Environ. Sci. Technol. **2006**, *40,* 4253−4260

Reactivity of Substituted Benzotrichlorides toward Granular Iron, Cr(II), and an Iron(II) Porphyrin: A Correlation Analysis

TAMAR KOHN,[‡,†]
WILLIAM A. ARNOLD,[§] AND
A. LYNN ROBERTS*,[‡]

Department of Geography and Environmental Engineering, Johns Hopkins University, 313 Ames Hall, 3400 North Charles Street, Baltimore, Maryland 21218-2686, and Department of Civil Engineering, University of Minnesota, 500 Pillsbury Drive, SE, Minneapolis, Minnesota 55455

Cross-correlations of rate constants between a system of interest and a better-defined one have become popular as a tool in studying transformations of organic pollutants. A slope of unity (if the correlation is conducted on a log−log basis) in such plots has been invoked as evidence of a common mechanism. To explore this notion, benzotrichloride and several of its substituted analogues were reacted with $Cr(H_2O)_6^{2+}$, an iron(II) porphyrin (iron *meso*-tetra(4-carboxyphenyl)porphine chloride, Fe(II)TCP), and granular iron. The first two reductants react with organohalides by dissociative inner sphere single-electron transfer, while mechanism(s) for organohalide reduction by granular iron are still debated. Apart from sterically hindered compounds, good correlations were obtained in comparing any two systems, although slopes (on a log−log basis) deviated from unity. We argue that a slope of unity is neither necessary nor sufficient evidence of a common mechanism. Overall rate constants may be composite entities, consisting in part of rate or equilibrium constants for adsorption onto surfaces or for precursor formation in solution; these components may differ between systems in their susceptibility to substituent effects. Cross-correlations may prove useful in predicting reactivity in the absence of steric effects, but additional evidence is required in deducing reaction mechanisms.

Introduction

Predicting the reactivity of compounds for which experimental data are unavailable remains an important if sometimes elusive goal in environmental chemistry. Such predictions can be provided by linear free energy relationships (LFERs), which relate reactivity to an appropriate molecular descriptor. Many LFERs have been developed for transformations of redox-active contaminants in natural environments or approximations thereof. Two well-investigated examples, as summarized in a recent review (*1*), are the reduction of organohalides and nitroaromatic compounds. Popular molecular descriptors in LFERs for such cases are the standard free energy of one-electron reduction ($\Delta G°$), one-electron reduction potentials (E_1 values), bond dissociation energies (BDEs), lowest unoccupied molecular orbital (LUMO) energies, Hammett substituent constants (σ), or a combination of several descriptors (*1*).

The utility of such LFERs may extend beyond their predictive capability. Depending on the molecular descriptors chosen, information about the rate-limiting steps in a reaction can also be deduced. Perlinger and co-workers (*2*) demonstrated that rate constants for reduction of polyhalogenated alkanes by iron porphyrin (FeP) or juglone correlate well with a combination of the computed BDE and $\Delta G°$, invoked as evidence that the rate-limiting step involves the homolytic cleavage of the carbon−halogen bond. Similar conclusions were drawn from correlations of reactivity with BDE in the reduction of halogenated alkanes by iron sulfide (*3*), and at nickel electrodes (*4*).

Perlinger and co-workers (*5*) further suggested that reaction mechanisms can be deduced from LFERs by comparing the rate constants observed in a well-characterized system to those determined in the system under investigation. The underlying assumption is that the rate constants for a set of compounds in two systems should be linearly proportional to one another, provided that the reaction occurs by a common mechanism with the same rate-limiting step. The proportionality between $k_1(i)$ (rate constants for all compounds i in system 1) and $k_2(i)$ (system 2), which can be expressed as

$$k_1(i) = ak_2(i)^b \qquad (1)$$

can be tested by conducting a linear regression of log $k_1(i)$ against log $k_2(i)$:

$$\log k_1(i) = \log a + b \log k_2(i) \qquad (2)$$

Perlinger and co-workers (*5*) maintain that if the resulting slope b is unity, the two systems can be assumed to react via a common mechanism. If the slope deviates from unity, different mechanisms must be operating.

In their study, Perlinger and co-workers reacted polyhalogenated methanes with a cysteine-reduced iron(II) porphyrin (*meso*-tetrakis(*N*-methylpyridyl) iron porphyrin, FeP). Rate constants were correlated to those determined (*6*) for the reaction of polyhalogenated methanes with the known outer sphere reductant $Co(II)W_{12}O_{40}^{7-}$. A correlation of log k_{FeP} with log $k_{Co(II)W_{12}O_{40}^{7-}}$ yielded a slope of unity, a result cited in support of an outer sphere mechanism for reduction by cysteine-reduced FeP.

This approach was expanded by Pecher and co-workers (*7*) in studying organohalide reduction in heterogeneous systems, consisting of Fe(II) adsorbed onto goethite (α-FeOOH). A correlation of logarithmic rate constants obtained in this system against those obtained in a homogeneous system in which juglone served as the reductant yielded a slope of unity, whereas one with cysteine-reduced FeP as the reductant had a slope different from unity. These results were interpreted as an indication that Fe(II) adsorbed onto goethite reacts in a manner analogous to juglone but not to FeP, namely by combined one- and two-electron transfer.

