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**ALKYL BROMIDES AS MECHANISTIC PROBES
OF REDUCTIVE DEHALOGENATION:
REACTIONS OF VICINAL DIBROMIDE
STEREoisomers WITH ZERO-VALENT
METALS**

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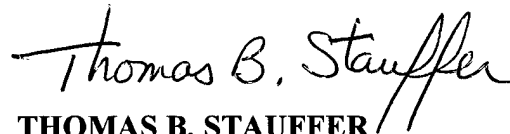
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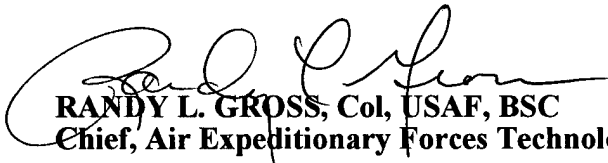
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Alkyl Bromides as Mechanistic Probes of Reductive Dehalogenation: Reactions of Vicinal Dibromide Stereoisomers with Zero-Valent Metals

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Abstract

The mechanism through which zero-valent metals (most notably iron and zinc) reduce alkyl polyhalides in aqueous solution at room temperature was investigated using several stereoisomers of vicinal dibromides as probe compounds: *2R-3S*-2,3-dibromopentane (DBP) (and its stereoisomeric enantiomer, *2S-3R*-2,3-dibromopentane), *2R-3R*-2,3-dibromopentane (and its stereoisomeric enantiomer, *2S-3S*-2,3-dibromopentane), and *1R-2R*-1,2-dibromo-1,2-diphenylethane [(±)-SBr₂]. All of the probes react with zero-valent metals to give approximately the same *E:Z* ratio of olefins as observed during dehalogenation by iodide (a classic nucleophilic reductant). Reductions promoted by Cr(II) (a one-electron reductant) yield distinctly different proportions of *E*- and *Z*-olefins. Despite these differences, it cannot be definitively concluded that zero-valent metals reduce vicinal dibromides via nucleophilic two-electron pathways rather than via two sequential single electron transfer (SET) steps. This is because the reactions are heterogenous in nature, occurring at a surface which may possess locally elevated concentrations of reducing equivalents. Transfer of one electron may thus be rapidly followed by a second SET step. Estimates of energy barriers for C-C bond rotation in intermediate radicals suggest that if the zero-valent metals studied reduce the vicinal dihalide probe compounds via SET, the intermediate radicals must be reduced to the final olefin products with rate constants of about 10⁸ to 10¹⁰ s⁻¹. Steady-state concentrations of free radicals in these systems would be extremely low, and reactions such as coupling of free radicals would therefore be unlikely to compete with reduction to olefins.

Key words: reductive dehalogenation, zero-valent metals, stereochemical probes, reductive elimination, permeable barriers, rotational barriers.

Introduction

Zero-valent metals have been the focus of much recent attention in the environmental community because they offer great promise in treating contaminated groundwater through their ability to promote abiotic reductive dehalogenation (1-12). Nevertheless, many basic questions about the mechanism of these reactions remain unanswered. Reductions promoted by zero-valent metals include hydrogenolysis (replacement of halogen by hydrogen), reductive β-elimination (removal of two vicinal halogens, accompanied by an increase in bond order), reductive α-elimination (e.g., reduction of carbon tetrachloride to dichlorocarbene) and hydrogenation of double or triple bonds. Each of these involves a net transfer of two electrons. The principal goal of this research was to investigate the degree of concertedness of electron transfer in metal-promoted reductive β-elimination.

Theoretically, electron transfer may occur either via single electron transfer (SET) (which may occur via outer-sphere or inner-sphere pathways) or via inner-sphere two-electron

(nucleophilic) pathways (13). If reduction occurs via SET, the resulting radicals might persist long enough to undergo characteristic free-radical reactions, such as coupling and hydrogen atom abstraction. Whether reactions proceed via one- or two-electron pathways can affect the ultimate distribution of products, which in turn may exert a major influence on the success of treatment approaches based on zero-valent metals.

For example, Balko and Tratnyek (11) argue that a shift toward a two-electron mechanism in the reduction of carbon tetrachloride by iron metal caused by photoirradiation (which increases the production of conduction band electrons in the oxide which coats the metal) is responsible for a corresponding change in the product distribution: photoirradiation favors carbon monoxide (which results from reductive α -elimination to dichlorocarbene) at the expense of the hydrogenolysis product, chloroform. Criddle and McCarty (14) also invoked a near simultaneous transfer of two electrons to account for electrolytic reduction of carbon tetrachloride to dichlorocarbene. In contrast, Buschmann *et al.* (15) attributed haloforms produced in the reduction of tetrahalomethanes by cysteine to a two-electron pathway.

A better understanding of the mechanism through which zero-valent metals reduce organohalides may also help explain the results of recent investigations (16) of the reduction of 1,1,1-trichloroethane (1,1,1-TCA) by iron metal, which revealed that a significant portion (up to 9%) of the carbon mass balance may be found in the form of C_4 hydrocarbons which apparently arise via the coupling of reactive intermediates. In contrast, no coupling products were observed when zinc served as the reducing agent. This shift in product distribution may reflect a difference in the mechanism of reduction. Sivavec (17) has hypothesized that C_4 products resulting from chlorinated ethylene reduction by iron arise from the coupling of intermediate radicals. To date, however, techniques designed to confirm the existence of free radicals have not been successfully applied to the study of reaction of organohalides with zero-valent metals in aqueous solution.

In order to explore the mechanism by which zero-valent metals reduce alkyl halides, the distribution of products arising from reduction of a series of stereochemical probe compounds (Figure 1) has been examined. These probe compounds include 2*R*-3*S*-2,3-dibromopentane (DBP) and its stereoisomeric enantiomer, 2*S*-3*R*-2,3-dibromopentane (the mixture of the two stereoisomers is hereafter referred to as *erythro*-DBP), as well as 2*R*-3*R*-2,3-dibromopentane and

1 its stereoisomeric enantiomer, 2*S*-3*S*-2,3-dibromopentane (hereafter referred to as *threo*-DBP).
2 The other stereochemical probe employed was 1*R*-2*R*-1,2-dibromo-1,2-diphenylethane [and its
3 enantiomeric isomer, abbreviated as (±)-SBr₂].

