delta S°(RX)_g - \Delta S°(R^\bullet)_g] - \Delta H°(X^\bullet)_g + \Delta G°(X^-)_{aq} + RT \ln\left[\frac{K_H(R^\bullet)}{K_H(RX)}\right] \qquad (12)$$

the Marcus equation for eq 1 is expressed as

$$k = C \exp\left\{\frac{-1}{4RT}\left[3D_{(R-X)} + 2T[\Delta S°(RX)_g - \Delta S°(R^\bullet)_g] - 2\Delta H°(X^\bullet)_g + 2\Delta G°(X^-)_{aq} + 2RT \ln\left(\frac{K_H(R^\bullet)}{K_H(RX)}\right)\right]\right\} \qquad (13)$$

The largest contributors to $\Delta G°'$ are the enthalpy terms in eq 11. All final enthalpy values used in our calculations were estimated using a single theory/basis set. This approach can be expected to decrease random error in $\Delta G°'$ values as compared to previously reported estimates of $\Delta G°'$.[6]

Linear Regressions. A multiple linear regression was performed between the dependent variable (log(k)) and the descriptors used to predict log(k) (the independent variables $D_{(R-X)}$ and $\Delta G°'$). The regression expression was split into three parts to give it the same form as eq 8:

$$\log(k) = \log(C) - \frac{1}{4 \times 2.303RT}[D_{(R-X)}] - \frac{2}{4 \times 2.303RT}\left[D_{(R-X)} + T[\Delta S°(RX)_g - \Delta S°(R^\bullet)_g] - \Delta H°(X^\bullet)_g + \Delta G°(X^-)_{aq} + RT \ln\left[\frac{K_H(R^\bullet)}{K_H(RX)}\right]\right] \qquad (14)$$

The general form of this equation is

$$\log(k) = \beta_0 + \beta_1 D_{(R-X)} + \beta_2 \Delta G°' \qquad (15)$$

where β_0, β_1, and β_2 are the unbiased estimated regression coefficients. A regression of the form of eq 15 produced good fits, as evidenced by high r^2 values. Additionally, in an effort to improve the degree of correlation, regressions of the form of eq 15 were also performed after (i) either $D_{(R-X)}$ or $\Delta G°'$ was eliminated, (ii) one or more descriptors were added to eq 15, or (iii) compounds were grouped into those containing the same leaving group or those containing no and at least one β-halogen.

Regression Analysis. Accurate prediction of log(k) values depends on a variety of factors, including which descriptors are included in the regression, the number of variables used in the regression, and the accuracy of the dependent and independent variables. To increase the accuracy of prediction of the model presented in eq 15, an additional term is sometimes included in multiple linear regression equations to account for errors (ref 37, Chapters 3 and 6):

$$\log(k)_i = \beta_0 + \beta_1 D_{(R-X),i} + \beta_2 \Delta G_i°' + \epsilon_i \qquad (16)$$

where β_0, β_1, and β_2 are unbiased estimated regression coefficients, i represents an individual PHA, and ϵ_i is the error term that includes systematic, theoretical, and random errors. An example of a theoretical error is the use of $D_{(R-X)}$ to approximate the overall reorganization energy, λ. In reality other forces contribute to λ to a relatively small extent, and these forces may vary from compound to compound. A second example is the values employed for the reduction potential, which factors into the constant C in eq 8. For mercaptojuglone this value was estimated, while for iron porphyrin it was measured in the absence of axial ligands. However, in the latter system, iron porphyrin is expected to have two axial cysteine ligands.[2] Therefore, the value of C is an estimate for both systems. While systematic errors can be reduced through improved experimental procedures and theoretical errors eliminated by incorporating the correct theoretical variables, random errors are indeterminate in nature. The error term in eq 16 lumps all of these sources of error; the importance of each error source may vary for different compounds.

In addition, although eq 16 can be used to predict the value of k for a particular PHA, it is necessary to first transform the predicted log(k) value by taking the antilogarithm. In doing so, bias can be introduced, and this bias has been shown to systematically underestimate the mean predicted k value.[33,38] Suggested correction factors include multiplying the predicted k value by 10^ϵ, where ϵ represents variability in k not explained by the predictor variables. The correction factor is, in turn, estimated from the following expression:[33,38]

$$10^\epsilon = 10 \exp\left(\frac{{}^1/_2 \sum_{i=1}^{N} e_i^{\,2}}{N-2}\right) \qquad (17)$$

where N is the number of data points used to fit the model in eq 16 and e_i is the residual. The correction reportedly reduced the bias in the dependent variable by as much as 57% in one case.[33,46] The residual is the difference between the predicted log(k) and measured log(k), and hence is a measure of the sums of the systematic, theoretical, and random errors mentioned previously. The residuals must be unbiased as per the requirements of the model.[37] While we acknowledge the necessity of a correction factor to eliminate the sometimes biased estimates of predicted k values, we feel that the correction factor introduced in eq 17 is not representative of the bias of the predicted k value because the separation of systematic, theoretical, and random errors is not possible for the data considered here. Hence, we have not incorporated the correction factor into the final expression for k, but have left β_0 and ϵ_i unseparated, as implied by eq 15. The recommended equation to predict k values from the LFERs is

$$k = 10^{\beta_0} 10^{\beta_1 D_{(R-X)}} 10^{\beta_2 \Delta G°'} \qquad (18)$$

Sources of Descriptors used in the LFERs. Various descriptors were tested individually and in combination for correlation with rate constants. The descriptors tested were the electron affinity (EA) of the PHA, energy of the lowest unoccupied molecular orbital (LUMO) of the PHA, standard free energy of two-electron reduction in the case when hydrogenolysis ($\Delta G°_{2H}$), elimination ($\Delta G°_{2E}$), and carbene ($\Delta G°_{carbene}$) products of C_2-compounds were formed, standard free energies for DET reactions ($\Delta G°'$; eq 7), and bond dissociation energies of the weakest R−X bond in the PHA ($D_{(R-X)}$; eq 7). Because the measured rate constants were found to be very sensitive to $D_{(R-X)}$ values, and because measured $D_{(R-X)}$ values are not available for a number of the studied compounds, this parameter was used to test the method by which the other descriptors would be computed.

Source of $D_{(R-X)}$ Values. Density functional calculations were carried out using the Gaussian 92,[13] Gaussian 94,[14] and Gaussian 98[15] suite of programs on an SGI Indigo workstation containing a R4000 processor. Computational methods of determination of the bond dissociation energy of a molecule involve calculation of the difference in the total energies between the molecule and its free radical(s). Total energies can be calculated using a particular level of theory and basis set depending upon the molecule, the amount of time one is willing to spend to run the calculation, and the desired degrees of precision and accuracy.

To determine the accuracy of the calculations using Gaussian, calculations were compared for haloalkanes whose bond dissociation energies are tabulated in the literature.[30,50] (Tables 1S−4S, Supporting Information). Calculations were performed using HF, MP2, MP3, G1, G2, SVWN5, and B3LYP theories. The basis sets used varied from 6-31g to 6-311++g(3df,2p) depending on the level of theory used. Later, to correct the electronic energy of the molecules for the effects of molecular vibrations that persist at 0 K (zero-point energy, ZPE), a frequency analysis was performed at the same level of theory and basis set as the optimization, and the result was added to the electronic energy calculated using optimization.

Source of EA Values. EAs of the PHAs were computed as the difference in the total energies between the PHA and its anion. Calculations were performed using the same theory and basis set as in the calculation of the bond dissociation energies, B3LYP/6-311++g(d,p).

Source of LUMO Values. The LUMO values of the PHAs were obtained by first optimizing the molecular structures using the B3LYP/6-311++g(d,p) theory/basis set and then performing a population analysis of their molecular orbitals. The energy of the first virtual (unoccupied) molecular orbital corresponded to the LUMO.

