DECHLORINATION OF SUBSTITUTED TRICHLOROMETHANES BY AN IRON(II) PORPHYRIN

RICHARD A. LARSON* and JAVIERA CERVINI-SILVA
Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, 1101 West Peabody Drive, Urbana, Illinois 61801, USA

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Abstract—Iron(II) porphyrins complex with many organochlorine compounds and oxidize by dechlorinating them. For a series of trichloromethyl derivatives, CCl₃R (R = NO₂, CHCl₂, CN, Cl, COO⁻, CH₃, H, C(O)NH₂, and CH₂OH), heme oxidation occurred in two consecutive steps: heme-CCl₃R complexation, and (usually slower) inner-sphere electron transfer. Stability of the intermediate CCl₃R radical, which is strongly correlated with the ability of the R group to delocalize electron density, governed the overall electron transfer rate.

Keywords—Trichloromethanes  Inner-sphere electron transfer  Group electronegativity

INTRODUCTION

Chlorinated organic compounds have very different susceptibilities toward reduction [1–3]. Iron(II) acts as an electron-transfer mediator either at mineral surfaces or in solution. Metallic iron surfaces contain regions including iron(II) and iron(III) minerals as well as iron(0), but the chemical importance of the various species is not fully understood [4,5].

Previous studies have examined reactions of the biologically and environmentally important iron(II) porphyrins with several classes of chlorinated compounds, including CCl₃ R with R = Cl, CHCl₂, CCl₃, and CH₃) in the presence of an iron(II) porphyrin. Castro et al. [6,7] proposed that dechlorination of alkyl halides occurs in two consecutive steps: heme-CCl₃R complexation, and (usually slower) inner-sphere electron transfer. Stability of the intermediate CCl₃R radical, which is strongly correlated with the ability of the R group to delocalize electron density, governed the overall electron transfer rate.

In contrast, Perlinger et al. [10] studied dehalogenation of polyhalomethanes and ethanes (including CCl₃ R with R = H, CH₃, CH₂Cl, CCl₃, and CH₄) in the presence of an iron(II) porphyrin (meso-tetrakis[N-methylpyridyl] iron porphyrin) and cysteine, and they suggested an outer-sphere electron transfer, in which the first step was an electron transfer to the halogenated alkanes (R – X) followed by either formation of a carbaniion [R – X]⁻ (Eqn. 3), dissociation of the weakest carbon-halogen bond (Eqn. 4), or both:

\[
\text{Fe}^{II} + RX \leftrightarrow \text{Fe}^{II}(RX) \rightarrow [\text{Fe} \cdots X \cdots R]^- \rightarrow \text{Fe}^{III}X + R^- \quad \text{(slow) (1)}
\]

\[
\text{Fe}^{II} + R^- \rightarrow \text{Fe}^{III}(R^-) + H^+ \rightarrow \text{Fe}^{III} + RH \quad \text{(fast) (2)}
\]

To our knowledge, however, little attention has been paid to how the electronic properties of substituents in chlorinated compounds affect the mechanisms of their reaction toward iron(II) in solution. Molecular structure may be important for predicting their rates of reduction by zero-valent iron [1,2], iron(II)-containing clays [3] and minerals [4], and iron(II) in solution [5–7]. In this study, we examine the reactivity of an iron(II) complex, heme, toward a series of chlorinated compounds, CCl₃ R, possessing different R electronic properties. We use linear free-energy relationships to help explain our observations.

MATERIALS AND METHODS

Pentachloroethane (98%), carbon tetrachloride (99%), chloroform (99%), trichloroacetonitrile (99%), 1,1,1-trichloroethane (99%), 2,2,2-trichloroacetamide (99%), 2,2,2-trichloroethanol (99%), hematin (+99%; Fig. 1), and sodium dithionite (98%) were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Trichloroacetic acid (99%), sodium bicarbonate, and sodium carbonate were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Trichloronitromethane (98%) was purchased from Mallinckrodt (Paris, KY, USA), industrial ethanol (USP) from McCormick Distilling Company (Weston, MO, USA), and pentane for THM analysis HP; from Burdick and Jackson (Muskegon, MI, USA).