4 If these vicinal dihalides undergo reduction via an SET process, the first one-electron
5 reduction would yield a radical (Figure 1a), which is partially stabilized by delocalization of the
6 unpaired electron over the remaining bromine. This "bridged" bromine radical could experience
7 rotation around the C-C bond before being further reduced, resulting in a mixture of *E*- and *Z*-
8 olefins. The *E/Z* ratio of the products is a function of the rate at which the second electron is
9 transferred to the intermediate radical relative to the rate of C-C bond rotation, as well as the
10 distribution of different conformers within the population of radicals. Assuming that C-C bond
11 rotation rates are fast relative to the rate of transfer of the second electron, the *E*- olefin may only
12 be favored slightly over the *Z*- isomer (if the R groups are small enough such that adverse steric
13 interactions are minor), or the *E*- olefin may be formed exclusively (as in the case of bulky R
14 groups). The same ratio of *E*- to *Z*- olefins should however be attained, regardless of whether the
15 starting material was the *threo*- or the *erythro*- isomer (or the *meso*- or the (±)- pair).

16 In contrast to the SET mechanism, if vicinal dihalides were to undergo reduction via a
17 more-or-less concerted transfer of two electrons (Figure 1b), the reaction typically demonstrates
18 a strong preference for an *anti* stereochemistry, and is characterized by high stereospecificity
19 (18). *Threo*-DBP reacts to *Z*-2-pentene, and *erythro*-DBP to *E*-2-pentene. This "two electron"
20 reaction may be envisioned as a nucleophilic "X-philic" attack of the reductant on one of the
21 bromines, rather than on carbon as in a typical S_N2 reaction. Reductive elimination of vicinal
22 dihalides by the strong nucleophile iodide has commonly been attributed to just such a concerted
23 nucleophilic mechanism (18, 20, 21).

24 Numerous exceptions to an *anti* stereoselectivity have, however, been observed for (±)-
25 SBr₂. These exceptions have been most commonly attributed to a halonium ion mechanism (18),
26 as discussed subsequently.

27 The phrase "two-electron reduction" is somewhat misleading because electrons can only
28 be transferred one at a time (19). Products characteristic of a two-electron reduction may arise
29 either from an SET mechanism (either inner-sphere or outer-sphere) in which the transfer of the
30 second electron is much faster than C-C bond rotation, or from an inner-sphere attack of the

1 reductant on the dihalide.

2 Vicinal dibromides have been extensively used in the past to investigate a variety of
3 reduction reactions; Baciocchi (18) provides an excellent review. The mechanism through which
4 reductive β -elimination occurs is a function not only of the reductant, but also of the structure of
5 the dihalide probe, the solvent, and the temperature. Thus, although the reactions of zero-valent
6 metals with vicinal dihalides have in some cases already been investigated, these experiments
7 were generally conducted in organic solvents or at high temperatures (21, 22). The principal goal
8 of this research was to investigate reactions of a variety of zero-valent metals under
9 environmentally relevant conditions (*i.e.*, at room temperature, in water). A further goal was to
10 assess the overall feasibility of applying vicinal dihalide probes to the investigation of a broad
11 range of environmentally relevant reduction reactions. Reactions promoted by reductants other
12 than zero-valent metals were therefore also investigated, including a model one-electron
13 reductant [Cr(II) (aq)], and a model nucleophilic reductant (I⁻). Some researchers have suggested
14 that Fe(II) species adsorbed to oxides coating iron surfaces may represent important reductants in
15 the Fe(0) system (2, 10, 11, 17). Reductions promoted by Fe(II) species adsorbed to a Fe(III)
16 mineral surface (goethite) were thus also studied. Hydrolysis of the probe compounds, which
17 competes with reduction, was also examined.

18 **Experimental Methods**

19 **Reagents.** All chemicals were obtained from commercial sources and used as received, except as
20 noted. *Threo*- and *erythro*-DBPs and ($\pm$)-SBr₂ were synthesized from the *Z*- and *E*-2-penten-3-ols and
21 *Z*-stilbene, respectively, by stereospecifically brominating the olefins with pyridinium tribromide
22 (23). The ($\pm$)-SBr₂ product was purified by recrystallization in methanol, and was found by gas
23 chromatographic/mass spectrometric (GC/MS) analysis to contain no significant impurities. The
24 *threo*- and *erythro*-2,3-DBPs each contained less than 0.5% impurity of the undesired isomer.
25 The identities of the synthesis products were verified by MS and proton nuclear magnetic
26 resonance analysis (24).

27 **Preparation of metals.** Each metal was cleaned to remove surface oxides using a cleaning
28 solution (Table 1) (25) (see ref. 24 for details). In order to avoid reoxidation of the metal
29 surfaces, all cleaning procedures were conducted in an anaerobic glove box (90% N₂, 10% H₂
30 atmosphere).

Goethite. Goethite slurry (44.2 g goethite/L) was synthesized by Barbara Coughlin (26) and was provided by Alan T. Stone. The goethite had a specific surface area of 47.5 m²/g, and adsorption isotherms demonstrated that it is able to adsorb a maximum of 2.8 atoms of Fe(II) per nm² (26). Experiments were conducted with 1.4 mmol Fe(II) and 10 g of goethite slurry (0.442 g goethite). The Fe(II) was present at 5 times molar excess to the number of available sites. Some experiments were conducted at pH 7.5 using 5 mM tris(hydroxymethyl)aminomethane (Tris) buffer. Others were conducted at pH 10.5 using 5 mM 2-amino-2-methyl-1-propanol (AMP) buffer. At pH above 6, all of the surface sites on the goethite should be occupied by Fe(II) (26).

Cr(II) solutions. Cr(II) solutions were synthesized in an inert atmosphere by the method of Castro (27). Cr(II) reactions were carried out in 5 mM H₂SO₄ (pH 2.0-2.1) in a constant temperature water bath at 25.0 (± 0.1)°C. Initial Cr(II) concentrations were determined independently by reaction with Fe(III), with quantitation of the resulting Fe(II) by a bathophenanthroline disulfonic acid (BPDS) colorimetric assay (28).

Iodide. Reactions with iodide were conducted in 1 M KI, 0.1 M NaCl, 50 mM sodium tetraborate buffer (pH 9.3) in a constant temperature water bath at 25.0 (± 0.1)°C. This pH value was employed to provide consistency with other experiments involving strong nucleophiles (29).