Source of $\Delta G°_{2H}$ and $\Delta G°_{2E}$ (or $\Delta G°_{carbene}$) Values. Semiempirical calculations were carried out using the Project Leader interface of CAChe Worksystem software (Oxford Molecular Group, U.K.), version 3.9, running on a PowerMac. Computational methods of determination of $\Delta G°_{2H}$ of a molecule involve calculation of the difference in the free energies between the reactants (R−X and H_2) and its 2H products (R−H and HX) followed by correction for partitioning between the gaseous and aqueous phases. The free energies of the molecules were determined by first optimizing the molecular geometry using Augmented MM2, followed by MOPAC with PM3 parameters (CAChe procedure MM/PM3$_-$Geo$_-$IR). The same approach was used for computation of $\Delta G°_{2E}$ (for ethanes) and $\Delta G°_{carbene}$ (for methanes and ethanes), except that the energy differences were between those of the molecule R−X and its 2E product or between those of the molecule R−X and the carbene, respectively.

Source of $\Delta G°'$ Values and Terms Therein. Quantum chemical theories were used to estimate all quantities in eq 12 except for the following: Henry's law constants were computed using the group contribution method of Hine and Mookerjee;[21] measured $\Delta H°(X^\bullet)_g$ and $\Delta G°(X^-)_{aq}$ values reviewed by Wagman *et al.*[51] were used. The $\Delta G°(X^-)$ and $\Delta H(X^\bullet)$ values from Wagman *et al.* were at STP (1 atm of pressure, 25 °C, unit activity). As mentioned earlier, because rate constants are particularly sensitive to bond dissociation energies, $D_{(R-X)}$ values computed using seven different theories and six different basis sets were compared with the best available measured and computed values in the literature as discussed below. The remainder of the descriptors were computed using the best theory, as indicated by comparison of the $D_{(R-X)}$ values. Entropies of each PHA and the corresponding radical were taken from the thermodynamic properties section of a frequency calculation on the optimized molecule. All parameters needed to compute *f*, the correction term for electrostatic interactions, were taken from ref 17.

Results

Descriptors Used in the Correlation Analysis. *Bond Dissociation Energies.* Hartree−Fock theories predicted dissociation energies that were more than 100% different from the experimental values (data not shown). Calculations using the same basis set but with higher levels of theory showed significant improvements over Hartree−Fock values. The MPn methods are one of the least expensive methods that improve upon the Hartree−Fock theory. Bond dissociation energies computed using MP2/6−31g* and MP2/6−311g* theories/basis sets showed a 0−10% deviation from literature values (Table 1S; all $D_{(R-X)}$ values for comparison with literature values were computed according to eq 11 and are reported in Tables 1S−4S of the Supporting Information). Bond dissociation energies of R−F and R−Cl computed using MP2/6−311g* theory/basis set gave consistently good results for all bonds, and deviations from literature values were less than 3%. Similar patterns were observed for R−H bond dissociation energies (data not shown). Calculations were also performed using the Gaussian-1 (G1) and Gaussian-2 (G2) theories. The R−F bond dissociation energies of some fluorocarbons were calculated using these theories (Table 2S). The calculated values are within 1−2% of the literature values, except in the case of CCl_4.

Although most of the theories investigated predicted bond dissociation energies that were close to the literature values, the amount of computational resources increased tremendously with an increase in the number of halogens. Keeping in mind the necessity to calculate the bond dissociation energies of chlorinated and brominated ethanes, a method that required moderate computational time and yet was accurate was selected.

A theory that is not very expensive in terms of computation time and resources but which gave precise results is the density functional theory. Two types of functionals were studied: traditional functionals (SVWN5) and hybrid functionals (B3LYP) (Table 3S). As is evident from the table, the traditional functionals overestimated bond dissociation energies by 10−20%. The hybrid functionals predicted bond dissociation energies that were underestimated by approximately 10%. This overestimation/underestimation is the result of improper implementation of exchange functionals in the calculation of the exchange-correlation energy part of the total energy in the parent and dissociated molecules.[11,25,24] The differences in $D_{(R-X)}$ values reported by Slayden *et al.*[50] and those computed using B3LYP/6-311++g(3df,2p) and using MP2/6−311g* were both nearly constant, as is apparent from regressions of the two data sets vs the data of Slayden *et al.* (Figure 1). MP2/6−311g* theory gave slightly more precise and accurate results. However, B3LYP/6-311++g(3df,2p) theory gave results that were nearly as precise as MP2/6−311g* in one-fourth the computation time. To further reduce the computation time, a smaller basis set, 6-311++g(d,p), was used instead of the 6−311++g(3df,2p) basis set, resulting in time savings on the order of 30% while providing reasonable accuracy. Therefore, B3LYP/6-311++g(d,p) theory/basis set was used in computation of $D_{(R-X)}$ values of the studied compounds as well as in computation of all other parameters that were used in the LFERs (Table 1).

$D_{(R-X)}$ values were corrected for correlation energy effects by using the correction factors presented in eqs 19−21 in Table

TABLE 1: Descriptors Used in the Correlation Analyses[a]

molecule	$D_{(R-X)}'$ [b] (kJ/mol)	$\Delta G^{\circ\prime}$ [c] (kJ/mol)	LUMO[d] (kJ/mol)	EA[e] (kJ/mol)	2H product[f]	ΔG°_{2H} [g] (kJ/mol)	carbene product[h]	$\Delta G^{\circ}_{2E,carbene}$ [i] (kJ/mol)
$CFCl_3$	292.2	48.4	−377.4	115.6	$CHFCl_2$	−102.92	$:CFCl_2(-)$	54.77
$CHBrCl_2$	262.1	70.5	−393.0	136.3	CH_2Cl_2	−128.01	$:CHCl_2(-)$	98.80
CCl_4	263.4	19.6	−437.1	125.0	$CHCl_3$	−106.57	$:CCl_3(-)$	74.58
$CHBr_3$	260.5	66.2	−483.6	141.8	CH_2Br_2	−127.07	$:CHBr_2(-)$	60.45
$CHBr_2Cl$	261.3	69.7	−443.8	134.6	CH_2BrCl	−120.86	$:CHBrCl(-)$	79.67
$CFBr_3$	253.5	53.2	−561.4	185.3	$CHFBr_2$	−128.63	$:CFBr_2(-)$	−67.04
$CBrCl_3$	240.1	54.3	−513.1	184.8	$CHCl_3$	−114.93	$:CCl_3(-)$	5.20
CBr_2Cl_2	238.2	45.6	−558.7	184.1	$CHBrCl_2$	−117.08	$:CBrCl_2(-)$	−12.40
$CH_2Cl-CCl_3$	270.5	32.0	−316.5	169.5	$CH_2Cl-CHCl_2$	−102.82	$CH_2Cl-:CCl_2(-)$	−29.43
CH_3-CCl_3	288.2	47.8	−243.3	65.4	CH_3-CHCl_2	−97.38	$CH_3-:CCl_2(-)$	148.41
$CF_2Cl-CFCl_2$	295.1	51.9	−301.6	153.1	$CF_2Cl-CHFCl$	−112.89	$CF_2Cl-:CFCl(-)$	37.98
$CHCl_2-CHCl_2$	294.2	54.0	−280.3	161.3	$CHCl_2-CH_2Cl$	−112.32	$CHCl_2-:CHCl(-)$	−10.50
CF_3-CCl_3	272.2	28.1	−359.4	102.9	CF_3-CHCl_2	−114.65	$CF_3-:CCl_2(-)$	45.02
$CHCl_2-CCl_3$	262.2	22.2	−332.7	177.4	$CHCl_2-CHCl_2$	−103.93	$CHCl_2-:CCl_2(-)$	−61.07
$CF_2Cl-CCl_3$	264.5	20.0	−350.7	178.1	$CF_2Cl-CHCl_2$	−114.53	$CF_2Cl-:CCl_2(-)$	−9.27
CCl_3-CCl_3	259.4	10.2	−340.6	193.4	CCl_3-CHCl_2	−115.03	$CCl_3-:CCl_2(-)$	0.47

[a] The descriptors listed in columns 2−5 were calculated using the Gaussian software package and B3LYP/6−311++g(d,p) theory/basis set. The descriptors listed in columns 7 and 9 were calculated using the PM3 theory in the MOPAC interface of the CAChe software package. [b] Corrected bond dissociation energy. [c] Free energy of one-electron-transfer reaction including a correction for changes in electrostatic effects. [d] Energy of the lowest unoccupied molecular orbital. [e] Electron affinity of the PHA as calculated by the difference in energies between the PHA and its corresponding anion. [f] Hydrogenolysis product of the PHA, [g] Free energy of reaction for formation of hydrogenolysis product from the PHA. [h] Carbene intermediate of the PHA. [i] Free energy of reaction for formation of carbene from the corresponding PHA.