A similar approach was pursued by Kenneke and Weber (*8*) in studying halomethane reduction in iron- and sulfate-reducing sediments. Rate constants measured in sediment suspensions were compared to data from two better-defined systems (Fe(II) adsorbed onto goethite and FeS). Correlations

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* Corresponding author phone: (410)516-4387; fax: (410)516-8996; e-mail: lroberts@jhu.edu.

[‡] Johns Hopkins University.

[†] Current address: Department of Civil and Environmental Engineering, Univeristy of California, Berkeley, Berkeley, CA 94720.

[§] University of Minnesota.

10.1021/es051737x CCC: $33.50

based on logarithmic surface-area normalized rate constants in iron- and sulfate-reducing sediments yielded slopes of unity when compared to the Fe(II)/goethite model system, but not when compared to the FeS system. This was interpreted as evidence of a common mechanism of reduction in the two sediments and the Fe(II)/goethite model system, implicating adsorbed Fe(II) as the principal reductant in the sediments.

An important example of organohalide reduction in heterogeneous systems is that which takes place in the presence of granular iron. Although such reactions have been studied extensively (*9−16*), the identity of the principal reductant(s), as well as the mechanism of electron transfer, are still a matter of some debate. For example, it has been suggested that the reactive sites could comprise Fe(II) adsorbed to oxides on the iron surface (*12*). Fe(II)-bearing corrosion products such as magnetite (Fe_3O_4) or green rust (e.g., $[Fe_4^{2+}Fe_2^{3+}(OH)_{12}][CO_3\cdot 2H_2O]$) have also been found to reduce organohalides (*17−20*) and may act as additional redox-active phases in granular iron systems. Alternative suggestions include electron transfer in corrosion pits, in which Fe(0) could be exposed to solution (*12*, *21*), electrons originating from adsorbed hydrogen on the iron surface (*22*), or reaction at the surface of graphite impurities in the iron (*23*). Both inner and outer sphere pathways have been proposed (*24*) for reduction of organohalides by granular iron. Although the description of reactions as inner sphere or outer sphere was originally developed from studies of electron-transfer reactions of coordination complexes of transition metal ions (*25*), it has also been extended to reactions of organic compounds. Following the conventions articulated by Savéant (*26*), a reaction of an organohalide can be viewed as outer sphere from the perspective of the electron donor if no bond between the donor and the electron acceptor is formed or cleaved during electron transfer, even if a carbon−halogen bond undergoes cleavage in concert with electron transfer (making the reaction one that is inner-sphere from the perspective of the electron acceptor). We refer to such reactions herein as “outer sphere”. A counterexample, in which transfer of an electron from the donor to the acceptor occurs via a “bridging” halogen (coordinated to the electron donor and bonded to the electron acceptor via a bond that undergoes cleavage in concert with electron transfer) is referred to as “inner sphere” (from the perspective of the donor and acceptor alike).

The purpose of the present study was to develop experimental data for reaction of a set of organohalides with granular iron, as well as with two better-defined model reductants, one consisting of $Cr(H_2O)_6^{2+}$ and the second comprising an iron porphyrin (iron *meso*-tetra(4-carboxyphenyl)porphine chloride, FeTCP). Comparing two well-defined homogeneous systems with the more poorly characterized granular iron system allows us to draw inferences about factors governing reactivity of organohalides toward granular iron and to test the utility of cross-correlations.

$Cr(H_2O)_6^{2+}$ was selected as a model reductant by virtue of the extent to which the mechanism with which it reacts with organohalides has been previously characterized (*27−32*). $Cr(H_2O)_6^{2+}$ is a one-electron donor, and its reactions with organohalides have been shown (*27*, *28*) to take place by an inner-sphere mechanism. FeTCP was chosen as a second model system because its reactive center is Fe(II), a metal ion that may also serve as the reactive center in the granular iron system (*12*). Various Fe(II) reaction centers have been shown to respond similarly to changes in contaminant structure, independent of their chemical environment (*33*). FeTCP can thus be viewed as a very crude approximation of the putative reactive entity on the surface of granular iron. Reduction of organohalides and nitroaromatic compounds in aqueous solution by iron porphyrins have been extensively investigated by others (*5*, *34−38*).

The set of organohalides investigated consisted of benzotrichloride (BTC) and eight of its substituted analogues. This compound class has to date received relatively little scrutiny. It was chosen for this study because it is likely to undergo reduction via pathways similar to other chlorinated hydrocarbons; it also enables us to investigate the effect of ring substituents on reactivity, as previously explored for nitroaromatic compounds (*33*, *38*). Moreover, the selection of BTC derivatives enables comparison with other $R{-}CCl_3$ compounds such as 1,1,1-trichloroethane and chloroform. Molecular descriptors tested in developing LFERs included computationally derived bond dissociation energies (BDE values), as well as Hammett substituent constants (σ values).