Reactions of DBP isomers. Reaction flasks were prepared in a glove box to minimize contamination with oxygen. Reactions with metals were carried out in 1-L flasks. Reactions with goethite, Cr(II), iodide, and hydrolysis experiments were carried out in 125-mL flasks. Each flask was equipped with a stopcock adapter which was plugged with an NMR-type septum. The reaction solution (typically 0.1 M NaCl) was deoxygenated via sparging with purified argon. The reductant was weighed or pipetted into each flask, which was then filled completely with aqueous solution. For reactions with zero-valent metals, an aliquot of the solution was removed for pH measurement after equilibrating with the metal overnight. The flask was then filled completely with aqueous solution, leaving no headspace. Flasks were spiked with either *threo*- or *erythro*-DBP in methanol to achieve an initial dibromide concentration of about 0.2 mM and a methanol concentration of 0.025 M. Flasks were then placed on a roller table at 40 RPM for mixing at room temperature. Samples (1 mL) were taken without introducing headspace by periodically injecting an aliquot of deoxygenated solution through the septum, which forced the sample into a second sampling syringe. Aqueous samples (1 mL) were extracted into 1 mL

hexane and were analyzed on a Carlo-Erba Mega 2 GC equipped with a flame-ionization detector (FID). Hexane extracts were injected via an AS 800 autosampler by a direct cold on-column technique onto a capillary guard column connected to a 30 m, 0.32 mm ID, 5 μ m film thickness Rtx-1 capillary column (Restek). The same analytical column was used to conduct GC-MS confirmation of the identity of the reaction products.

Reactions of ($\pm$)-SBr₂. Experimental procedures were the same as those for the DBPs except that all reactions were conducted in 1-L bottles. Each bottle was spiked with a methanolic solution of ($\pm$)-SBr₂ to give an initial dibromide concentration of about 4 μ M (and a methanol concentration of 0.025 M). No attempt was made to keep these systems headspace free, since the parent compound and olefin products have relatively low Henry's law constants. Aqueous samples (10 mL) were taken from each bottle, with the volume being displaced by purified nitrogen or a nitrogen/hydrogen mixture instead of deoxygenated aqueous solution. The aqueous samples were extracted with 1 mL of hexane, and 1 μ L hexane samples were injected onto a 15 m, 0.25 mm ID, 0.25 μ m film thickness EC-5 capillary column (Alltech) with an FID for GC analysis. Selected samples were also analyzed by GC-MS using a Hewlett-Packard (HP) 5890 GC equipped with an HP 5970 mass selective detector.

Computational estimates of rotational energy barriers. The heights of the barriers to C-C bond rotation for the 2-bromopentyl, 3-bromopentyl, and bromostilbene radicals were estimated via computational chemistry techniques using *Spartan v. 5.0* (Wavefunction Inc., Irvine, CA) on a Silicon Graphics Indigo workstation. The dihedral angle centered on the radical carbon and the carbon containing the remaining bromine was rotated through 360° in 30 steps, with the geometry of the radical optimized at each step using the AM1 semi-empirical basis set. The energy of each rotational conformer was then calculated by density functional theory using the perturbative Becke-Perdew (pBP) method with the DN** basis set.

Results and Discussion

Rotational barriers. With any computational technique, it is essential that the output of the model be checked against experimentally measured values. For this purpose, the rotational barriers for a series of substituted ethanes were also calculated by the same method. The results were generally in reasonable agreement with experimental values (30), differing in the worst case by 4 kJ/mol.

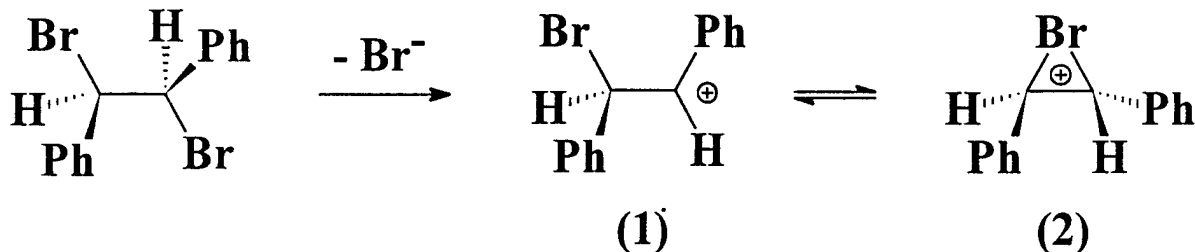
Barriers for rotation about the C-C bond in the intermediate bromopentyl and bromostilbene radicals were estimated to be 21.1 kJ/mol for the 2-bromopentyl radical, 18.1 kJ/mol for the 3-bromopentyl radical, and 27.1 kJ/mol for the bromostilbene radical. The estimated rotational energy barriers can be used to calculate rate constants for C-C bond rotation of about 10^9 s^{-1} for the bromopentyl radicals and 10^8 s^{-1} for the bromostilbene radical. These results are in good agreement with those of Lund *et al.* (31), who assumed a rotational barrier of 25 kJ/mol for the bromostilbene radical based on the measured value for butane. These researchers used this barrier height to estimate that an intermediate bromoalkyl rotational conformer would have a lifetime of at least 10^{-8} s before undergoing C-C bond rotation.

The computational calculations of the relative energies of rotamers can also be used to estimate their equilibrium distribution. The computational calculations suggest that the energy difference between the most stable *E*- and *Z*-like rotamers is about 8.3 kJ/mol for the dibromopentyl radicals, and about 31 kJ/mol for the bromostilbene radicals. Assuming an error of $\pm 8 \text{ kJ/mol}$, these computed relative energies suggest that *Z*-like rotamers represents 0.1-47% of the bromopentyl radicals and $< 0.001\%$ of the bromostilbene radicals at rotational equilibrium.

Hydrolysis of the probe compounds. All of the dibromide probe compounds hydrolyzed relatively rapidly at a rate essentially independent of pH between 7 and 9.3. Hydrolysis rate constants for the DBPs were 0.02 hr^{-1} (*erythro*) and 0.006 hr^{-1} (*threo*) at pH 7.5 (5 mM Tris buffer). The hydrolysis products were tentatively identified by GC-MS after extraction into hexane as 2-bromo-pentan-3-ol and 3-bromo-pentan-2-ol.