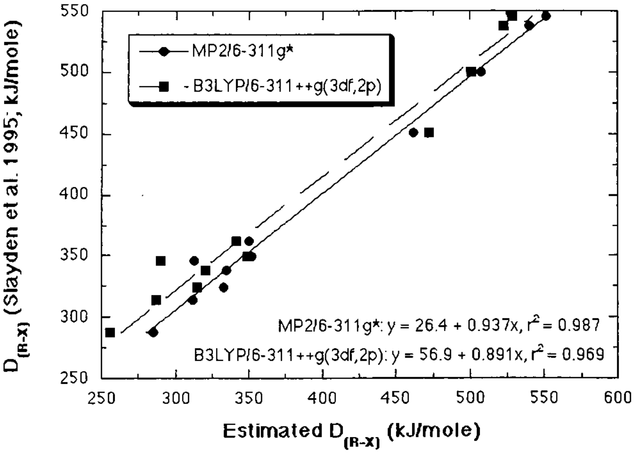


Figure 1. $D_{(R-X)}$ values from Slayden *et al.* (1995) versus $D_{(R-X)}$ values for polyhalogenated methanes computed using B3LYP/6-311++g(3df,2p) and MP2/6−311g* theories.

TABLE 2: Suggested Conversion Factors to Correct for the Underestimation of Bond Dissociation Energies by B3LYP/6-311++G(d,p) Theory/Basis Set[a]

eq	leaving group	suggested correction factor	*n*	r^2
19	F	$D_{(R-X)}' = 1.083D_{(R-X)} - 32.12$	6	0.924
20	Cl	$D_{(R-X)}' = 0.9266D_{(R-X)} + 33.32$	6	0.898
21	Br	$D_{(R-X)}' = 0.5994D_{(R-X)} + 120.7$	9	0.900

[a] $D_{(R-X)}$ values from ref 30.

2. Figure 2 shows the regressions for a training set of compounds containing chlorine or bromine as leaving group. These corrected values are referred to as $D_{(R-X)}'$ below.

Entropies. Calculated entropies were in excellent agreement with those of Wagman *et al.*[51] as shown by the following relation between the two (values in parentheses are 95% CI):

$$S_{computed} = 1.0052(\pm 0.0915)S_{literature} - 1.3285(\pm 32.1342)$$

$$n = 11,\ r^2 = 0.9957 \qquad (22)$$

where $S_{computed}$ = entropy calculated using B3LYP/6-311++g(d,p) and $S_{literature}$ = entropy from Wagman *et al.*[51]

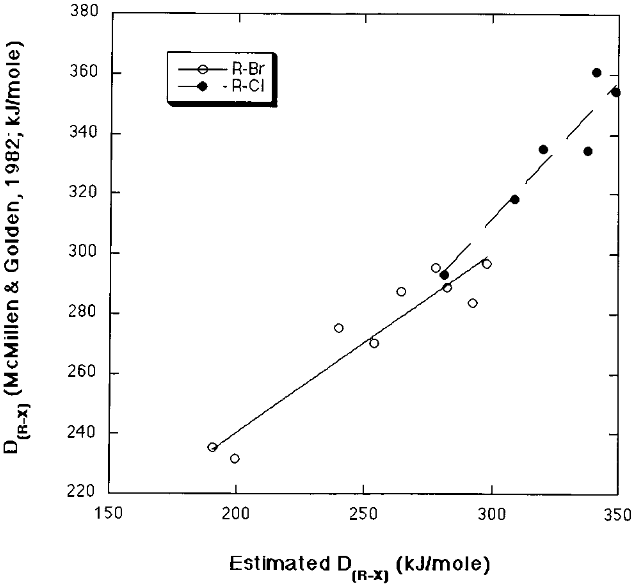


Figure 2. $D_{(R-X)}$ values from McMillen and Golden (1982) versus $D_{(R-X)}$ values of polyhalogenated methanes and ethanes computed using B3LYP/6-311++g(d,p) theory/basis set for PHAs having bromine and chlorine as leaving groups. The equations of the lines in the figure are given in Table 2.

Correlation Analysis. Examination of the descriptors presented in Table 1 and Figure 3 demonstrates which parameters are correlated. Of the descriptors included in the plots, $\Delta G^{\circ\prime}$ and $D_{(R-X)}'$ are highly correlated with one another when all compounds are separated into those containing bromine as leaving group and those containing chlorine as leaving group (Figure 3). For example, the correlation coefficients for the brominated compounds alone increases to 0.816, while that for chlorinated compounds alone increases to 0.966. Of the other descriptors in Figure 3, there is a slight correlation between $D_{(R-X)}'$ and LUMO values. The compounds containing β-halogens ($r^2 = 0.929$) show a separate correlation between LUMO and EA from those that do not contain β-halogens ($r^2 = 0.630$).

Plots of log(k) values (Table 4) versus the descriptors (Table 1) suggest which initial reaction (1−4) may occur in each model system, and which of the parameters in Table 1 is best correlated