Hematin stock solution

A procedure modified from that reported elsewhere [1] was used to prepare the stock solution of hematin, an iron(III) porphyrin. Hematin (10 mg, 1.6 × 10⁻¹⁹ mol) was added to 100 ml of 1:1 v/v aqueous NaHCO₃ (5.2 × 10⁻³ M; pH, 8): ethanol and stirred for 4 h. The green solution was then decanted from the insoluble residue; its concentration was 1 × 10⁻¹⁰ M. Later, it was purged with argon (99.9%) for 15 min and used to prepare a solution of heme (Fig. 1).

Heme preparation

From the stock solution, a 5-ml aliquot of hematin was added to 0.02 g (1.15 × 10⁻¹⁴ mol) of solid sodium dithionite (Na₂S₂O₄) in a 6-ml, oxygen-free vessel and shaken manually. Dithionite serves as a source of reducing sulfoxyl radical anions, SO₂⁻, which forms when the salt is dissolved in water at alkaline pHs [13]. A rapid change of color from dark green (hematin) to bright red (heme, the iron[II] form) indicated the

* To whom correspondence may be addressed (ralarson@uiuc.edu).
change in oxidation state (solution A). Concentrations of hematin (λ = 575 nm, ε = 34.4 L/mol cm [6,7,14]) and heme (λ = 566 nm, ε = 29.1 L/mol cm) were determined spectroscopically.

**Reaction of trichloromethanes and heme**

Solutions of CCl₃R (solution B) were prepared in 1:1 v/v water:ethanol. The vessels were shaken manually until no emulsion was visibly detected (final concentration, 0.01 M).

Solution A (1.5 ml), solution B (0.5 ml), and 1:1 v/v bicarbonate-ethanol (1.0 ml) were added to a screw-capped cuvette to adjust the concentration of sodium bicarbonate to 4.5 × 10⁻³ M, CCl₃R to 1.7 × 10⁻³ M, and heme to approximately 5 × 10⁻⁵ M, respectively. The rate of heme loss was determined using a Beckman 7400 DU diode-array spectrometer (Beckman, Fullerton, CA, USA).

**Chlorohemin identification**

Hematin (λ = 575 nm) and chlorohemin (λ = 490 and 615 nm, ε = 34 L/mol cm [15]) were differentiated by ultraviolet spectroscopy and thin-layer chromatography. The elution solvent consisted of the mixture of two solutions prepared separately. Solution 1 was prepared by adding cetyltrimethylammonium bromide (3%) in water, acetonitrile, and methanol in a ratio of 55:3:42 v/v/v; solution 2 was 0.02 M aqueous HCl prepared just before use with reverse osmosis-distilled water. Five milliliters of solution 1 and 2 ml of solution 2 were mixed, placed in a 150-ml closed beaker, and equilibrated for 30 min before introduction of the plate. Samples of hematin stock solution and the reaction mixture were spotted on a 8- × 4-cm sheet of Whatman flexible plates for thin-layer chromatography (layer, 250 μm) coated with silica gel 1.2 cm above the lower edge. The spots were dried with argon before elution of the plates. The elution time was 20 min, and the plates were revealed in a 150-ml covered beaker containing 30% NH₃. Samples of hematin and chlorohemin in a mixture of acetonitrile, methanol, and distilled water (50:25:25) were used as reference to estimate Rₚ values, which corresponded to 0.30 and 0.38, respectively. Two major spots (Rₚ = 0.31 and 0.37, respectively) were observed after the elution of the reaction mixture (discussed previously) and suggested the formation of both chlorohemin and hematin.

**RESULTS AND DISCUSSION**

The oxidation of heme in the presence of CCl₃R (R = NO₂, CHCl₃, CN, Cl, COO⁻, CH₄, H, C[O]NH₂, and CH₂OH) was correlated with the decrease in absorbance of the signal corresponding to the iron(II) form (λ = 566 nm) coupled with buildup of the iron(III) form. We confirmed the formation of chlorohemin, an iron(III) porphyrin bearing a chlorine atom as a ligand, by its absorption at a λ of 490 and 615 nm. During the reaction, a smooth change occurred isosbestically, from the heme to the chlorohemin spectrum (Fig. 2), which was consistent with the formation of chlorohemin (λ = 490 and 605 nm [6,7]) and not with the formation of a stable heme-CCl₃R complex (λ = 470 nm [9]) reported elsewhere. The formation of chlorohemin from heme was crosschecked using thin-layer chromatography; in these experimental conditions, Rₚ values were comparable in magnitude that those reported elsewhere [16].