The hydrolysis rate constant for ($\pm$)-SBr₂ was 0.17 hr^{-1} at pH 8-9. The major hydrolysis product was the epoxide, *E*-stilbene oxide (95%). Traces of *Z*-stilbene oxide (less than 10% of the total epoxide yield; confirmed by GC/MS) were also formed, along with minor amounts of the reduction product *E*-stilbene. *Z*-stilbene was not detected as a hydrolysis product. Both the *E*- and *Z*-stilbene oxide were found to be stable in buffered aqueous solutions at pH 7.5, and no isomerization of *Z*-stilbene oxide to the *E*-isomer was observed.

The mixture of epoxide products obtained from ($\pm$)-SBr₂ and the rapid nature of the hydrolysis together point to an S_N1 mechanism (Scheme 1) involving the loss of a bromide ion to form a relatively stable benzylic cation with an open structure (1), which may be in equilibrium with a bridged halonium ion (2).



Scheme 1

Open cations (unlike halonium ions) are thought to be capable of extensive C-C bond rotation (18). In this scheme, they presumably persist for a sufficient length of time for rotation to come to an equilibrium in which the phenyl groups are likely to be located *trans* to one another for a large proportion of the molecules. Thus hydrolysis of ($\pm$)-SBr₂ results predominantly in *E*-stilbene oxide. This is an important observation because nucleophilic reduction of ($\pm$)-SBr₂ may also involve intermediate benzylic cations.

Reductive dehalogenation of the probe compounds. The stereospecificity of the reductive elimination reactions can be expressed as the percent *E*-olefin present in the total olefin yield. The results for the dehalogenation of *threo*-DBP and ($\pm$)-SBr₂ promoted by a variety of reductants are summarized in Figure 2. Some of the reactivity parameters are listed in Table 2.

Reductions promoted by Cr(II). Cr(II) was used as a model reducing agent because it has been demonstrated to act as a one-electron reductant of vicinal dibromides, at least in mixed dimethylsulfoxide/water solution (20-22, 32). For both the DBPs and ($\pm$)-SBr₂, the rate of reduction by Cr(II) was fast relative to hydrolysis, and disappearance exhibited pseudo-first order kinetics. The *E*- and *Z*-olefin products were stable under the reaction conditions.

($\pm$)-SBr₂ reacted with 0.06 mM Cr(II) to give *E*-stilbene as the sole observed product, consistent with the results of Mathai *et al.* (21). The second-order rate constant for this reaction was 3.7 M⁻¹s⁻¹. The high percentage of *E*-stilbene produced from ($\pm$)-SBr₂ results from the steric strain in the *Z*-configuration of the intermediate radical, which drives bond rotation (see Fig. 1). These radicals apparently persist long enough to approach rotational equilibrium, in which essentially 100% of the radicals are in the *E*-like configuration.

The second-order rate constants for reaction of Cr(II) with *threo*- and *erythro*-DBP were approximately 0.012 M⁻¹s⁻¹ and 0.018 M⁻¹s⁻¹, respectively. Reduction of 0.2 mM 2,3-DBPs by 10

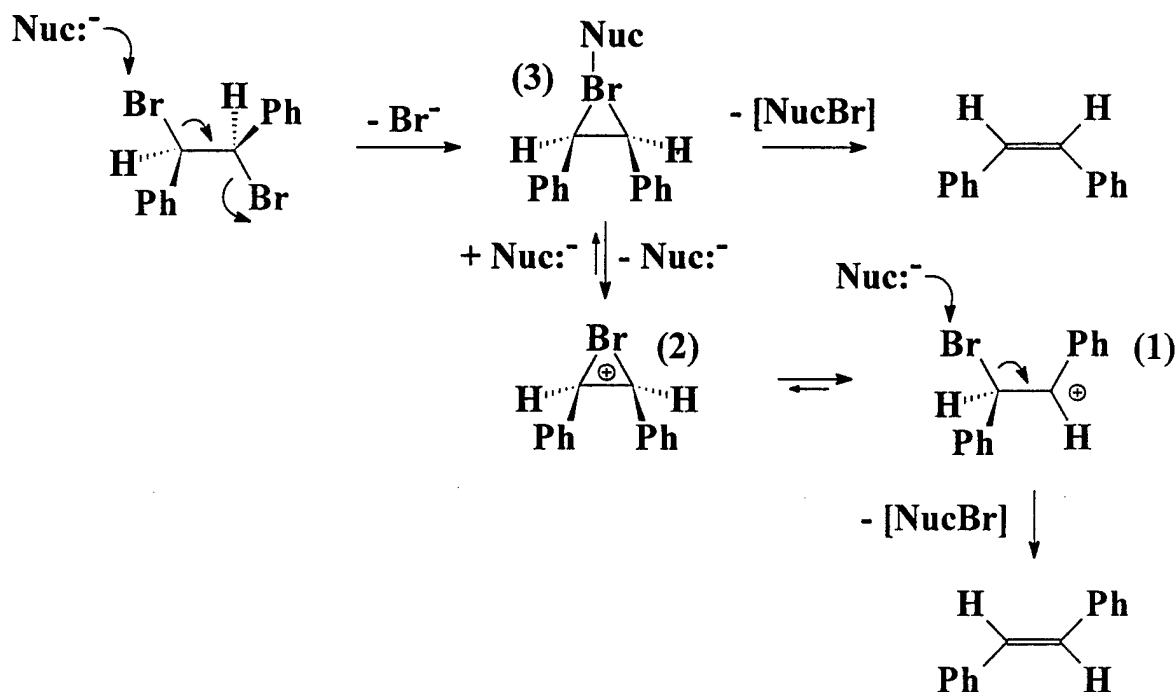
1 mM dissolved Cr(II) resulted in 68% *E*-2-pentene from the *threo* isomer and 73% from the
2 *erythro* isomer. These results are in good agreement with those of Kochi and Singleton (33) who
3 observed a similar ratio of *E*- and *Z*-olefins from the reduction of ($\pm$)-2,3-dibromobutane by 68
4 mM Cr(II) in (30/10) acetonitrile/water. The formation of both *Z*- and *E*-2-pentenenes during the
5 reduction of *threo*-DBP by Cr(II) indicates that the radical formed from the first one-electron
6 reduction of this probe can, at least under some circumstances, persist long enough to undergo
7 C-C bond rotation. Unlike ($\pm$)-SBr₂, aliphatic vicinal dibromides are reduced to a mixture of *E*-
8 and *Z*-olefin because the *E*-like and *Z*-like rotational conformers of the bromopentyl radicals are
9 closer in energy and therefore significant amounts of each exist at equilibrium.