Experimental Section

Chemicals. Compounds investigated included benzotrichloride (BTC, 99%, TCI), 2-chlorobenzotrichloride (2-Cl-BTC, 98%, TCI), 3-chlorobenzotrichloride (3-Cl-BTC, Sigma-Aldrich), 4-chlorobenzotrichloride (4-Cl-BTC, 99%, Aldrich), 2,4-dichlorobenzotrichloride (2,4-diCl-BTC, Sigma-Aldrich), 3,4-dichlorobenzotrichloride (3,4-diCl-BTC, 98%, TCI), 2-fluorobenzotrichloride (2-F-BTC, 99%, TCI), α,α,α,α′,α′,α′-hexachloro-*p*-xylene (hexaCl-*p*-xylene, TCI), and α,α,α,α′,α′,α′-hexachloro-*m*-xylene (hexaCl-*m*-xylene, 98%, TCI). Products of BTC and 4-Cl-BTC included benzal chloride (BC, 98%, TCI), benzaldehyde (BA, 99%, Aldrich), benzyl alcohol (Supelco), toluene (reagent grade, J. T. Baker), 4-chlorobenzaldehyde (4-Cl-BA, 97%, Aldrich), 4-chlorobenzyl alcohol (4-Cl-benzyl alcohol, Fluka), and 4-chlorotoluene (4-Cl-toluene, 98%, Aldrich). Concentrated stock solutions of individual BTC compounds and reaction products were prepared in deaerated acetonitrile (HPLC grade, J. T. Baker). The reductants were electrolytic iron powder (100 mesh, Fisher), Cr(III) sulfate hydrate ($Cr_2(SO_4)_3\cdot xH_2O$, Aldrich) reduced to Cr(II) by zinc powder (100 mesh, Alfa Aesar), and Fe(III) *meso*-tetra(4-carboxyphenyl)porphine chloride (Fe(III)TCP, Frontier Scientific) reduced to Fe(II)TCP by palladized iron. A detailed description of the preparation of all three reductant systems is provided in the Supporting Information.

Kinetic Experiments. Reactions were followed by analyzing organohalides in hexane extracts of subsamples that were obtained at regular intervals. Details are provided in the Supporting Information. Because BTC and its substituted analogues readily hydrolyze (*39*), experiments in all three reductant systems were conducted in a 50:50 (v/v) acetonitrile:aqueous buffer matrix. This slowed hydrolysis to rates that were negligible relative to those of the reductions investigated.

Kinetic experiments with Cr(II) were conducted at a Cr(II) concentration of 2.5 mM, prepared by diluting a 0.5 M Cr(II) stock with appropriate amounts of deaerated acetonitrile and 5 mM H_2SO_4. Aliquots of the Cr(II) solution were spiked with 40 μL of a stock solution of the BTC compound of interest (in deaerated acetonitrile) to an initial concentration of 40 μM. Reactions with Fe(II)TCP were performed using a solution with an actual reduced Fe(II)TCP concentration of 6.4 μM (and an Fe(III)TCP concentration of 18.6 μM), prepared in 50:50 (v/v) deaerated acetonitrile and water. The initial BTC concentration was 1 μM. All experiments using these homogeneous systems were carried out in a glovebox (95% N_2/5% H_2 atmosphere). Granular iron reactions were carried out in a deaerated solution of 50:50 (v/v) acetonitrile and aqueous buffer (50 mM Tris buffer and 0.1 M NaCl at pH 7.2). The iron loading was 1.56 g/L, and the initial oxidant concentration was 40 μM.

Analytical Methods. Disappearance of BTC and its substituted analogues was monitored by gas chromatography

TABLE 1. Reaction Rate Constants for the Compounds under Investigation for Reactions in 50:50 (v/v) Aqueous Acetonitrile with Fe(0), Cr(II), and FeTCP, along with Summed Hammett Constants for the Ring Substituents Relative to Unsubstituted BTC, and Computed Bond Dissociation Energies for the Reaction RX → $R^\bullet + X^\bullet$ [a]

compd	k_{obs} Fe(0) (s^{-1})	k_{red} Cr(II) (M^{-1} s^{-1})	k_{red} FeTCP (M^{-1} s^{-1})	$\Sigma\sigma$ [b]	BDE [c] (kJ mol^{-1})
BTC	$3.82 (\pm 0.38) \times 10^{-4}$	$2.19 (\pm 0.09)$	$861 (\pm 29)$	0	255
2-Cl-BTC	$4.58 (\pm 0.61) \times 10^{-4}$	$1.16 (\pm 0.13)$	$809 (\pm 69)$	NA [d]	237
3-Cl-BTC	$5.19 (\pm 0.58) \times 10^{-4}$	$2.62 (\pm 0.08)$	$1070 (\pm 97)$	0.37	254
4-Cl-BTC	$7.29 (\pm 0.47) \times 10^{-4}$	$3.17 (\pm 0.14)$	$1910 (\pm 244)$	0.23	255
2,4-diCl-BTC	$6.16 (\pm 0.36) \times 10^{-4}$	$1.83 (\pm 0.06)$	$1630 (\pm 146)$	NA [d]	237
3,4-diCl-BTC	$7.89 (\pm 0.77) \times 10^{-4}$	$3.57 (\pm 0.23)$	$2510 (\pm 250)$	0.60	256
2-F-BTC	$2.51 (\pm 0.20) \times 10^{-4}$	$1.24 (\pm 0.09)$	$391 (\pm 47)$	NA [d]	248
hexaCl-*p*-xylene	$1.27 (\pm 0.23) \times 10^{-3}$	$6.48 (\pm 0.63)$	$5410 (\pm 2168)$	0.46	256
hexaCl-*m*-xylene	$4.26 (\pm 0.28) \times 10^{-4}$	$4.07 (\pm 0.28)$	$2600 (\pm 471)$	0.40	252