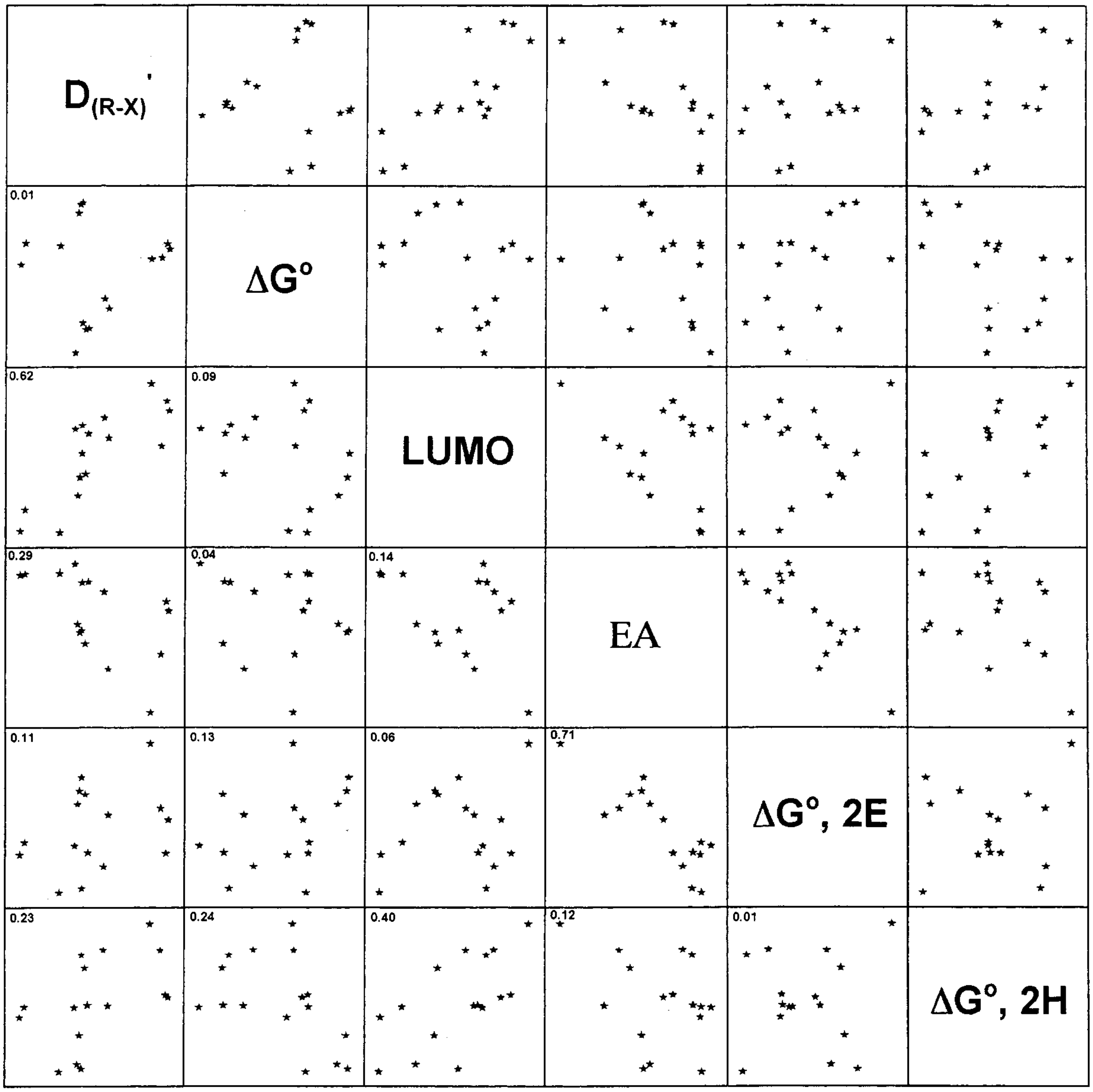


Figure 3. Scatter plots of the indicated descriptors. Numbers in the upper left-hand corner of the panels refer to r^2 values.

with the energy of the transition state (Figure 4). Correlation of log(k) values with $\Delta G^{\circ\prime}$, LUMO, EA, and $D_{(R-X)}'$ indicates that reaction 1 may occur, whereas correlation with $\Delta G^{\circ\prime}$, EA, and LUMO, but not $D_{(R-X)}'$, indicates that reaction 2 may occur. Correlation of log(k) values with ΔG°_{2H} and ΔG°_{2E} (or $\Delta G^{\circ}_{carbene}$) values may indicate that reaction 3 or 4 may occur. Figure 4 shows that log(k) values are highly correlated with $\Delta G^{\circ\prime}$ and $D_{(R-X)}'$ values. There is a clear division of log(k) versus $\Delta G^{\circ\prime}$ among compounds containing bromine and chlorine as leaving groups. Correlation coefficients for the brominated compounds increase to 0.916 and 0.943 for the iron porphyrin and juglone systems, respectively. For the chlorinated compounds, the coefficients increase to 0.957 and 0.876 in the two systems, respectively. This separation into R−Br and R−Cl mimics the inverse of the plot of $\Delta G^{\circ\prime}$ vs $D_{(R-X)}'$ shown in Figure 3, and results from the $\Delta G^{\circ}(X^-)_{aq}$ term in eq 9. Log(k) values are slightly correlated with LUMO values (Figure 4; r^2 = 0.72 and 0.61 in the iron porphyrin and juglone systems, respectively). The correlations suggest that the mechanism of transformation in the rate-limiting step is dissociative electron transfer in both the iron porphyrin and juglone systems. Accordingly, LFERs were developed that account for the reactions according to the Marcus equation for dissociative electron transfer as shown in eq 8.

LFERs. As expected from Marcus theory for dissociative electron transfer, correlation coefficients for regressions of log(k) values with $\Delta G^{\circ\prime}$ values alone were low (Table 5, eqs 23 and 24). Examination of the contributions of the terms in the Marcus expression in eq 14 and the values of the descriptors (Table 3) multiplied by their coefficients indicates that the $D_{(R-X)}'$ term is the largest contributor to the transition-state energy, but that $\Delta G(X^-)_{aq}$ and $\Delta H(X^\bullet)_g$ are not insignificant contributors. Correlations with $D_{(R-X)}'$ values alone were much higher than with $\Delta G^{\circ\prime}$ alone (eqs 25 and 26, Table 5), while the correlations of log(k) with both $\Delta G^{\circ\prime}$ and $D_{(R-X)}'$ (eqs 27 and 28, Table 5) were slightly higher (FeP) or slightly lower (mercaptojuglone) than with $D_{(R-X)}'$ alone. Separation of the compounds into those containing chlorine as leaving group and those containing bromine as leaving group led to even higher correlations of log(k) values with $\Delta G^{\circ\prime}$ (eqs 29−32), suggesting that the literature values of $\Delta G(X^-)_{aq}$ used to compute $\Delta G^{\circ\prime}$ were incorrect. Very small differences in $\Delta G^{\circ}(X^-)_{aq}$ were found upon examination of various literature sources,[52] suggesting that $\Delta G^{\circ}(X^-)_{aq}$ values are not uncertain, and that this uncertainty

TABLE 3: Descriptors Used in the LFER Analyses Presented in Tables 5 and 6 and in Figures 4 and 5[a]