10 **Reductions promoted by iodide.** The stereospecificity encountered in reduction of the dibromide
11 probe molecules by iodide was explored because prior work has shown that this species serves as
12 a nucleophilic (two-electron) "X-philic" reductant, at least in organic solvents (20-22, 32).

13 ($\pm$)-SBr₂ was reduced by iodide to form both *Z*- and *E*-stilbene with a second-order rate
14 constant of approximately $5.9 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$. Hydrolysis competed with reductive elimination.
15 Stilbenes comprised 55% of the total products, of which 70% was *E*-stilbene. Mass balances
16 were good (100-110%).

17 The observation of *E*-stilbene from the iodide-promoted reduction of ($\pm$)-SBr₂ might
18 initially appear at odds with a nucleophilic mechanism. As depicted in Figure 1b, a concerted
19 "X-philic" mechanism should yield only *Z*-stilbene, while [by analogy with the results obtained
20 for Cr(II)] a one-electron pathway would be expected yield only the *E* isomer. Understanding the
21 mechanism of hydrolysis for ($\pm$)-SBr₂ helps to reconcile this apparent discrepancy, as described
22 below.

23 Elimination of the two halogens need not be concerted for the reaction to represent a two-
24 electron process. Baciocchi (18) notes that nucleophilic dehalogenation of ($\pm$)-SBr₂ in organic
25 solvents may occur via a halonium ion mechanism (Scheme 2).



Scheme 2

Note that the bromonium ion (2) and the open carbocation (1) are identical to intermediates postulated during the hydrolysis of (±)-SBr₂ (Scheme 1). The existence of the open carbocation (1), which is in equilibrium with the bromonium ion (2) was inferred from the mixture of *E*- and *Z*-epoxides produced during hydrolysis. It is equally likely to coexist with a bromonium ion generated during iodide-promoted reduction. Rotation about the C-C bond of such an open carbocation is hypothesized to occur freely (18). A halonium ion mechanism involving an open carbocation may therefore account for the formation of large amounts of *E*-stilbene during the reduction of (±)-SBr₂ by nucleophilic reductants such as iodide in aqueous systems. A problematic *syn*-elimination pathway (34, 35) thus need not be invoked to account for the observed product distribution. A halonium ion mechanism may also account for the apparent increase in hydrolysis products that we have observed with increasing concentrations of dissolved nucleophiles (29).

Other researchers have found (smaller proportions of) *E*-stilbene resulting from reduction of (±)-SBr₂ by iodide in organic solvents, with *E*-stilbene (as a percent of total stilbene) ranging from 4% to 35% (21). Although the relatively small *E*-stilbene yields observed by other researchers may seem at odds with the larger proportions of *E*-stilbene produced in the aqueous systems employed in this work, close scrutiny of the published data reveals that the % *E*-stilbene

increases as the solvent becomes more polar. This most likely reflects increasing stabilization of charged intermediates in more polar solvents, favoring the halonium ion mechanism.

In contrast to the results obtained with ($\pm$)-SBr₂, *threo*-DBP was reduced by iodide to form exclusively *Z*-2-pentene (with a second-order rate constant k_1 of approximately $6 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$), and *erythro*-DBP was reduced by iodide to form exclusively *E*-2-pentene (with $k_1 \sim 1 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$). Mass balances were essentially complete (100%). This result is in agreement with previous studies which demonstrated that *aliphatic* bromides react with iodide primarily via concerted nucleophilic reductive elimination pathways (Figure 1b), rather than via a halonium ion mechanism (Scheme 2) (18). For example, reduction of ($\pm$)-2,3-dibromobutane by iodide yields 95-100% *Z*-2-butene in 90/10 methanol/water (59°C) (32). The greater tendency to react via a concerted nucleophilic mechanism probably reflects lesser stabilization of a charged intermediate by the alkyl substituents of the DBPs vs. the phenyl substituents of ($\pm$)-SBr₂.

Reduction by zero-valent metals. Reduction of the DBPs followed good pseudo-first order kinetics with Fe, Zn, Cu, and Al. Reaction rate constants normalized to metal surface area (k_{SA}) generally followed the order Zn>Fe>>Cu (Table 2), although absolute values of k_{SA} varied somewhat with metal loading and with mixing speed. The pseudo-first order rate constant for reaction of *threo*-DBP with 5.0 g of Al was 0.05 hr^{-1} (after accounting for hydrolysis). Mass balances were close to 100% for all metals except aluminum. The *Z*- and *E*-pentene products were stable under the reaction conditions with all metals. No hydrogenolysis products (2- or 3-bromopentanes) were detected.

Each of the zero-valent metals reduced both *threo*- and *erythro*-2,3-DBP in a highly stereospecific manner, resulting in >95% of the *anti* elimination product (Figure 3), similar to the results obtained for reaction with iodide. Earlier studies conducted in various organic solvents also demonstrate that aliphatic vicinal dibromides are reduced to characteristic *anti* elimination products by zero-valent metals (22). This has been interpreted to reflect a nucleophilic attack on the halogen by the metal (18).

The pH dependence of the stereospecificity of reaction with iron was investigated by adjusting the initial pH of the reaction solution with either NaOH or HCl. Although the initial pH was not maintained, the rate of reaction was affected. The reaction was roughly 2 times faster at either high or low pH than at neutral pH. The stereoselectivity changed at best only slightly with

1 pH (Figure 2a).