[a] Stated uncertainties on rate coefficients correspond to 95% confidence limits. [b] Values for Hammett constants taken from Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley: Hoboken, NJ, 2003. [c] Computed via B3LYP methods using the 6-311G basis set, as described in the Supporting Information. [d] Hammett constants for ortho-substituted compounds are not available because of steric interactions with the reaction center.

(GC) with electron capture detection (ECD). The GC (Fisons HRGC Mega 2 series) was equipped with an RTX-1 column (30 m × 0.32 mm i.d. × 5 μm film thickness, Restek). Samples (1 μL) were injected by means of an AS 800 liquid autosampler (Fisons) in on-column mode. The system was calibrated using external standards prepared in hexane. Calibration curves were obtained by analyzing 1 μL aliquots of the standards using the same GC system employed for samples.

The reaction products of BTC and 4-Cl-BTC were analyzed using a Thermo Finnigan Trace quadrupole GC/MS with an Equity-5 column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, Supelco). Samples (2 μL) in hexane or ethyl acetate were injected on-column, and spectra were obtained in full scan (m/z 61 to 441) electron ionization (EI) mode. Calibration curves were obtained using ethyl acetate standards of the corresponding benzyl alcohols, and hexane standards of all other products.

Electron-transfer mechanisms in the Cr(II) system were investigated by capillary electrophoresis (see Supporting Information).

Data Analysis. Pseudo-first-order rate constants (k_{obs} values) for all systems were determined by regressing the natural logarithm of the organohalide concentration against elapsed time. The R^2 values for the model fits were generally 0.99 or greater. Second-order rate constants (k_{red} values) for the homogeneous systems were obtained by dividing the relevant k_{obs} value by the measured initial Cr(II) or Fe(II)TCP concentration.

Results and Discussion

Reactions with Cr(II). Under our experimental conditions, Cr(II) exists as the substitution labile $Cr(II)(H_2O)_6^{2+}$ complex, with a standard reduction potential of −0.424 V vs NHE (*40*). If BTC were to react with Cr(II) by an inner sphere process, chloride would act as a bridging ligand (*31*). One-electron oxidation of Cr(II) leads to Cr(III), which is substitution-inert. The bridging ligand should therefore remain associated as $CrCl^{2+}$ following R−X bond cleavage rather than dissociate as Cl^-_{aq}. The $CrCl^{2+}$ species has a lifetime of a few days at low pH (*41*). In the case of an outer sphere reaction, in which the electron is transferred without actual bonds being formed between Cr(II) and BTC, no chloro complexes of chromium should be observed. Their rate of formation from Cl^-_{aq} and $Cr(H_2O)_6^{3+}$ is very slow (*42*), especially at the low Cl^-_{aq} concentration present in these experiments.

Capillary electrophoretic (CE) analyses of products originating from BTC reduction by Cr(II) revealed the generation of $CrCl^{2+}$ (see Supporting Information, Figure S1) at a rate much more rapid than expected for its formation from $Cr(III)(H_2O)_6^{3+}$ and Cl^-. This demonstrates that BTC reduction by $Cr(II)(H_2O)_6^{2+}$ proceeds via an inner sphere mechanism. Evidence for the formation of $CrCl^{2+}$ and thus for an inner sphere mechanism has previously been presented by others in the reduction of benzyl chloride (*27*, *29*) and alkyl polyhalides (*28*, *43*).

Second-order rate constants for reduction of BTC compounds by $Cr(H_2O)_6^{2+}$, shown in Table 1, varied by a factor of 5. Products observed from the reactions of BTC and 4-Cl-BTC with Cr(II) were the corresponding BA species and, in the case of BTC, trace amounts of benzyl alcohol (Supporting Information, Figure S2a). In contrast to the findings of Castro and Kray (*31*), no toluene was detected. Measured reduction products are consistent with a scheme outlined by Castro and Kray (*31*) for reaction of *gem*-trihalides with Cr(II) (Figure 1a).

Reactions with Fe(II)TCP. $E_{1/2}$ for the reduction of Fe(III)TCP to Fe(II)TCP in water at pH 9.9 was measured as approximately −0.133 V vs NHE (see Supporting Information). Fe(II)TCP reacted relatively rapidly with BTC (Supporting Information, Figure S2b). The second-order rate constants for reactions of BTC compounds with Fe(II)TCP (Table 1) are 2 to 3 orders of magnitude greater than those for reaction with Cr(II), despite the higher reduction potential of Fe(II)TCP. This indicates that reaction with Fe(II)TCP also proceeds by an inner sphere mechanism; such reactions are typically faster than outer sphere reactions, and the increased reactivity of Fe(II)TCP relative to $Cr(II)(H_2O)_6^{2+}$ is inconsistent with the higher reduction potential of the former if reaction with Fe(II)TCP were to proceed via an outer sphere process.