molecule	$D_{(R-X)}'$ [b] (kJ/mol)	$\Delta G^{\circ\prime}$ [c] (kJ/mol)	S(RX)[d] (cal/K/mol)	S(R•)[e] (cal/K/mol)	H(X•)[f] (kJ/mol)	G(X^-)[g] (kJ/mol)	K_H(RH)[h] (atm•m³/mol)	K_H(RX)[i] (atm•m³/mol)	ln(K_H(RH)/K_H(RX))[j]	LUMO[k] (kJ/mol)
$CFCl_3$	292.2	48.4	74.1	71.3	121.7	−131.2	0.0182	0.0509	−1.0	−377.4
$CHBrCl_2$	262.1	70.5	75.8	67.2	111.9	−104.0	0.0091	0.0011	2.2	−393.0
CCl_4	263.4	19.6	79.1	74.2	121.7	−131.2	0.0032	0.0254	−2.1	−437.1
$CHBr_3$	260.5	66.2	79.3	72.8	111.9	−104.0	0.0010	0.0001	2.2	−483.6
$CHBr_2Cl$	261.3	69.7	78.7	70.0	111.9	−104.0	0.0030	0.0003	2.2	−443.8
$CFBr_3$	253.5	53.2	82.9	77.1	111.9	−104.0	0.0020	0.0018	0.1	−561.4
$CBrCl_3$	240.1	54.3	87.5	74.2	111.9	−104.0	0.0032	0.0004	2.2	−513.1
CBr_2Cl_2	238.2	45.6	84.9	77.1	111.9	−104.0	0.0011	0.0001	2.2	−558.7
$CH_2Cl{-}CCl_3$	270.5	32.0	85.5	82.5	121.7	−131.2	0.0043	0.0015	1.0	−316.5
$CH_3{-}CCl_3$	288.2	47.8	76.4	74.9	121.7	−131.2	0.0121	0.0043	1.0	−243.3
$CF_2Cl{-}CFCl_2$	295.1	51.9	90.1	86.8	121.7	−131.2	0.0955	0.2670	−1.0	−301.6
$CHCl_2{-}CHCl_2$	294.2	54.0	84.7	83.0	121.7	−131.2	0.0043	0.0015	1.0	−280.3
$CF_3{-}CCl_3$	272.2	28.1	87.8	85.2	121.7	−131.2	0.0955	0.2670	−1.0	−359.4
$CHCl_2{-}CCl_3$	262.2	22.2	91.5	89.7	121.7	−131.2	0.0015	0.0005	1.0	−332.7
$CF_2Cl{-}CCl_3$	264.5	20.0	92.3	90.0	121.7	−131.2	0.0169	0.0473	−1.0	−350.7
$CCl_3{-}CCl_3$	259.4	10.2	95.5	95.0	121.7	−131.2	0.0005	0.0042	−2.1	−340.6
$CHCl_3$	296.5	50.7	70.7	67.2	121.7	−131.2	0.0091	0.0032	1.0	−304.2
CH_2Cl_2	324.2	77.7	66.0	60.6	121.7	−131.2	0.0082	0.0091	−0.1	−174.9
CH_3Cl	349.2	116.4	58.2	50.0	121.7	−131.2	0.4140	0.0082	3.9	−89.4
$CH_2Cl{-}CHCl_2$	296.5	51.4	79.7	75.5	121.7	−131.2	0.0121	0.0043	1.0	−215.3
$CHCl_2{-}CH_3$	319.1	70.8	74.7	66.1	121.7	−131.2	0.0109	0.0121	−0.1	−117.4
$CH_2Cl{-}CH_2Cl$	329.2	81.1	74.0	68.0	121.7	−131.2	0.0109	0.0121	−0.1	−135.4
$CH_3{-}CH_2Cl$	346.5	108.6	65.7	61.5	121.7	−131.2	0.5500	0.01090	3.9	−69.7
$CHBr_2{-}CHBr_2$	256.6	48.5	96.5	91.1	111.9	−104.0	0.00015	0.0000172	2.2	−411.6
$CH_3{-}CHBr_2$	276.1	69.9	78.3	71.2	111.9	−104.0	0.0113	0.0013	2.2	−299.1
$CCl_2Br{-}CCl_2Br$	235.0	23.5	101.0	98.2	111.9	−104.0	0.000173	0.00002	2.2	−466.1
$CCl_2{=}CCl_2$	345.4	99.0	84.3	79.7	121.7	−131.2	0.0230	0.0165	0.3	−259.3
$CCl_2{=}CHCl$	350.2	104.6	77.6	72.4	121.7	−131.2	0.0319	0.0230	0.3	−223.4
cis-$CHCl{=}CHCl$	381.5	137.0	70.6	64.4	121.7	−131.2	0.0444	0.0319	0.3	−159.3
trans-$CHCl{=}CHCl$	374.8	130.4	70.8	64.6	121.7	−131.2	0.0444	0.0319	0.3	−192.4
$CH_2{=}CCl_2$	357.4	113.0	70.2	64.0	121.7	−131.2	0.0444	0.0319	0.3	−191.2
$CH_2{=}CHCl$	384.2	142.2	63.0	55.8	121.7	−131.2	0.0978	0.0444	0.8	−127.9

[a] The descriptors listed in columns 2, 4, 5, and 11 were calculated using the Gaussian software package and B3LYP/6-311++g(d,p) theory/basis set. Descriptors listed in columns 6 and 7 are from ref 51. Henry's law constants in columns 8 and 9 were calculated on the basis of the method developed in ref 21. [b] Corrected bond dissociation energy. [c] Free energy of one-electron-transfer reaction including a correction for changes in electrostatic effects. [d] Gas-phase entropy of the PHA. [e] Gas-phase entropy of the free radical. [f] Gas-phase enthalpy of formation of halide radical. [g] Aqueous-phase free energy of formation of the halide ion. [h] Henry's law constant for the free radical formed through one-electron reduction of the PHA. It is assumed to be equal to the Henry's law constant of RH. [i] Henry's law constant of the PHA. [j] Natural logarithm of the ratio of RH and RX. [k] Energy of the lowest unoccupied molecular orbital.

TABLE 4: Second-Order Rate Constants (±95% CI) Measured by Perlinger *et al.* (1998) and for This Study for the Reaction of Polyhalogenated Methanes and Ethanes with Iron Porphyrin and Mercaptojuglone

molecular formula	k (M^{-1} s^{-1}) (iron porphyrin)	k (M^{-1} s^{-1}) (juglone)	molecular formula	k (M^{-1} s^{-1}) (iron porphyrin)	k (M^{-1} s^{-1}) (juglone)
$CFCl_3$	$(1.0 \pm 0.1) \times 10^{-1}$	$(1.4 \pm 0.3) \times 10^{-4}$	$CFCl_2{-}CF_2Cl$	$(3.8 \pm 0.60) \times 10^{-2}$	
$CHBrCl_2$	$(5.8 \pm 0.9) \times 10^{0}$	$(9.4 \pm 5.3) \times 10^{-2}$	CHCl2 − CHCl2	$(1.0 \pm 0.25) \times 10^{-2}$	
CCl_4	$(5.9 \pm 0.9) \times 10^{0}$	$(9.5 \pm 0.3) \times 10^{-1}$	$CF_3{-}CCl_3$	$(8.6 \pm 3.3) \times 10^{0}$	$(2.2 \pm 0.3) \times 10^{-2}$
CHBr3	$(8.9 \pm 2.1) \times 10^{0}$	$(1.6 \pm 0.2) \times 10^{0}$	$CCl_3{-}CHCl_2$	$(9.5 \pm 2.8) \times 10^{0}$	
$CHBr_2Cl$	$(1.2 \pm 0.3) \times 10^{1}$	$(1.2 \pm 0.7) \times 10^{-1}$	$CF_2Cl{-}CCl_3$	$(1.3 \pm 0.3) \times 10^{1}$	$(4.0 \pm 1.7) \times 10^{-2}$
$CFBr_3$	$(6.9 \pm 2.8) \times 10^{1}$	$(1.6 \pm 0.5) \times 10^{2}$	$CCl_3{-}CCl3$	$(4.8 \pm 0.4) \times 10^{1}$	$(5.5 \pm 0.3) \times 10^{-1}$
$CBrCl_3$	$(2.5 \pm 0.6) \times 10^{2}$	$(8.0 \pm 0.1) \times 10^{2}$	$CHBr_2{-}CHBr_2$[a]	$(1.3 \pm 0.1) \times 10^{1}$	$(2.1 \pm 2.0) \times 10^{0}$
CBr_2Cl_2	$(6.1 \pm 2.2) \times 10^{2}$	$(1.6 \pm 1.4) \times 10^{3}$	$CBrCl_2{-}CBrCl_2$[a]		$(3.0 \pm 1.1) \times 10^{4}$
$CCl_3{-}CH_2Cl$	$(1.2 \pm 0.5) \times 10^{0}$	$(2.0 \pm 0.10) \times 10^{-3}$	$CHBr_2{-}CH_3$[a]		$(1.1 \pm 1.0) \times 10^{-2}$
$CCl_3{-}CH_3$	$(3.2 \pm 0.24) \times 10^{-2}$				

[a] This study.

cannot account for the systematic deviation of compounds with bromine and chlorine leaving groups from regressions of the two classes together.

Plots of the measured and predicted log(k) values for the iron porphyrin and juglone systems for the LFERs in eqs 27 and 28 are shown in part a and b, respectively, of Figure 5. The sign and magnitude of log(C) and the coefficient of $D_{(R-X)}'$ are statistically significant in each case and are within a factor of 2.5 of the expected values in eq 8 (∼11.8 and 0.0438, respectively). The coefficient of $\Delta G^{\circ\prime}$ is of the same sign as and approximately an order of magnitude lower than that expected from the theoretical value of 0.0876 in eq 8 for the iron porphyrin system. It is not significantly different from zero at the 95% confidence limit, but it is significantly different from zero at the 90% confidence limit. In the juglone LFER, this coefficient is not significantly different from zero at the 95% or the 90% confidence limit.