The shift of absorbance from 566 to 600 nm in the presence of chloropicrin (CCl₃NO₂) and trichloroacetonitrile (CCl₃CN) was found to be extremely fast, and in these cases, the rates of heme loss were extrapolated from an additional study of the loss rate as a function of [RCCl₃]₀. Products of CCl₃NO₂ loss were not determined (either one or two chlorine atoms could have been displaced). Data for CCl₄, however, suggested that one chlorine at a time was removed. The rate of dechlorination of CHCl₃ was much slower than that of CCl₄.

In most experiments where chlorohemin was formed, stoichiometric heme loss was faster than chlorohemin formation, suggesting that CCl₃R-heme complexation occurs at a comparable rate to that of electron transfer (Fig. 2) and that the heme-mass balance may be described as...
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Fig. 3. Profiles of heme loss in the presence of trichloromethanes. Circles refer to the trend observed when \( R = \text{NO}_2, \text{CHCl}_3, \text{Cl}, \text{COO}^-, \text{CH}_3, \text{H} \) (profile I). Squares refer to the trend when \( R = \text{CN} \) (profile II). Triangles refer to the trend when \( R = \text{CONH}_2 \) or \( \text{CH}_2\text{OH} \) (profile III).

\[
[heme]_T = [heme]_{\text{free}} + [heme]_{\text{complexed}} \quad \text{and} \quad (5)
\]

\[
[heme]_T - [heme]_{\text{free}} = [heme]_{\text{complexed}} \quad \text{where} \ [heme]_{\text{free}} \text{refers to the total heme present in solution formed during hematin reduction,} [heme]_{\text{complexed}} \text{to complexed heme, and} [heme]_{\text{free}}(??) \text{to uncomplexed heme. If} [heme]_{\text{free}} \ll [heme]_{\text{complexed},} \text{then the heme rate law expression may be approximated as}
\]

\[
\frac{d[heme]_T}{dt} \approx \frac{d[heme]_{\text{complexed}}}{dt} \quad \text{(7)}
\]

We identified three apparently different courses of reaction between \( \text{CCl}_3\text{R} \) and heme (Fig. 3). For most of the compounds (\( R = \text{NO}_2, \text{CHCl}_3, \text{Cl}, \text{COO}^-, \text{CH}_3, \text{H} \); profile I), heme concentration decreased rapidly and then remained constant over time. In the presence of trichloroacetoniitrile (\( R = \text{CN} \)), however, heme concentration showed no change for a period of time but then a sharp decrease (profile II), whereas in the presence of 2,2,2-trichloroacetamide (\( R = \text{CONH}_2 \)) and 2,2,2-trichloroethanol (\( R = \text{CH}_2\text{OH} \)), heme concentration showed little or no variation (profile III). In these three cases, heme loss was attributed to the complexation and later oxidation (except in profile III) of the iron(II) center to form chlorohem in. In all the experiments, trihalomethane was present in molar excess regarding heme, or \( [\text{CCl}_3\text{R}]_0 \gg [\text{heme}]_0 \) and heme oxidation for profiles I and II was approximated as a pseudo–first order reaction regarding heme.

A kinetic mechanism consistent with the results depicted in Figure 3 would involve two consecutive steps: fast complexation of \( \text{CCl}_3\text{R} \) with heme, followed by heme oxidation via inner-sphere electron transfer (Eqn. 8). Applying the steady-state principle to formation of the precursor complex [17], the heme rate law expression can be rewritten as Equation 9:

\[
\text{heme} + \text{CCl}_3\text{R} \xrightarrow{k_{i}} \text{heme} - \text{CCl}_3\text{R} \xrightarrow{k_{ii}} \text{P} \quad \text{(8)}
\]

\[
\frac{-d[heme]}{dt} = \frac{d[heme \cdot \cdot \cdot \text{CCl}_3\text{R}]}{dt} = k_i [\text{heme}][\text{CCl}_3\text{R}]
\]

\[
-(k_{i} + k_{ii})[\text{heme} \cdot \cdot \cdot \text{CCl}_3\text{R}] \quad \text{(9)}
\]

where heme \( \cdot \cdot \cdot \text{CCl}_3\text{R} \) refers to the precursor complex that results from the binding of \( \text{CCl}_3\text{R} \) to heme, \( k_i \) to the adsorption rate constant of \( \text{CCl}_3\text{R} \), \( k_{ii} \) to the precursor complex dissociation rate, and \( k_{i} \) to the loss of the precursor complex and heme oxidation.