2 The disappearance of ($\pm$)-SBr₂ in the presence of iron and zinc displayed good pseudo-
3 first order behavior. Hydrolysis did not contribute significantly to the loss of ($\pm$)-SBr₂. Mass
4 balances were essentially 100%. ($\pm$)-SBr₂ was reduced to a mixture of *Z*- and *E*-stilbenes (Figure
5 4). The percentage of *E*-stilbene in the olefin mixture was 71% for iron and 70% for zinc. The
6 similarity in the product distribution resulting from reduction of ($\pm$)-SBr₂ by metals and by iodide
7 is striking: the percent of the *E*-isomer in the total stilbene yield is the same (within experimental
8 error) for reductions promoted by iodide, Fe(0), and Zn(0), as demonstrated by the error bars in
9 Figure 2. Furthermore, reduction of ($\pm$)-SBr₂ in water by a variety of strong nucleophiles
10 (including bisulfide and polysulfides) at varying concentrations has been observed to result in a
11 similar percentage of *Z*-stilbene (29). It is possible that the mechanism of the reaction is different
12 for these various reductants but that exactly the same product distribution nevertheless results. It
13 may be more plausible, however, to assume that these reactions all involve a common (or at least
14 a similar) intermediate.

15 ***Reduction by surface-associated Fe(II).*** Several researchers have suggested that Fe(II) species
16 adsorbed to oxides coating iron surfaces may represent important reductants in the Fe(0) system
17 (2, 10, 11, 17). For this reason, the stereochemistry of reduction of probe compounds promoted
18 by Fe(II) species adsorbed to goethite was investigated.

19 Because reduction of DBPs in the presence of goethite plus Fe(II) was slow, hydrolysis of
20 the probe compounds consumed most of the spiked mass. At pH 7.5, the yield of pentenes was
21 less than 10%, but only the stereospecific isomer (*Z*-2-pentene from *threo*-DBP and *E*-2-pentene
22 from *erythro*-DBP) was detected.

23 In order to speed up the reaction between the Fe(II)/goethite and the DBPs, some
24 experiments were conducted at pH 10.5 using 5 mM AMP buffer. Modest (17%) conversion of
25 *threo*-DBP to 2-pentenenes was achieved in 8 hours. *E*-2-pentene represented 3% of the 2-pentene
26 products. The mass balance was 95% (consisting mostly of unreacted *threo*-DBP). At this high
27 pH, however, Fe(II) is expected to precipitate as Fe(OH)₂ (s). Control experiments in which a
28 solution of Fe(II) at pH 10.5 was spiked with *threo*-DBP showed no production of pentenes
29 despite the formation of a cloudy gray-green precipitate [presumably Fe(OH)₂ (s)].

(±)-SBr₂ was not dehalogenated in goethite/Fe(II) systems. The DBPs and (±)-SBr₂ were not dehalogenated in goethite suspensions which did not contain Fe(II), or in Fe(II) solutions which did not contain goethite (*i.e.*, olefins and bromoalkanes were not detected as products in these systems).

The reduction of the DBPs via stereospecific *anti* elimination by Fe(II) adsorbed to goethite might initially seem somewhat surprising, since Fe(II) would presumably serve as a one-electron reductant. Reduction of the vicinal dibromides by Fe(II) adsorbed to goethite may be comparable to reduction of these compounds by Li(0), for which elimination is highly stereospecific (in tetrahydrofuran) despite the fact that Li(0) is presumably oxidized by a single electron to Li⁺ (22). A comparable situation may occur in the photoreductive degradation of CCl₄ on TiO₂ investigated by Choi and Hoffmann (36). Detailed study of the kinetics of these reactions suggested that CCl₄ reduction to dichlorocarbene occurred via a sequence of two single-electron transfers rather than via a concerted two-electron transfer step. In all of these cases, reduction occurs at a surface containing an excess of available reductant. Given the Fe(II) binding site density on goethite (2.8 sites/nm² from ref. 26), a simple calculation shows that the sorbed Fe(II) atoms are only about 0.44 nm apart on average. For a bromopentyl radical, the characteristic diffusion time t_D (computed as $L^2/2D$, where D is the aqueous diffusion coefficient, estimated according to refs. 37 and 38) over such a distance is 10⁻¹⁰ s. This is less than the characteristic time for C-C bond rotation in a bromopentyl radical of 10⁻⁹ s. The rate of C-C bond rotation may therefore be sufficiently slow relative to the transfer of the second electron at an oxide surface that the intermediate bromopentyl radicals are reduced to alkenes before undergoing significant C-C bond rotation.

Mechanistic Interpretation. For both the DBPs and (±)-SBr₂, the products observed from reduction by iron and zinc have essentially the same *E/Z* ratio as those encountered with the classic nucleophilic reductant, iodide. It cannot be definitively concluded, however, that these probe compounds are reduced by zero-valent metals via a nucleophilic two-electron mechanism, because the reactions are heterogeneous in nature and occur at a surface which possesses a high density of reducing equivalents. For the DBPs, similar products were obtained when Fe(II)/goethite served as the reductant, suggesting that the reactions with zero-valent metals could equally well occur via a mechanism in which initial SET yields a radical which is rapidly

1 reduced by a second electron to the alkene at a rate that is rapid relative to C-C bond rotation.

2 The computational estimates of the energy barriers for C-C bond rotation in the
3 intermediate radicals allow approximate limits to be placed on the pseudo-first order rate
4 constants corresponding to transfer of a second electron to the radical (k_2). If C-C bond rotation
5 occurs with an estimated rate constant of 10^9 s^{-1} for the bromopentyl radicals, then k_2 would have
6 to be on the order of 10^{10} s^{-1} in order to produce 95% *Z*-2-pentene from *threo*-DBP. Similarly, if
7 C-C bond rotation occurs with an estimated rate constant of 10^8 s^{-1} for the bromostilbene radical,
8 k_2 would have to be on the order of 10^8 s^{-1} in order to produce 70% *E*-stilbene via an SET
9 pathway.

10 In order for other bimolecular reactions to compete with transfer of the second electron,
11 they would have to be extremely fast. Even a diffusion-limited reaction, such as self-coupling of
12 free radicals (which occurs with a bimolecular rate constant on the order of $10^{10} \text{ M}^{-1}\text{s}^{-1}$) could
13 only begin to compete with the second one-electron transfer if the local concentration of the
14 radical species was greater than 10^{-2} to 10^{-3} M . Such a high concentration of reactive transients is
15 extremely unlikely in the presence of powerful reductants such as zero-valent metals.

16 These stereochemical studies therefore suggest that if radical intermediates are in fact
17 generated during reduction of vicinal dibromides by zero-valent metals, they do not escape the
18 surface before undergoing rapid further reduction.