Three compounds that were not included in the training set were used to verify the LFERs in eqs 27 and 28 for use in predicting rate constants. The rate constants measured for disappearance of 1,1,2,2-tetrabromoethane, 1,1-dibromoethane, and 1,2-dibromotetrachloroethane are included in Table 4 and indicated by open circles in Figure 5. The correlation (measured log(k) for $CHBr_2{-}CHBr_2$ is 1.11 and 0.32 vs a predicted log(k)

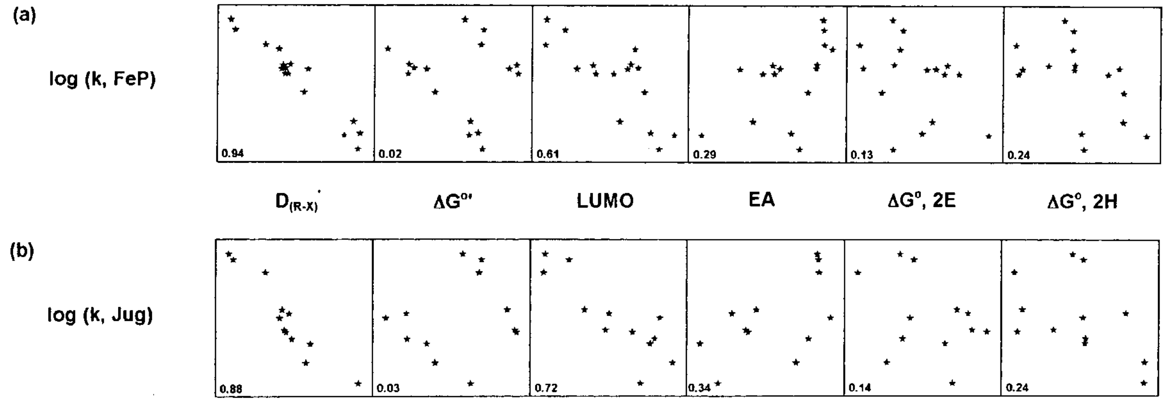


Figure 4. Scatter plots of (a) $\log(k_{\mathrm{FeP}})$ and (b) $\log(k_{\mathrm{Jug}})$ versus the indicated descriptors. Numbers in the lower left-hand corner of the panels refer to r^2 values.

TABLE 5: Equations of Linear Regressions of $\log(k_{\mathrm{FeP}})$ and $\log(k_{\mathrm{Jug}})$ versus the Indicated Descriptors[a]

eq	regression equation	n	adj r^2	r^2
23	$\log(k_{\mathrm{FeP}}) = -0.0109(\pm0.0419)\Delta G^{\circ\prime} + 1.07(\pm1.97)$	16		0.0220
24	$\log(k_{\mathrm{Jug}}) = 0.0179(\pm0.0723)\Delta G^{\circ\prime} - 0.828(\pm2.66)$	12		0.0294
25	$\log(k_{\mathrm{FeP}}) = -0.0781(\pm0.0112)D_{(\mathrm{R-X})}{}' + 21.5(\pm3.00)$	16		0.942
26	$\log(k_{\mathrm{Jug}}) = -0.144(\pm0.0355)D_{(\mathrm{R-X})}{}' + 37.3(\pm9.29)$	12		0.891
27	$\log(k_{\mathrm{FeP}}) = -0.0777(\pm0.0105)D_{(\mathrm{R-X})}{}' - 0.00804(\pm0.00961)\Delta G^{\circ\prime} + 21.7(\pm2.82)$	16	0.946	0.953
28	$\log(k_{\mathrm{Jug}}) = -0.143(\pm0.0383)D_{(\mathrm{R-X})}{}' + 0.00301(\pm0.0262)\Delta G^{\circ\prime} + 37.0(\pm10.2)$	12	0.867	0.891
29	chlorinated: $\log(k_{\mathrm{FeP}}) = -0.0815(\pm0.0142)\Delta G^{\circ\prime} + 2.69(\pm0.519)$	10		0.957
30	brominated: $\log(k_{\mathrm{FeP}}) = -0.0777(\pm0.0326)\Delta G^{\circ\prime} + 6.29(\pm1.98)$	6		0.916
31	chlorinated: $\log(k_{\mathrm{Jug}}) = -0.100(\pm0.0526)\Delta G^{\circ\prime} - 0.210(\pm0.995)$	6		0.876
32	brominated: $\log(k_{\mathrm{Jug}}) = -0.181(\pm0.0617)\Delta G^{\circ\prime} + 9.67(\pm2.98)$	6		0.943
33	$\log(k_{\mathrm{FeP}}) = -0.0765(\pm0.0191)D_{(\mathrm{R-X})}{}' - 0.000367(\pm0.00343)\mathrm{LUMO} + 20.9(\pm6.22)$	16	0.932	0.942
34	$\log(k_{\mathrm{Jug}}) = -0.103(\pm0.0308)D_{(\mathrm{R-X})}{}' - 0.00958(\pm0.00513)\mathrm{LUMO} + 22.7(\pm9.72)$	12	0.955	0.963
35	no β: $\log(k_{\mathrm{FeP}}) = -0.0758\ (\pm0.0133)D_{(\mathrm{R-X})}{}' - 0.000344(\pm0.0155)\Delta G^{\circ\prime} + 20.8(\pm3.65)$	9	0.961	0.971
36	β: $\log(k_{\mathrm{FeP}}) = -0.00413(\pm0.117)D_{(\mathrm{R-X})}{}' - 0.0780(\pm0.106)\Delta G^{\circ\prime} + 3.82(\pm28.9)$	7	0.948	0.965
37	no β: $\log(k_{\mathrm{Jug}}) = -0.136(\pm0.0398)D_{(\mathrm{R-X})}{}' - 0.0209(\pm0.0399)\Delta G^{\circ\prime} + 36.5(\pm10.5)$	8	0.917	0.940
38	β: $\log(k_{\mathrm{Jug}}) = 0.183(\pm0.476)D_{(\mathrm{R-X})}{}' - 0.197(\pm0.276)\Delta G^{\circ\prime} - 48.2(\pm124)$	4	0.989	0.996
39	no β: $\log(k_{\mathrm{FeP}}) = -0.0565(\pm0.0107)D_{(\mathrm{R-X})}{}' - 0.00417(\pm0.00197)\mathrm{LUMO} + 13.9(\pm3.58)$	9	0.993	0.995
40	β: $\log(k_{\mathrm{FeP}}) = -0.0606(\pm0.0261)D_{(\mathrm{R-X})}{}' - 0.0198(\pm0.0137)\mathrm{LUMO} + 10.3(\pm11.0)$	7	0.987	0.986
41	no β: $\log(k_{\mathrm{Jug}}) = -0.0887(\pm0.0418)D_{(\mathrm{R-X})}{}' - 0.0139(\pm0.00996)\mathrm{LUMO} + 16.7(\pm14.9)$	8	0.968	0.977
42	β: $\log(k_{\mathrm{Jug}}) = -0.140(\pm0.663)D_{(\mathrm{R-X})}{}' - 0.0247(\pm0.210)\mathrm{LUMO} + 27.4(\pm193)$	4	0.719	0.906

[a] Plots of residuals versus each of the descriptors (not shown) indicated no systematic variations in residuals with the variables in any of the cases. Numbers in parentheses are ±95% CI. For the sake of precision, three significant figures have been included in the coefficients in the regression equations. When used in a predictive mode, computed *k* values should contain only two significant figures.

of 1.29 and 0.48 in the iron porphyrin and juglone systems, respectively; measured log(*k*) of −1.96 vs a predicted log(*k*) of −2.25 for $CH_3{-}CHBr_2$ in the juglone system; measured log(*k*) of 4.45 vs a predicted log(*k*) of 3.46 for $CCl_2Br{-}CCl_2Br$ in the juglone system) between the predicted and measured rate constants indicates the utility of the LFERs in predicting relative reactivity of PHAs with these commonly encountered reductants. The higher measured value in the latter case may be the result of a higher preexponential factor if the reaction mechanism is an elimination reaction (ref 48, pp 348−352).