If the concentration of the precursor complex that may form is limited by the amount of heme in solution (Eqn. 8), the initial concentration of \( \text{CCl}_3\text{R} \) is the same in all the experiments. Thus, \( k_1[\text{CCl}_3\text{R}] \) may be written as \( k'_1 \), and in the case where \( k_2 \gg k_{ii} \), Equation 9 simplifies to Equation 11:

\[
[heme] \cong [heme \cdot \cdot \cdot \text{CCl}_3\text{R},(10)
\]

\[
\frac{-d[heme]}{dt} = \frac{d[heme \cdot \cdot \cdot \text{CCl}_3\text{R}]}{dt} = (k'_1 - k_2)[heme] \quad \text{(11)}
\]

where heme \( \cdot \cdot \cdot \text{CCl}_3\text{R} \) is proportional to the amount of total heme, \( [heme]_T \). Thus, Equation 11 may also be written as Equation 13:

\[
[heme \cdot \cdot \cdot \text{CCl}_3\text{R}] \propto [heme] \quad \text{(12)}
\]

\[
\frac{-d[heme]}{dt} \propto [heme](k'_1 - k_2) \quad \text{(13)}
\]

The rate of heme oxidation depends on the heme and \( \text{CCl}_3\text{R} \) concentrations, and it is limited by the stability of the precursor complex (Eqn. 13). The lifetime of the precursor complex (\( \tau \)) [17,18] or \( \tau^{-1} = k'_1 - k_2 \), varies from one \( \text{CCl}_3\text{R} \) compound to another and depends on the molecular structure. Profile I (\( R = \text{NO}_2, \text{CHCl}_3, \text{Cl}, \text{COO}^-, \text{CH}_3, \text{H} \)) illustrates the case where electron transfer is the rate-limiting step and \( \tau^{-1} \approx k'_1 \). In profile II (\( R = \text{CN} \)), complexation is the rate-limiting step, and \( \tau^{-1} \approx k_2 \). Profile II may be considered to be a particular case of profile I, in which the nitrile group and chlorine atoms may compete to complex with iron(II) center via a lone-pair interaction (Fe:N=C and Fe:Cl, respectively) and retard the electron transfer [19]. Profile III (\( R = \text{CONH}_2, \text{CH}_2\text{OH} \)) corresponds to the case in which the concentration of heme remained relatively constant, no electron transfer was observed, \( k_2 = 0 \), and \( \tau^{-1} \) could be written as \( \tau^{-1} \approx k'_1 \). In this latter case, heme and \( \text{CCl}_3\text{R} \) may participate in a type of interaction other than electron transfer. It is possible that the nonbonding-pair electrons on the oxygen [20] and/or nitrogen atoms [21] of the substituent can preferentially complex with the Fe(II) site in competition with their chlorine atoms or participate in pi-lone pair bonds with the ethylene groups located at the side chains (\( k_{ii} \)) so that \( \tau^{-1} = k'_1 + k_{ii} \).

**Mechanism**

A detailed mechanism to explain these results is depicted in Figure 4. The first step is the complexation of the \( \text{CCl}_3\text{R} \) molecule to the heme axial site through a chlorine atom. Chlorine atom charge transfer to the iron(II) center via overlap of an empty \( p \) and \( d^8 \) orbital, respectively, will form a Fe-Cl covalent bond. As [Fe(II)-Cl-CCl_3R] forms, the Fe(II) transfers an electron to the bound chlorine to form Fe(III)Cl (chlorohem in) and ‘‘CCl_3R. The radical ‘‘CCl_3R could then complex with another heme molecule to form Fe(II)--CCl_3R and undergo a second inner-sphere electron transfer to form Fe(III)--CCl_3R [6,7]. The participation of the chlorine as a bridging ligand supports the inner-sphere redox mechanism [22].

