Reaction of 1,1,1-Trichloroethane with Zero-Valent Metals and Bimetallic Reductants

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Information concerning the pathways and products of reaction of 1,1,1-trichloroethane (1,1,1-TCA) with zero-valent metals may be critical to the success of in situ treatment techniques. Many researchers assume that alkyl polyhalides undergo reduction via stepwise hydrogenolysis (replacement of halogen by hydrogen). Accordingly, 1,1,1-TCA should react to 1,1-dichloroethane (1,1-DCA), to chloroethane, and finally to ethane. Experiments conducted in laboratory-scale batch reactors indicate, however, that with zinc, iron, and two bimetallic reductants (nickel-plated iron and copper-plated iron) this simplistic stepwise scheme cannot explain observed results. 1,1,1-TCA was found to react rapidly with zinc to form ethane and 1,1-DCA. Independent experiments confirmed that 1,1-DCA reacts too slowly to represent an intermediate in the formation of ethane. In reactions with iron, nickel/iron, and copper/iron, *cis*-2-butene, ethylene, and 2-butyne were also observed as minor products. Product ratios were dependent on the identity of the metal or bimetallic reductant, with zinc resulting in the lowest yield of chlorinated product. For reactions with iron and bimetallic reductants, a scheme involving successive one-electron reduction steps to form radicals and carbenoids can be invoked to explain the absence of observable intermediates, as well as the formation of products originating from radical or possibly from carbenoid coupling.

Introduction

Until its use in applications such as vapor degreasing, cold metal cleaning, printed circuit board manufacture, aerosols and as a solvent for inks, coatings, and adhesives was curtailed under provisions of the Montreal Protocol (and subsequent amendments), 1,1,1-trichloroethane (1,1,1-TCA) was the single most extensively employed chlorinated solvent, with a U.S. demand in 1989 of 338 000 t (*1, 2*). In keeping with its widespread former use, this solvent has been detected at about 20% of the sites on the National Priorities (Superfund) List as identified by the U.S. EPA (*3*).

Groundwater contaminated with 1,1,1-TCA (as with other dense chlorinated solvents) is difficult to remediate using conventional pump-and-treat methods, which are inefficient at extracting organic contaminants from heterogeneous subsurface environments (*4*). This provides a substantial incentive for development of innovative and cost-effective alternative methods for minimizing the risks associated with contaminants in the subsurface. The possibility of trans-forming contaminants in situ through permeable "barriers" employing zero-valent metals, in particular, has received considerable scrutiny as a replacement for pump-and-treat approaches (*5*−*12*). The success of this technique is, however, contingent on the reaction products being relatively innocuous.

At present, little information is available concerning the pathways through which 1,1,1-TCA reacts with zero-valent metals, including the distribution of the products that result. Many researchers assume that organohalides react with zero-valent metals via hydrogenolysis, involving stepwise replacement of halogen by hydrogen (*5, 6, 13*). According to this paradigm, 1,1,1-TCA should react to 1,1-dichloroethane (1,1-DCA), to chloroethane, and finally to ethane. The data that do exist concerning products of 1,1,1-TCA reaction with metals are somewhat contradictory and do not always accord with this sequence.

An early report by Archer (*14*) indicated that the reaction of 1,1,1-TCA with Al(0) was complicated by a side reaction of the solvent with $AlCl_3$ or Al_2O_3 present at the metal surface, which served as Lewis acids to catalyze dehydrohalogenation to 1,1-dichloroethylene (1,1-DCE). Such a product would be of considerable concern in a zero-valent metal treatment scheme if it were to arise from Fe(0): 1,1-DCE tends to be more persistent in the presence of Fe(0) than is 1,1,1-TCA (*5, 15*), and drinking water standards for 1,1-DCE are 20 times more stringent (on a molar scale) than for 1,1,1-TCA (*16*). Archer further noted that 1,1,1-TCA reacts with Al(0), Sn(0), and Fe(0) to form 2,2,3,3-tetrachlorobutane, which in turn reacts with metals via reductive elimination to *cis*- and *trans*-2,3-dichloro-2-butene.

More recently, Gillham and O'Hannesin (*5*) studied reactions of Fe(0) with 14 halogenated organic contaminants including 1,1,1-TCA. Products of 1,1,1-TCA reaction were not however reported. Schreier and Reinhard (*13*) found that 1,1,1-TCA reacts with both Fe(0) and Mn(0) in HEPES buffer. No increase in 1,1-DCA concentration accompanying 1,1,1-TCA degradation was detected; rather, it was noted that 1,1-DCA (added as a cosubstrate) was stable under reaction conditions. Finally, Wilson (*17*), citing work conducted by the U.S. EPA National Exposure Research Laboratory, reported that 1,1,1-TCA reacts with Fe(0) to form 1,1-DCA. 1,1-DCA is on the U.S. EPA 1991 Drinking Water Priority List and must be monitored by all drinking water systems (*18*), but at this time, no maximum contaminant levels have been established by the EPA for this organohalide. Considerable ambiguity therefore exists concerning the products likely to be encountered in a zero-valent metal-based treatment system, leading to uncertainties in the human health risk that might be associated with the presence of partially dehalogenated reaction products in effluent from a subsurface treatment wall.