Discussion

The factor of approximately 2 greater dependence of the rate constants on $D_{(\mathrm{R-X})}{}'$ in the juglone system indicated by the LFER in eq 28 as compared to the iron porphyrin LFER in eq 27 suggests a greater sensitivity of the reaction to the R−X bond. This sensitivity to bond strength may be linked to mercaptojuglone's function as a one-electron-transfer agent *and* a nucleophile.[41,42] However, the lack of correlation of measured rate constants with free energies of two-electron transfer (Figure 4) suggests that an X-philic reaction (eq 3) is not of primary importance in determining the rate.

The comparison of k_{jug} values with rates of reaction of PHAs with a known outer-sphere reductant[42] summarized above and the lack of correlation with $\Delta G^{\circ}_{2\mathrm{E}}$ (or $\Delta G^{\circ}_{\mathrm{carbene}}$) suggest that the reaction may rather be an inner-sphere, one-electron-transfer *versus* two, separate outer-sphere one-electron-transfer and X-philic reactions. This reaction could result in homolytic R−X bond breakage and later formation of the carbenes detected by Buschmann.[2] An inner-sphere one-electron-transfer reaction is possible if the reactant is the mercaptojuglone semiquinone (detected by EPR at pH values greater than 7.0 in the absence of dithioerythritol[39,40]) rather than the hydroquinone form, because the product of a reaction with the latter would be a very unstable radical anion.[2] The outer-sphere, one-electron-transfer and X-philic reactions with the hydroquinone, an inner-sphere, one-electron-transfer with the semiquinone, or a combination of these reactions could explain the greater sensitivity of the measured rate constants to $D_{(\mathrm{R-X})}{}'$ in the juglone system relative to the iron porphyrin system.

Comparison of the correlation of log(*k*) with $D_{(\mathrm{R-X})}{}'$ and LUMO with that for correlation with $D_{(\mathrm{R-X})}{}'$ and $\Delta G^{\circ\prime}$ also may indicate that an inner-sphere reaction occurs in the juglone system. Replacing $\Delta G^{\circ\prime}$ with LUMO did not significantly alter the equation or the correlation coefficient for the iron porphyrin system (*cf.* eqs 27 and 33, Table 5). On the other hand, for the juglone system, the LUMO coefficient is significantly different from zero and the correlation coefficient increases when LUMO

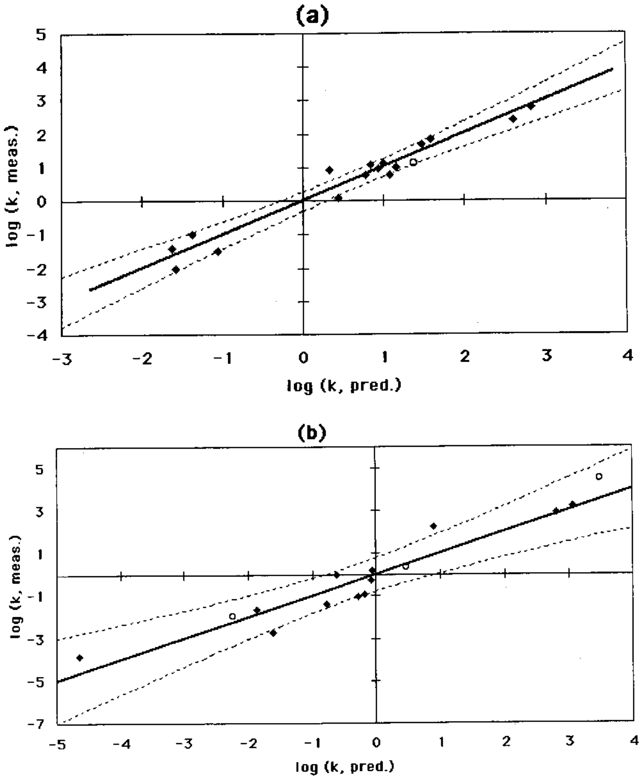


Figure 5. Measured (Table 4) versus predicted log(k) values for (a) iron porphyrin and (b) juglone systems. Predicted log(k) values were computed using the LFERs in eqs 27 and 28 and the descriptors in Table 3. Dashed lines indicate 95% confidence limits of the estimates of log(k). Open circles indicate measured rate constants for disappearance of 1,1,2,2-tetrabromoethane, 1,1-dibromoethane, and 1,2-dibromotetrachloroethane, which were not included in the training set, giving an indication of the ability of the LFERs to predict rate constants.

is substituted for $\Delta G^{\circ\prime}$ (*cf.* eqs 28 and 34, Table 5). LUMO appears to better describe the relative potential energy of the PHAs' reaction with mercaptojuglone.

Different behavior of compounds containing β-halogens compared to those with no β-halogens in the juglone system may also suggest inner-sphere reaction at the halogen due to formation of bridged radicals[26] in the transition state. Although correlation coefficients increased when the compounds were separated into those containing β-halogens and those containing none for both systems in all regressions except one (eq 42 in eqs 35−42), the uncertainty of the coefficients tended to increase due to the lower number of data points in each class. Accordingly, we draw no conclusions as to the occurrence of bridged radical formation in the transition state from these results.

The use of the two descriptors in eqs 27 and 28 to describe reaction of polyhalogenated alkanes in the model systems is different from that of LFERs developed in an earlier study employing the same model systems for reaction of the electron-transfer mediators with nitroaromatic compounds.[49] In contrast to reaction of the electron shuttles with PHAs, the one-electron reduction of nitroaromatic compounds to form the anion is reversible, and no bond is broken in the transition state. Therefore, the overall reorganization energy shown in eq 5 was constant for the model systems, and was in the range of 150−200 kJ mol^{-1}, much lower than the reorganization energies needed to describe PHA reduction, as expected. An LFER was developed involving $E_{\mathrm{h}}^{1'}$, the one-electron reduction potential of the nitroaromatic compound in water:

$$\log(k) = a\frac{E_{\mathrm{h}}^{1'}(\mathrm{ArNO_2})}{0.059\ \mathrm{V}} + b \qquad (43)$$

where a and b are constants. Because the reorganization energy was constant, it factored into the intercept in eq 43. For irreversible electron transfer involving homolytic bond dissociation, eq 43 is not useful unless all compounds in the training set used to develop the LFER have very similar bond strengths, or unless the bond strength varies systematically with the one-electron reduction potential (or free energy of one-electron transfer).

As previously mentioned, Figure 3 demonstrates that $\Delta G^{\circ\prime}$ values were correlated with $D_{(\mathrm{R-X})}{}'$ values for compounds having the same leaving group in our training set, but there was no correlation when all PHAs in the training set were considered. In recent studies, polyhalogenated aliphatic transformation rate constants were correlated with the one-electron reduction potential (or the corresponding free energy) alone, rather than explicitly including the bond dissociation energy.[4,46] Although the large majority of the compounds included in the training sets in these studies were chlorinated, both alkanes and alkenes were included in the LFERs. Alkenes have significantly higher bond dissociation energies than the alkanes (Table 3), so a general relationship of the rate constant to the one-electron reduction potential alone is not expected (eq 7). The correlations obtained are likely the result of a systematic variation in the one-electron reduction potential with bond dissociation energy among the compounds that happened to be included in the training sets. Indeed, for all chlorinated aliphatic compounds presented in Table 3, linear regression of a plot of $\Delta G^{\circ\prime}$ vs $D_{(\mathrm{R-X})}{}'$ had $r^2 = 0.991$, supporting this conclusion.