Support for an inner sphere mechanism is given by Wade and Castro (*36*), who propose that the reduction of alkyl polyhalides by an FeP (deuterohemin IX) is initiated by an axial inner sphere electron transfer, analogous to that observed for the reaction with Cr(II). A similar mechanism was postulated by Ong and Castro (*37*) for the reaction of an FeP (iron deuteroporphyrin IX) with nitroaromatic compounds. These researchers further found that reactivity of nitroaromatic compounds was suppressed by the presence of good axial ligands, which was interpreted as evidence of an axial inner sphere electron-transfer mechanism.

The principal reaction products observed after four half-lives were various coupling products (inferred from mass spectra). Lacking authentic reference materials, these were not quantified. The proposed reaction scheme is depicted in Figure 1b.

Reactions with Granular Iron. The major products observed from the reduction of BTC by granular iron are BC (Supporting Information, Figure S2c) and coupling products (which again were not quantified). Trace amounts of toluene were also observed. We propose that BTC degradation occurs in a manner analogous to the reduction of 1,1,1-TCA by

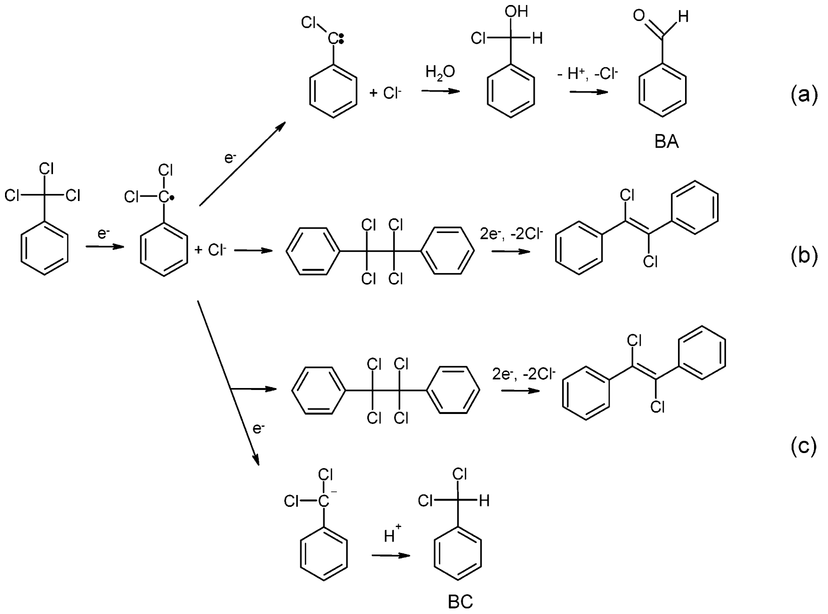

FIGURE 1. Proposed major reaction pathways and products for the reduction of BTC by (a) $Cr(H_2O)_6^{2+}$, (b) FeTCP, and (c) granular iron. BA = benzaldehyde, BC = benzal chloride.

granular iron (*15*), as depicted in Figure 1c. Pseudo-first-order rate constants are given in Table 1.

Relationship between Reactivity and Bond Dissociation Energies. Perlinger and co-workers (*2*) have shown that rate constants for the reduction of alkyl halides by an iron porphyrin or juglone correlate well with BDE values, as well as with the one-electron reduction potentials for dissociative electron transfer. Similarly, Kochi and Davis (*44*) observed a good correlation between the reaction rate constants for the reduction of benzyl bromides by Cr(II) and gas-phase pyrolysis rate constants. The latter reaction leads to homolytic bond cleavage, and these rate constants were interpreted to reflect R−X BDE values. In our systems, however, no pronounced correlation between BDE values and rate constants from any system investigated was evident (see Table 1 and Supporting Information, Figure S3). Correlations exhibited R^2 values of 0.57 (Cr(II)), 0.11 (FeTCP), and 0.01 (Fe(0)), respectively.

Most of the compounds investigated in this study have very similar BDE values, between 252 and 256 kJ/mol (Table 1). Only ortho substituents appreciably lower BDE values. Were R−X bond cleavage to represent the sole factor involved in the rate-determining step, the ortho-substituted compounds should be the most reactive, with the unsubstituted and meta- and para-substituted compounds exhibiting similar reactivities. In our systems, however, ortho substituents tended to reduce reactivity. This is evident in comparing rate constants for 2-Cl-BTC with those for 3- or 4-Cl-BTC, rate constants for 2,4-diCl-BTC with those for 3,4-diCl-BTC, and rate constants for 2-F-BTC relative to BTC in any system. In contrast, meta and para substituents led to increased reactivity relative to BTC, despite their lack of influence on BDE values.

The absence of a correlation between BDE and reactivity can be explained by a concept introduced by Davis and Pryor (*45*, *46*). These researchers hypothesize that substituent effects are best rationalized by separate consideration of their influence on (1) BDE values and (2) the stability of the transition state. This is because substituents influence BDE values through their effect on the ground state (RX) or the radical state ($R^•$), while the transition state is a structurally different entity from the former two. The two influences can counteract one another. For example, substituents may increase BDE by stabilizing the R−X bond in the ground state, but they may stabilize the transition state through resonance interactions. The latter may be especially important in compounds possessing aromatic substituents.