At first glance, Figure 4 suggests that the \( \text{CCl}_3\text{R} \) molecule undergoes electron transfers involving two heme molecules and requires a minimum heme:CCl_3R ratio of 2:1 for full conversion. Pentachloroethane (\( R = \text{CHCl}_3 \)), however, undergoes dechlorination in the presence of excess dithionite and a de-
ficiency of heme (CCl₃CHCl₂:dithionite:heme, 100:260:3) with a yield of as much as approximately 75% ([23]; J. Cervini-Silva et al., unpublished data). These results suggest that instead of acting as stoichiometric reagent, heme serves as an electron-transfer mediator. In this scenario, sulfoxyl radicals act as reducing agents of Fe(III) and, perhaps, of Fe(III)Cl₂ to form Fe(II).

Blank experiments in which dithionite alone was incubated with pentachloroethane further showed that no dechlorination products were formed, only polar products and, perhaps, sulfonic acids of the type reported elsewhere [24]. These experiments demonstrated the necessity for heme to be present for reductive dechlorination to occur.

The stereochemistry of the bulk reductant may affect the mechanism of electron transfer between iron porphyrins and halogenated alkanes. For instance, dithionite is an efficient electron source for iron [13], which in turn serves as an electron-transfer mediator in the presence of halogenated alkanes [23]. In the presence of dithionite, the formation of chlorohemin supports the electron transfer between CCl₃R and heme occurring via an inner-sphere mechanism, in agreement with the “captodative effect” [32]. Heme oxidation in the presence of dithionite is followed by rupture of the Cl-C bond for the formation of chlorohemin and a CCl₃R radical. Presumably, the relative formation rate of the Fe-Cl bond is a function of (χₑ – χᵣ), and the rate of formation of chlorohemin and CCl₃R radical depends on the electronic contribution of R to stabilize the radical. For instance, π acceptor groups (NO₂, CN, COO⁻) are substituents that possess high electronegativity to promote formation of the Fe-Cl bond, but they can also provide a higher CCl₃R radical stability via odd-electron delocalization and form a three-electron bond [29]. On the other hand, σ acceptor groups (Cl, CH₂, H) have a moderate (χₑ – χᵣ) value and cannot contribute to CCl₃R radical stability, thus experiencing a slower dechlorination than the π acceptor groups.

Figure 5 shows that the heme oxidation rate follows a strong relationship with R electronegativity, or χᵣ. In agreement with the results of previous studies [29–31], the electronegativity of a substituent appears to be an important variable to predict a trend in the reactivity of homologous compounds in a reaction involving radical species (Table 1). The good correlation of ln kᵢ and χᵣ (r² = 0.88; Eqn. 14) suggests no significant deviation from this trend in reactivity that might cause the conjugation of the R and chlorine electronic contributions (i.e., the “captodative effect” [32]). Heme oxidation in the presence of trichloromethanes that follow profiles I and II may be char-

χᵣ. The carbon center acquires a different partial charge according to R’s group electronegative properties: A strongly electronegative group induces a charge deficiency in the carbon atom that translates to a large (χₑ – χᵣ) value, and the electron flow along the Fe-Cl-C bond shifts until (χₑ – χᵣ) approaches zero (i.e., the “electronegativity equalization” [25–28]). Equalization in electronegativity is followed by rupture of the Cl-C bond for the formation of chlorohemin and a CCl₃R radical. Presumably, the relative formation rate of the Fe-Cl bond is a function of (χₑ – χᵣ), and the rate of formation of chlorohemin and CCl₃R radical depends on the electronic contribution of R to stabilize the radical. For instance, π acceptor groups (NO₂, CN, COO⁻) are substituents that possess high electronegativity to promote formation of the Fe-Cl bond, but they can also provide a higher CCl₃R radical stability via odd-electron delocalization and form a three-electron bond [29]. On the other hand, σ acceptor groups (Cl, CH₂, H) have a moderate (χₑ – χᵣ) value and cannot contribute to CCl₃R radical stability, thus experiencing a slower dechlorination than the π acceptor groups.