19 **Implications for Zero-Valent Metal Based Remediation Technology.** Because zero-valent
20 metals (as well as Fe(II) adsorbed to iron (hydr)oxide surfaces) reduce vicinal dibromides via a
21 very rapid transfer of two electrons, any intermediate radical that is formed is short-lived and is
22 not likely to escape from the metal [or (hydr)oxide] surface before being reduced to a relatively
23 stable closed-shell species. In general, then, characteristic free-radical reactions such as hydrogen
24 atom abstraction from dissolved constituents and intermolecular dimerization of free radicals
25 should be rare events in zero-valent metal based remediation schemes. Radical coupling
26 (including the coupling of organic radicals with hydrogen atoms at the metal surface) is likely to
27 occur only if radicals are generated very close to one other at the metal-water interface. In order
28 for the coupling products observed, for example, during the reduction of 1,1,1-TCA by iron (16)
29 to originate from the coupling of free radicals, a large number of radicals would have to be
30 produced at specific highly reactive areas on the iron surface. Alternatively, coupling may take

1 place via a process other than the collision of two free radicals, perhaps by an intramolecular
2 mechanism involving rearrangement of a dialkyl organometallic intermediate.

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References

- (1) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958-967.
- (2) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045-2053.
- (3) Lipczynska-Kochany, E.; Harms, S.; Milburn, R.; Sprah, G.; Nadarajah, N. *Chemosphere* **1994**, *29*, 1477-1489.
- (4) Boronina, T.; Klabunde, K. J. *Environ. Sci. Technol.* **1995**, *29*, 1511-1517.
- (5) Helland, B. R.; Alvarez, P. J. J.; Schnoor, J. L. *J. Haz. Mater.* **1995**, *41*, 205-216.
- (6) Warren, K. D.; Arnold, R. G.; Bishop, T. L.; Lindholm, L. C.; Betterton, E. A. *J. Haz. Mater.* **1995**, *41*, 217-227.
- (7) Burris, D. R.; Campbell, T. J.; Manoranjan, V. S. *Environ. Sci. Technol.* **1995**, *29*, 2850-2855.
- (8) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654-2659.
- (9) Scherer, M. M.; Westall, J. C.; Ziomekmoroz, M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, *31*, 2385-2391.
- (10) Johnson, T. L.; Fish, W.; Gorby, Y. A.; Tratnyek, P. G. *J. Contam. Hydrol.* **1998**, *29*, 379-398.
- (11) Balko, B. A.; Tratnyek, P. G. *J. Phys. Chem. B* **1998**, *102*, 1459-1465.
- (12) Arnold, W. A.; Ball, W. P.; Roberts, A. L. *J. Contam. Hydrol.* **1998**, in press.
- (13) Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987.
- (14) Criddle, C. S.; McCarty, P. L. *Environ. Sci. Technol.* **1991**, *25*, 973-978.
- (15) Buschmann, J.; Angst, W.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1999**, *33*, 1015-1020.
- (16) Fennelly, J. P.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*, 1980-1988.
- (17) Sivavec, T. M. In *IBC International Symposium on Biological Dehalogenation*, Annapolis, MD; 1995.
- (18) Baciocchi, E. In *The Chemistry of Halides, Pseudo-halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley and Sons: New York, 1983; Vol. 1, 161-201.
- (19) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212-219.
- (20) Winstein, S.; Pressman, D.; Young, W. G. *J. Am. Chem. Soc.* **1939**, *61*, 1645-1647.
- (21) Mathai, I. M.; Schug, K.; Miller, S. I. *J. Org. Chem.* **1970**, *35*, 1733-1736.
- (22) Sicher, J.; Havel, M.; Svoboda, M. *Tetrahedron Letters* **1968**, *40*, 4269-4272.
- (23) Fieser, L. F.; Williamson, K. L. *Organic Experiments*; 4th ed.; DC Heath and Co.: Lexington, MA, 1979.
- (24) Totten, L. A. PhD Thesis, The Johns Hopkins University, 1999.
- (25) In *Metals Handbook*; Wood, W. G., Ed.; American Society for Metals: Metals Park, OH, 1982; Vol. 5.
- (26) Coughlin, B. R.; Stone, A. T. *Environ. Sci. Technol.* **1995**, *29*, 2445-2455.
- (27) Castro, C. E. *J. Am. Chem. Soc.* **1961**, *83*, 3262-3264.
- (28) Diehl, H. *The Iron Reagents*; 3rd ed.; G. Frederick Smith Chemical Company: Columbus, Ohio, 1980.
- (29) Jans, U.; Roberts, A. L. In *216th ACS National Meeting*, Vol. 38, Boston; Division of Environmental Chemistry, 1998; pp 123-124.

- (30) Lowe, J. P. *Prog. Phys. Org. Chem.* **1968**, *6*, 1-80.
- (31) Lund, T.; Bjorn, C.; Hansen, H. S.; Jensen, A. K.; Thorsen, T. K. *Acta Chem. Scand.* **1993**, *47*, 877-884.
- (32) Schubert, W. M.; Steadly, H.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1955**, *77*, 5755.
- (33) Kochi, J. K.; Singleton, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1582-1589.
- (34) Fawell, P.; Avraamides, J.; Hefter, G. *Aust. J. Chem.* **1990**, *43*, 1421-1430.
- (35) Inesi, A.; Rampasso, L. *J. Electroanal. Chem.* **1974**, *54*, 289.
- (36) Choi, W.; Hoffmann, M. R. *J. Phys. Chem.* **1996**, *100*, 2161-2169.
- (37) Hayduk, W.; Laudie, H. *AIChE J.* **1974**, *20*, 611-615.
- (38) Reid, R. C.; Prausnitz, J. M.; Polling, B. E. *The Properties of Gases and Liquids*; 4th ed.; McGraw-Hill: New York, 1987.

Table 1: Properties of metals used in these experiments.

Metal	Mesh		Source	Surface	
	Size	Purity		Area (m ² /g)	Cleaning Solution
Al	40	>99%	Baker	ND ^a	chromic ^b
Cu	40	99.5%	Aldrich	0.13 ^c	0.4% sulfuric
Fe	100	95.3%	Fisher	0.76 ^c	1N HCl
Zn	30	100.5%	Baker	0.035 ^d	0.4% sulfuric

^a not determined. ^b 2 g chromic acid + 4 mL concentrated sulfuric acid in 100 mL distilled water. ^c by nitrogen BET. ^d by krypton BET.