Substituent Effects on Reactivity. In considering the potential influence of substituents on reactivity, it may be instructive to recognize that rate constants for reduction in both homogeneous and heterogeneous systems may represent composite parameters. For electron transfer between an electron donor *D* and an acceptor *A* in homogeneous solution, the rate of reaction of *A* can be written (*47*) as

$$\text{rate} = \frac{-k_p}{1 + \dfrac{k_p}{K_p k_{el}}}[D][A] = -k_{red}[D][A] \qquad (3)$$

where k_{red} is a second-order rate constant for a given reductant that embodies k_p, the rate constant for precursor formation, k_{el}, the rate constant for electron transfer, and K_p, an equilibrium constant for precursor formation (see Supporting Information for derivation). In the case of a heterogeneous reaction for which the rate-limiting step is a surface reaction, the rate of reaction of *A* can be given (*16*) as

$$\text{rate} = \frac{-k_s S_t K_A [A]}{1 + K_A [A]} = -k_{obs}[A] \qquad (4)$$

where k_s is the surface reaction rate constant, which we assume to reflect dissociative electron transfer, S_t is the total number of sites, and K_A is an equilibrium constant for adsorption of *A* to a reactive surface site. If $K_A[A] \ll 1$, $k_{obs} \cong k_s S_t K_A$.

For heterogeneous reactions in which adsorption is rate-limiting, the corresponding rate expression (*16*) is

$$\text{rate} = -k_a[A][S_t] = -k_{obs}[A] \qquad (5)$$

where k_a is a rate constant for adsorption to a surface site.

The negligible influence of meta or para chlorine substituents on BDE values would imply a similarly negligible effect on the rate coefficient for electron transfer (k_{el} or k_s). Equations 3−5 therefore suggest that these substituents primarily manifest their tendency to increase reactivity by increasing k_p, K_p, k_a, or K_A values by favoring precursor formation in homogeneous systems or substrate adsorption in heterogeneous systems. In terms of the concept of Davis and Pryor (*45*, *46*), the electron-withdrawing properties of the meta and para substituents could influence reactivity through an effect on the precursor complex, which can be viewed as part of the transition state (see Supporting Information). Overall this increases the corresponding (potentially composite) rate constants (k_{red} or k_{obs}).

Contrariwise, the lower BDE values for the ortho-substituted compounds should produce an increase in k_{el} or k_s. The observed diminished reactivity of these compounds implies that any increase in k_{el} or k_s is more than offset by a decrease in k_p (or K_p) or (for the heterogeneous systems) by a smaller value of K_A (or k_a in the case of adsorption-limited reactions). The precursor complex is thus destabilized by ortho substituents. This should not be viewed as a polar effect; rather, it reflects steric hindrance introduced by the ortho substituents that limits access of the reductants to the $-CCl_3$ reaction center.

The rate-enhancing effects of $-CCl_3$ substituents we observed (Table 1) in all of the systems studied were accompanied by relatively minor changes in BDE values. Interestingly, the enhancement of reactivity toward compounds possessing two $-CCl_3$ centers encountered in the granular iron system was significantly smaller than in the homogeneous systems. (Note that the reaction of hexaCl-*p*-xylene in all systems was very fast and difficult to measure. Its reaction rate constants are therefore subject to a rather large error.) These bulky substituents, which are not in the plane of the ring, may limit the access of the BTC compounds to the iron surface such that K_A or k_a values are less than those otherwise anticipated, a steric effect that would not be manifested in the homogeneous systems.

For ortho substituents, the granular iron system exhibits a lesser apparent sensitivity to steric hindrance, as is evident in comparing the relative reactivity of 2-Cl-BTC to BTC in the three systems. This may reflect competing effects. Adsorption to the iron may occur through electron donor−acceptor interactions with the aromatic ring, which are not necessarily inhibited by the presence of an ortho substituent in the same plane as the ring. It is even possible that ortho substituents could enhance the adsorption of BTCs to the iron surface by enhancing their Lewis basicity, and thereby enhancing k_a or K_A, similar to the effect of chlorine substituents on adsorption constants observed in the reduction of chlorinated ethylenes by granular iron (*16*). Enhanced electron donor−acceptor interactions may more than compensate for a potentially sterically hindered surface reaction, an effect that again would not be manifested in reactions in homogeneous solution.

Correlation of Reactivity with Hammett Constants. As is evident in Table 1, rate constants did not correlate particularly well with Hammett substituent constants. This is true even for reactions in homogeneous solution. Hammett correlations yielded R^2 values of 0.31 (Cr(II)), 0.51 (FeTCP), and 0.06 (Fe(0)), respectively.