This study was initiated to better characterize the pathways through which 1,1,1-TCA reacts with two metals (iron and zinc) and two bimetallic reductants (copper-plated iron and nickel-plated iron), with a particular emphasis on the identities of the organic products formed. Additional studies also were carried out with 1,1-DCA and 2-butyne to assess their potential roles as reaction intermediates. Finally, a limited suite of experiments was conducted with isotopically labeled 1,1,1-TCA-*2,2,2-d₃* in order to provide evidence in support of the hypothesized reaction pathways.

Experimental Section

Reagents. The following chemicals were used as received: 1,1,1-trichloroethane (99%; ChemService); 1,1-dichloro-

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ethane (95+%; TCI America); vinylidene chloride (1,1-dichloroethylene, 99%; Aldrich); 2-butyne (99%; Aldrich); chloroethane (in methanol; Supelco); ethane, ethylene, and cis-2-butene (Scott Specialty Gases); and 1,1,1-trichloroethane-2,2,2-d_3 (98%; Cambridge Isotope Laboratories). Spiking solutions of 1,1,1-TCA, 1,1-DCA, 2-butyne, and trideuterated 1,1,1-TCA were prepared in methanol (HPLC grade, J. T. Baker). Samples for additional analyses were extracted into hexane (95% n-hexane, ultra-resi analyzed grade, J. T. Baker).

Acid solutions for cleaning metals were prepared within an anaerobic chamber (containing an atmosphere of 10% H_2 and 90% N_2) using deoxygenated (argon-sparged) deionized water (Milli-Q Plus UV, Millipore). The argon stream was purified using an in-line molecular sieve and oxygen traps. Copper and nickel solutions for synthesis of bimetallic reductants were prepared by dissolving $CuCl_2$ (97%; Aldrich) or $NiCl_2$ (98%, Aldrich) in deoxygenated, deionized Milli-Q water under N_2/H_2. Reaction bottles were filled with an Ar-sparged solution consisting of 0.1 M NaCl (99%; J. T. Baker) and 50 mM Tris buffer (tris(hydroxymethyl)aminomethane, reagent grade; Sigma), pH 7.5.

Metal Preparation. The surfaces of the zero-valent metals (iron and zinc) used in these experiments were cleaned with acid according to methods recommended by ref 19 to remove any surface oxides present. All cleaning steps were carried out within an anaerobic chamber. Zinc metal (Baker, 30 mesh) was washed with 0.4% H_2SO_4 for 10 min, and iron metal (Fisher, 100 mesh electrolytic) was washed with 1 M HCl for 2 min. The acid-washed metals were rinsed 3 times with deoxygenated Milli-Q water, rinsed with acetone, removed from the anaerobic chamber, dried under argon at 100 °C for 30 min, and used within 24 h. Surface area analyses conducted via Kr and N_2 BET adsorption using a Micromeritics Flowsorb II 2300 device indicated a surface area of 0.16 m^2 g^{-1} for iron and 0.035 m^2 g^{-1} for zinc.

Preparation of Bimetallic Reductants. Iron was acid-washed and rinsed with deoxygenated water as described above. A dilute solution (50 μM) of $CuCl_2$ or $NiCl_2$ was added slowly (within an anaerobic chamber) to 2 g of iron that was suspended in water by agitation. Once the metal chloride solution had been added, the metal was agitated for an additional minute, rinsed with deoxygenated Milli-Q water, rinsed with acetone, and dried as described above. Assuming that all of the catalytic metal was reductively precipitated onto the iron base metal, the content of the Cu or Ni in the bimetallic reductant was calculated as 0.035 mol %.

Reactions of 1,1,1-TCA and 2-Butyne. Reactions of 1,1,1-TCA and 2-butyne with metals and bimetallic reductants were carried out in 125 mL (nominal volume; actual volume $\simeq$ 150 mL) glass bottles with glass stopcock adapters. The stopcocks were fitted with an NMR septum through which samples could be taken by syringe while maintaining anoxic reaction conditions; the stopcocks served to isolate the rubber septa from the flask contents except during the brief intervals required for sampling. For 1,1,1-TCA, reactions were run with 0.5 g of zinc, 1.0 g of iron, 1.0 g of nickel/iron, or 1.0 g of copper/iron. Metal loadings were the same for 2-butyne (except that reaction with zinc was not investigated). The bottles were filled with deoxygenated Tris/NaCl buffer under an anaerobic atmosphere. Initially, the reaction bottles contained no headspace; less than 2 mL of headspace (presumably resulting from reduction of protons to H_2 by the metal) evolved during the course of a typical experiment. The bottles were spiked with a 0.2 M methanolic solution of 1,1,1-TCA for an initial concentration of approximately 200 μM or with a 0.2 M solution of 2-butyne for an initial concentration of $\sim$10 μM. The bottles were rotated about their longitudinal axes on a rotator (Cole-Parmer) at 40 rpm throughout the course of the experiments. At regular intervals, a 1-mL sample was removed from the bottom of