Table 2: Reactivity of *threo*-DBP and (±)-SBr₂ with zero-valent metals.

Metal	<i>threo</i> -DBP			(±)-SBr ₂		
	metal (g/1.2 L)	pH trend ^a	k_{SA} (L·s ⁻¹ ·m ⁻²) ^b	metal (g/1.2 L)	pH trend ^a	k_{SA} (L·s ⁻¹ ·m ⁻²) ^b
Al	5.0	8.5, 8.5				
Cu	50	6.5, 6	3 × 10 ⁻⁶			
Fe	1.0	6.5, 8.5	1 × 10 ⁻⁴	0.5	7.8, 8.6	1 × 10 ⁻³
	2.4	6.5, 8.5	1 × 10 ⁻⁴			
	5.0	6.5, 8.5	7 × 10 ⁻⁵			
Zn	1.0	6, 7.5	6 × 10 ⁻³	1	7.7, 7.9	7 × 10 ⁻³
	2.5	6, 7.5	3 × 10 ⁻³			
	5.0	6, 7.5	3 × 10 ⁻³			

^a Initial, final. Values are approximate.

^b Reactivity is normalized to metal surface area and expressed as k_{SA} , calculated by dividing the observed pseudo-first order rate constant for reduction of the dibromide (in s⁻¹) by the metal loading (in m² per L of solution). k_{SA} could not be calculated for Al because its surface area was not determined.

Figure captions:

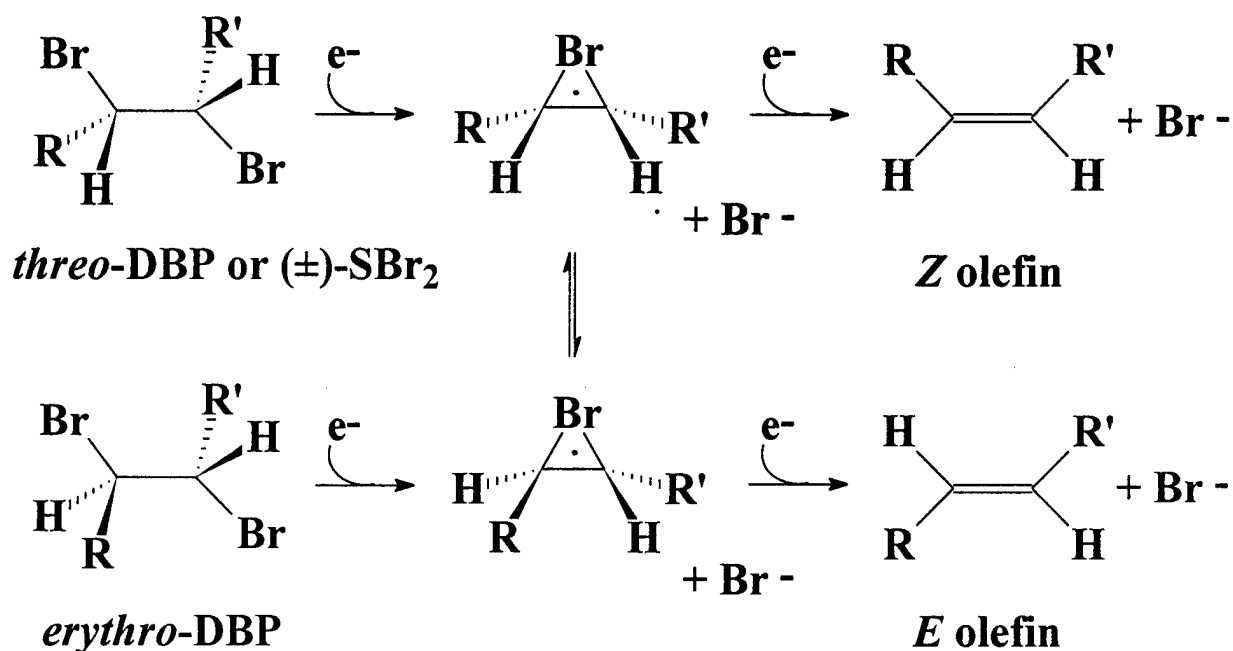
Figure 1: Idealized reaction schemes for the model compounds used in this study: a) single electron reduction pathway, and b) concerted nucleophilic pathway (Nuc^- = nucleophile). For DBPs, R = methyl, R' = ethyl (or vice versa). For ($\pm$)-SBr₂, R = R' = phenyl.

Figure 2: *E*- and *Z*-olefins (as a percent of total olefin) formed from the reaction of: (a) *threo*-DBP and (b) ($\pm$)-SBr₂ with various reductants. Fe (neutral) refers to the reduction carried out in 0.1 M NaCl without pH adjustment (see Table 2 for pH data). Fe (acidic) refers to the reduction carried out in 0.1 M NaCl solution initially adjusted to pH 4 with HCl. Fe (basic) refers to the reduction carried out in 0.1 M NaCl solution initially adjusted to pH 10 with NaOH. Fe(II)/goethite experiments were conducted at pH 10.5. See text for other reaction conditions. Error bars represent 95% confidence limits.

Figure 3: Reaction of *threo*-DBP (●) with (a) 5.0 g iron (3.26 m²/L) and (b) 1.0 g zinc (0.029 m²/L) in 0.1 M NaCl (pH 6.5-8.5). Products are *Z*-2-pentene (■) and *E*-2-pentene (□). Solid lines represent fits to data assuming pseudo-first order decay to observed products. Dashed lines represent mass balances measured at each timepoint.

Figure 4: Reaction of ($\pm$)-SBr₂ (○) with (a) 0.5 g iron (0.32 m²/L) and (b) 1 g zinc (0.028 m²/L) in 0.1 M NaCl (pH 7.8-8.6). Products are *E*-stilbene (▼) and *Z*-stilbene (◆). Solid lines represent fits to data assuming pseudo-first order decay to observed products. Dashed lines represent mass balances measured at each timepoint.

a) single electron reduction pathway



b) reduction via concerted nucleophilic pathway