In general, the thermochemical data presented in Table 3 give good correlations with measured rate constants for transformation of PHAs in various related systems (Table 6).[23,35,39,46] Jafvert *et al.*[23] examined the disappearance of five polyhalogenated ethanes from anoxic sediment−water systems. Peijnenburg *et al.*[39] measured rate constants for the disappearance of 15 polyhalogenated methanes, ethanes, ethenes, and hexachlorocyclohexanes (HCHs) in sediment−water slurries collected from ponds. We excluded the two HCHs from Peijnenburg *et al.*'s data set and diiodoethane from the data set of Jafvert *et al.* in our analysis, because we did not compute descriptors for these compounds. It must be assumed that rates of hydrolysis and reaction with other nucleophiles such as inorganic sulfur species in the slurries in these two studies were significantly lower than that of dissociative electron transfer.[40] Under this assumption, observed rate constants might be expected to be correlated with $\Delta G^{\circ\prime}$ and $D_{(\mathrm{R-X})}{}'$, as found.

Nastainczyk *et al.*[35] reported reduction rates of five polyhalogenated methanes and ethanes by cytochrome P450 *in vitro*. Although the correlation between the predicted and measured log(k) values was moderate ($r^2 = 0.649$), the correlation improved significantly ($r^2 = 0.971$) if the measured value of $D_{(\mathrm{R-X})}$ for $\mathrm{CCl_4}$ was substituted for the calculated $D_{(\mathrm{R-X})}{}'$. The erroneous $D_{(\mathrm{R-X})}{}'$ value for $\mathrm{CCl_4}$ appears to result from the higher/lower-than-average electron-correlation energy by B3LYP theory that was observed for both $\mathrm{CHCl_3}$ and $\mathrm{CCl_4}$ and/or their corresponding radical products. While the error in the calculated $D_{(\mathrm{R-X})}{}'$ for $\mathrm{CCl_4}$ appeared to be the result of use of the B3LYP theory, the calculated $D_{(\mathrm{R-X})}{}'$ value for $\mathrm{CHCl_3}$ was consistently lower than the value reported by Slayden *et al.*[50] by ca. 30 kJ/mol or more using any of the theories/basis sets (Figure 1, Table 1S). A possible reason for this deviation in $D_{(\mathrm{R-X})}{}'$ for $\mathrm{CHCl_3}$ is that the final optimized structure of $\mathrm{CHCl_3}$ is at a local

TABLE 6: LFERs of Polyhalogenated Aliphatic Compounds for Systems in Which Dissociative Electron Transfer Possibly Limits the Overall Disappearance Rate[a]

study	regression equation	*n*	adj r^2	r^2
Jafvert *et al.* (1987)	$\log(k) = -0.0781(\pm 0.201)D_{(R-X)}' + 0.0194(\pm 0.145)\Delta G^{\circ\prime} + 18.3(\pm 52.9)$	4	0.908	0.969
Peijnenburg *et al.* (1989)	$\log(k) = -0.0318(\pm 0.00742)D_{(R-X)}' + 0.0117(\pm 0.0101)\Delta G^{\circ\prime} + 4.83(\pm 1.80)$	13	0.905	0.921
Nastainczyk *et al.* (1982)	$\log(k) = -0.0112(\pm 0.280)D_{(R-X)}' - 0.0236(\pm 0.0585)\Delta G^{\circ\prime} + 4.35(\pm 73.6)$	5	0.298	0.649
Nastainczyk *et al.* (1982)[b]	$\log(k) = -0.0103(\pm 0.034)D_{(R-X)}' - 0.0280(\pm 0.0170)\Delta G^{\circ\prime} + 4.40(\pm 9.06)$	5	0.941	0.971
Scherer *et al.* (1998)	$\log(k) = 0.0302(\pm 0.131)D_{(R-X)}' - 0.0504(\pm 0.1226)\Delta G^{\circ\prime} - 8.80(\pm 33.0)$	12	0.866	0.890
Scherer *et al.* (1998)	$\log(k) = -0.0163(\pm 0.0133)D_{(R-X)}' - 0.00455(\pm 0.00742)\text{LUMO} + 1.24(\pm 6.06)$	12	0.879	0.901

[a] Numbers in parentheses are ±95% CI. [b] Correlation if the calculated $D_{(R-X)}'$ for CCl_4 is replaced with the measured $D_{(R-X)}$ in the original LFER.

minimum rather than a global minimum on the potential energy surface. Because $CHCl_3$ and CCl_4 are common subsurface contaminants, it is important to note that the use of the literature $D_{(R-X)}$ values rather than estimated $D_{(R-X)}'$ values for these two compounds may lead to better estimations of their rates of transformation.

Scherer *et al.*[46] tested correlation of reported rate constants of reduction of polychlorinated methanes, ethanes, and ethenes by Fe(0) with various descriptors. The r^2 values of the LFERs in Table 6 are as high or higher than the r^2 values reported by Peijnenberg *et al.* and Scherer *et al.* for their LFERs. If LUMO is substituted for $\Delta G^{\circ\prime}$ in the LFER for Scherer *et al.*'s data, the correlation coefficient increases very slightly (Table 6); for the other data sets, it decreases. The uncertainties in the coefficients of the descriptors in Table 6 are very high because of the number of data points and the necessary use of two descriptors for data sets containing alkanes having two different leaving groups, as well as alkenes. Although the predictive value of these LFERs is relatively low, the moderately high correlation coefficients suggest that a dissociative electron-transfer mechanism may, at least in part, be rate-limiting.

The LFERs reported in eqs 27 and 34 for polyhalogenated alkanes may not accurately predict rate constants for polyhalogenated alkenes if additional influences of the double bond cause a different reaction mechanism to occur for alkenes. Possible influences include the aforementioned higher R−X bond strength in the alkenes, sp^2- versus sp^3-hybridization, and back-bonding between nonbonded electrons in the halogens and the π-bond in alkenes. These influences may cause a consecutive rather than a concerted electron transfer−bond dissociation reaction, with formation of a discrete anion intermediate, or an elimination reaction, to occur. This may also be the case in the LFER for Scherer *et al.*'s results in Table 6. The linear regression analysis scales the alkenes to minimize error, masking the effect of a possibly different reaction mechanism of the alkenes.

Conclusions

The correlation analysis presented in Figure 4 supports earlier analyses of the kinetic results, intermediates, and products that concluded that a dissociative electron transfer is rate-limiting in transformation of C_1- and C_2-polyhalogenated alkanes in model aqueous solutions. This study demonstrates that LFERs based on Marcus theory can be used to predict rates of PHA reduction in aqueous solution by electron-transfer mediators that are representative of common environmental species. The bond dissociation energy and standard free energy of one-electron reduction are needed to accurately describe transformation rates. Training sets in recent studies have included few or no compounds that contain halogens other than chlorine, and/or that contain alkenes as well as alkanes, obscuring the importance of the bond dissociation energy in the reorganization energy of the transition state. Data sets for transformation rate constants of such common environmental pollutants as solvents, pesticides, flame retardants, and refrigerants that contain various leaving groups cannot be accurately predicted using LFERs that do not explicitly consider bond dissociation energy. The results suggest that the LFER containing $D_{(R-X)}'$ and LUMO rather than $D_{(R-X)}'$ and $\Delta G^{\circ\prime}$ can better describe the reaction of the PHAs with mercaptojuglone. Of the seven theories used to estimate $D_{(R-X)}$ values for comparison with literature values, the B3LYP theory estimated values that were of accuracy and precision comparable to those of MP2 theory at 4 times lower computational cost.

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Supporting Information Available: Table 1S containing values of C−Cl $D_{(R-X)}$ of chlorofluorocarbons computed using MP2/6−31g* and MP2/6−311g* theories/basis sets, Table 2S containing C−F $D_{(R-X)}$ values of chlorofluorocarbons computed using the G1 and G2 theories, Table 3S containing C−Cl $D_{(R-X)}$ values of chlorofluorocarbons computed using density functional theories with traditional (SVWN5) and hybrid (B3LYP) functionals, and Table 4S containing C−Br $D_{(R-X)}$ values of bromochlorofluorocarbons computed using B3LYP/6-311++g(d,p) theory/basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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