The applicability of Hammett correlations for radical reactions has not been fully clarified, and poor Hammett correlations have been previously reported in such cases. For example, Kochi and Davis (*29*, *44*) failed to discern any correlation between Hammett constants and rate constants for the reduction of substituted benzyl bromides by Cr(II). Other researchers note good correlations with Hammett constants for redox reactions of organic pollutants in a variety of homogeneous and heterogeneous systems that are likely to proceed via radical intermediates (*33*, *38*, *48*, *49*). Many of the substrates in question, however, are anilines or phenols with ionizable functional groups at the reaction center; good correlations in such cases may reflect the effect of substituents on basicity (and therefore substrate affinity for adsorption at surface sites) rather than on the electron transfer step, as previously noted (*48*).

Some Mechanistic Considerations. It is our contention that a slope different from unity in a correlation of logarithmic rate constants obtained from two systems does not necessarily indicate different reaction mechanisms. As shown in the derivation provided in the Supporting Information, for two sets of reactions that proceed via a simple elementary bimolecular process, the slope *b* in a correlation between logarithmic second-order rate constants is equal to $\Delta\Delta G_1^{\ddagger}/\Delta\Delta G_2^{\ddagger}$, where $\Delta\Delta G_1^{\ddagger}$ and $\Delta\Delta G_2^{\ddagger}$ represent the relative sensitivity of the activation energies in systems 1 and 2, respectively, to changes in structure of the common reactants. The slope *b* therefore includes both enthalpic and entropic contributions to the overall activation barrier in each system, as each $\Delta\Delta G^{\ddagger}$ can be expressed as $\Delta\Delta H^{\ddagger} - T\Delta\Delta S^{\ddagger}$. A slope of unity might certainly be expected if the enthalpic and the entropic barriers to reaction were to respond identically in the two systems to changes in structure of the common reactants, but this need not be true even for systems that react by the same mechanism.

A case in point involves second-order rate constants for reactions of methyl benzene sulfonate (CH_3OSO_2Ph) and alachlor with a common group of nucleophiles. Both sets of reactions are known to proceed by a simple elementary S_N2 mechanism, yet a correlation (*50*) of logarithmic second-order rate constants (k_{Nuc} values) in the two systems yields a slope *b* of 1.54 (± 0.36) that is different from unity at the 95% confidence level. This large slope reflects a high degree of activation of chloroacetanilides (large Swain-Scott *s* value) toward their S_N2 reactions with relatively strong nucleophiles (*50*, *51*); this activation, as well as the smaller $\Delta H^{\ddagger}$ values of S_N2 reactions of chloroacetanilides compared to methyl halides (*51*), has been interpreted as evidence of electronic interactions of the S_N2 reaction center with the α-anilide substituent (*52*).

As soon as reactions become more complex than simple elementary processes (as is the case in multistep reactions), second-order rate constants may represent composite entities. This is reflected in the rate expressions for electron transfer between an electron donor *D* and an acceptor *A* in homogeneous solutions such as the Cr(II) or FeTCP systems (eq 3), or for a heterogeneous reaction with a rate-limiting surface reaction (eq 4), such as the granular iron system investigated in this study. In such a case the slope *b* of a cross-correlation will reflect the aggregate effect of the relative sensitivity of each parameter that comprises the composite rate constant to both enthalpic and entropic factors. The different contributors to composite rate constants may exhibit varying susceptibilities to changes in the structure of one reactant. Reactants could be much more susceptible to steric factors in one system than in another, and this could easily be manifested by *b* values that differ from unity. If a linear proportionality (*b* value of unity) need not even be encountered in simple elementary reactions, then it would seem even more likely to reflect coincidence in the case of multistep reactions in homogeneous or heterogeneous systems.

Cross-Correlations. Figure 2 shows the individual cross-correlations of the three systems investigated. Once the most sterically hindered compounds indicated by open symbols (ortho-substituted compounds in the Cr(II) system, as well as compounds with a second $-CCl_3$ substituent in the granular iron system) were omitted from the regression, good cross-correlations were obtained between all three systems.

In all three cross-correlations the slopes of the linear regressions differ from unity. Even though the cross-correlation between granular iron and Cr(II) exhibits a slope that approaches unity, we would be hesitant to conclude that the two systems react by equivalent mechanisms,

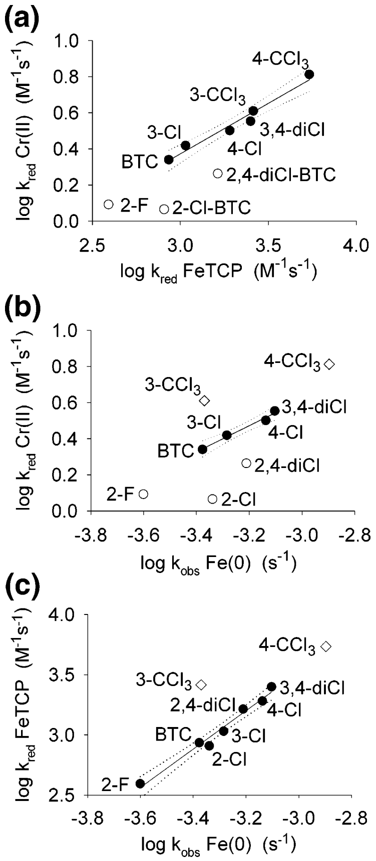

FIGURE 2. Cross-correlations obtained in the three reductant systems. The solid lines indicate the linear regressions through the solid symbols, the dotted lines represent 95% confidence intervals. Open symbols indicate compounds excluded from the correlations for reasons of steric hindrance. Regression parameters for the three panels are as follows: (a) log k_{red} Cr(II) = 0.56 (± 0.14) log k_{red} FeTCP − 1.31 (± 0.47); R^2 (adj) = 0.959, SE = 0.033; (b) log k_{red} Cr(II) = 0.72 (± 0.29) log k_{obs} Fe(0) + 2.78 (± 0.95); R^2 (adj) = 0.974, SE = 0.015; (c) log k_{red} FeTCP = 1.59 (± 0.29) log k_{obs} Fe(0) + 8.30 (± 0.95); R^2 (adj) = 0.971, SE = 0.046.