The inner-sphere electron transfer between heme and CCl₃R (kᵢ) includes the electron transfer and the formation of chlorohemin and CCl₃R radical. As CCl₃R and heme molecules approach each other and complex, there is charge transfer along the Fe-Cl-C bond that is driven by the difference in the electronegativity of the iron and the carbon atoms, or χₑ – χᵣ. The carbon center acquires a different partial charge according to R’s group electronegative properties: A strongly electronegative group induces a charge deficiency in the carbon atom that translates to a large (χₑ – χᵣ) value, and the electron flow along the Fe-Cl-C bond shifts until (χₑ – χᵣ) approaches zero (i.e., the “electronegativity equalization” [25–28]). Equalization in electronegativity is followed by rupture of the Cl-C bond for the formation of chlorohemin and a CCl₃R radical. Presumably, the relative formation rate of the Fe-Cl bond is a function of (χₑ – χᵣ), and the rate of formation of chlorohemin and CCl₃R radical depends on the electronic contribution of R to stabilize the radical. For instance, π acceptor groups (NO₂, CN, COO⁻) are substituents that possess high electronegativity to promote formation of the Fe-Cl bond, but they can also provide a higher CCl₃R radical stability via odd-electron delocalization and form a three-electron bond [29]. On the other hand, σ acceptor groups (Cl, CH₂, H) have a moderate (χₑ – χᵣ) value and cannot contribute to CCl₃R radical stability, thus experiencing a slower dechlorination than the π acceptor groups.

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acterized by the same function (Fig. 5), and this supports the hypothesis that profile II is a particular case of profile I. These results confirm that the electronegativity of a substituent is a helpful property in predicting the reduction rate of a homologous series of substrates by a metal center [28–30]:

\[
\ln k_r = 4.7x^8 - 15.8
\]

where \( r^2 \) is 0.88. For the particular case in which \( \tau^{-1} = k_r \) (profiles I and II), Equations 13 and 14 may be combined and \( \tau \) written as a function of \( x^8 \) according to

\[
\frac{1}{\tau} = \frac{1}{k_r} = \frac{1}{e^4 \cdot 66^8 - 15.5}
\]

Previous attempts to explain the trend in reactivity of halogenated alkanes during electron-transfer [33] and acid-base [34] reactions have included Taft parameters [35]. Taft postulated that polar properties (\( \sigma \)) of substituents attached to the reaction site promote a change in free energy at the transition state (\( \Delta G_s \)). According to the transition-state theory [18,35,36], this change in structure causes a change of the reaction rate. Our results (not shown) showed a poor correlation of the polar contributions of \( R \) and the two chlorine atoms (\( \Sigma \sigma = \sigma_R + 2\sigma_{Cl} \)) [35,36]) with the trend in dechlorination rates. These results may be explained because the electron transfer occurs along the Fe-Cl-C bond, where the chlorine atom serves as a bridging ligand between the iron(II) and the carbon centers during electron transfer. This reaction mechanism differs from the direct, nucleophilic attack on the carbon atom. Our results suggest that a Taft-like model would not apply in predicting the reactivity of \( CC_{1}\)R toward heme.

The order in reactivity observed for the \( CC_{1}\)R-heme-dithionite system was the same as that for the \( CC_{1}\)R-iron(II) porphyrin–cysteine system [10] according to \( CC_{1}ClCH_2 > CC_{1} > CC_{1}CH_3 > CHCl_3 \). Of particular interest is that rates of heme oxidation in the \( CC_{1}\)R-iron(II) porphyrin–cysteine system also show a strong correlation with \( x^8 \) (in \( k_{\text{dechlorination}} = 10.61x^8 - 31.16, r^2 = 0.96 \) and suggest that the trend in reactivity of \( CC_{1}\)R would be similar for inner- and outer-sphere electron-transfer pathways, because it depends on the \( R \) molecular structure and not on the bulk reductant present in solution (or on the electronic contribution of neighboring chlorine atoms substituents; Fig. 5).

The outcome of this work supports that idea that the group electronegativity, or \( x^8 \), is a useful substituent property in characterizing quantitatively the contribution of a substituent \( R \) to the stability of a forming radical, \( CC_{1}\)R, because of a carbon-chlorine bond homolysis, and the relative reactivity of trichloromethanes, \( CC_{1}\)R, toward electron transfer in the presence of iron(II) porphyrins and a bulk reductant.

**CONCLUSIONS**

Formation of chlorohemin as a terminal product of the reaction between heme and \( CC_{1}\)R suggests that electron transfer occurs via inner-sphere mechanisms. Our results show that heme serves as an electron-transfer mediator in the dithionite-hemin-CC1R system. The relative reactivity of CC1R toward heme can be predicted using R electronegativity values. The influence of R group electronic properties in the CC1R electron-transfer rate suggests that the overall reaction rate depends on the charge induced from R along the R-C \( \sigma \) bond to the carbon center.

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