because we lack evidence to support such a claim. We note that cross-correlations of Cr(II) and granular iron for other alkyl halides with a CCl_3 reaction center exhibit a very similar slope statistically different from unity (0.73 ± 0.08; see Figure 3 and Supporting Information, Table S1).

According to Perlinger et al. (*5*), the observation that the slopes differ from unity would imply that any two of these systems react by different mechanisms. We nevertheless maintain that both homogeneous systems react with substituted BTCs via dissociative inner sphere single electron transfer. We hypothesize instead that the nonlinear relationship between rate constants for the two homogeneous systems, along with the difference in their sensitivity to ortho substituents, reflects differences in k_p or K_p values associated with precursor formation and stability between the systems.

Even if the reaction mechanism for the heterogeneous granular iron system were equivalent to that of the homogeneous systems, the deviation of the slope from unity is not surprising. The different susceptibilities of the granular iron system and the two homogeneous systems to the effects of sterically hindering substituents may well signify differences in barriers to the individual steps in the reaction. The rate constants obtained in the homogeneous systems may wholly or in part be determined by precursor formation (eq 3 and Supporting Information, eqs S14 and S15). Precursor formation may be sterically hindered in the case of ortho-substituted BTCs, which may lead to smaller than expected overall rate constants. We speculate that adsorption is an important factor contributing to the rate constant in the granular iron system (eq 4 and Supporting Information, eq S23). In such a case, the bulky $-CCl_3$ substituents could impede the rate or extent of adsorption, explaining why these two compounds do not adhere to the cross-correlations.

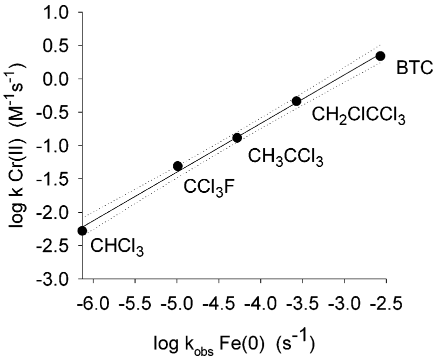

FIGURE 3. Comparison of reaction rate constants of several R−CCl_3 compounds in the granular iron and the Cr(II) systems. Data for reaction of Cr(II) with compounds other than BTC are from ref. *32*. The solid line indicates the linear regression. The reaction rate constant for BTC was obtained in 50% acetonitrile, whereas the other compounds were reacted in Tris buffer only. For this figure the BTC rate constant was therefore multiplied by a factor of 7, which was the inhibitory effect introduced by acetonitrile on the reactivity of iron toward 1,1,1-TCA. Regression parameters are as follows: log k_{red} Cr(II) = 0.73 (± 0.08) log k_{obs} Fe(0) + 2.24 (± 0.38); R^2 (adj) = 0.995, SE = 0.072.

Utility of Correlations. We have shown that the slope of a cross-correlation is not a reliable indicator of common mechanisms. A better indicator may be the quality of the cross-correlation. This was also noted by Canonica and Trantyek (*53*), who state that a strong correlation between rate constants observed in two systems suggests that the rate-determining step may be similar, even if the slope of the cross-correlation under consideration differs from unity. In weighing the quality of the cross-correlations, it is important to recognize, however, that different systems may vary in their sensitivity to steric hindrance. Claims about the prevalent reaction mechanisms must therefore be supported by other studies.

Acknowledgments

This material is based upon work supported by the National Science Foundation (Grant CHE-0089168) as part of the Collaborative Research Activities in Environmental Molecular Science in Environmental Redox-Mediated Dehalogenation Chemistry at the Johns Hopkins University. Sherine Obare and Gerald Meyer are gratefully acknowledged for their input on the FeTCP reactions. The help of Rich Carbonaro and Yun Wang with the capillary electrophoresis work is greatly appreciated. Computational resources were provided by the Minnesota Supercomputing Insitute.

Supporting Information Available

Supporting Information describes experimental details pertaining to the kinetic experiments and preparation of reductants; characterization of the FeTCP reductant (including determination of its half wave potential and the reduced Fe(II)TCP concentration); our investigation of electron transfer in reduction of BTC by Cr(II); typical time courses and product development; the computation of BDEs; the derivation of rate expressions; and data pertaining to reactions with other R−CCl_3 compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 1, 2005. Revised manuscript received January 28, 2006. Accepted April 18, 2006.

ES051737X