the reaction bottle using a syringe equipped with a long needle while simultaneously adding 1 mL of deoxygenated buffer solution to the top of the bottle with a second syringe. Samples were sealed in 2.6 mL crimp-cap autosampler vials for headspace analysis by gas chromatography (GC) with flame ionization detection (FID), as described below. A 10 μL sample aliquot was extracted into 1 mL of hexane for additional analysis of 1,1,1-TCA by GC with electron capture detection (GC/ECD). Efforts were made to follow the reaction of 1,1,1-TCA for at least 3 half-lives.

Reactions of 1,1-DCA. Reactions of 1,1-DCA with metals and bimetallic reductants were carried out in 160 mL serum bottles sealed with Teflon septa. Serum bottles were used in preference to the 125 mL reactors employed with 1,1,1-TCA because the pressure buildup caused by hydrogen gas evolution at high metal loadings or over long periods causes the glass stopcock adapters on the reactors to leak. Reactions were run with 2.5 g of zinc, 5.0 g of iron, 5.0 g of nickel/iron, or 5.0 g of copper/iron, i.e., at a 5-fold higher metal loading than employed with either 1,1,1-TCA or 2-butyne. The bottles were filled with deoxygenated Tris/NaCl buffer and sealed without headspace. Less than $\sim$5 mL of headpace evolved during these experiments. The bottles were spiked with 150 μL of a 0.2 M 1,1-DCA methanolic solution and were mixed and sampled as described for 1,1,1-TCA. Because of the dangers posed by the high pressures built up in the serum bottles, time courses could only be monitored for relatively low conversions (7−15%) of 1,1-DCA.

Reactions of Deuterated 1,1,1-TCA. To confirm hypothesized reaction pathways, additional experiments were conducted using Cl_3C-CD_3 as a starting material. Reactions were carried out in 25 mL serum bottles sealed with Teflon septa. The bottles contained 2 g of iron, 2 g of nickel/iron, or 2 g of copper/iron and were filled with 15 mL of deoxygenated Tris/NaCl buffer leaving approximately 10 mL of headspace in the bottle consisting of 10% H_2 and 90% N_2. The sealed bottles were spiked with 5 μL of a 0.7 M solution of trideuterated 1,1,1-TCA in methanol to give an initial concentration of approximately 200 μM. The bottles were mixed overnight to allow reaction products to accumulate before 50 μL headspace samples were taken directly from the reaction bottle for immediate analysis of reaction products by gas chromatography/mass spectrometry (GC/MS) as described below. Deuterium label retention in the parent compound was verified in separate experiments by monitoring the mass spectrum of the 1,1,1-TCA-2,2,2-d_3 over several hours during the course of its reaction with iron.

Sample Analysis. Headspace samples equilibrated with the 1-mL aqueous reaction aliquots were analyzed on a Carlo Erba GC 8000 gas chromatograph equipped with a Carlo Erba HS850 headspace autosampler, a J&W Scientific GS-Q PLOT column (30 m × 0.53 mm i.d.), and an FID. The samples were equilibrated in the autosampler at 60 °C for 30 min prior to injection of 200 μL of headspace in splitless mode. Data were acquired by a PC-based data acquisition system (XChrom v. 2.1; LabSystems, Beverly, MA).

Peak areas were converted to aqueous concentrations by the external standard method, using calibration curves prepared from aqueous standards or gas standards, as appropriate. For 1,1,1-TCA, 1,1-DCA, 1,1-DCE, and 2-butyne, aqueous standards were prepared in 20-mL glass syringes, which were analyzed as described for samples. For ethane, ethylene, and cis-2-butene, gas standards (Scott Specialty Gas) were employed. A 2-mL glass syringe with a wetted barrel and three-way stopcock (one end of which was fitted with a septum) was used to mix and dilute gas standards. A 200 μL aliquot of gas was removed and was manually injected in splitless mode. Results for samples were converted to aqueous concentrations using the appropriate Henry's law constant. The dimensionless Henry's law constant (ex-

pressed as [(mol/L$_{air}$)/(mol/L$_{water}$)] at 60 °C), measured in our laboratory by a modified EPICS method (20) in Tris/NaCl buffer, is 15.8 for ethane, 8.7 for ethylene, and 5.4 for cis-2-butene (15).

The existence of a small amount of headspace could, in principle, result in a partitioning of the volatile compounds under investigation, thereby influencing reaction mass balances. Based on 25 °C Henry's law constants (21) for 1,1,1-TCA (0.71 [(mol/L$_{air}$)/(mol/L$_{water}$)]), 1,1-DCA (0.26), and 1,1-DCE (1.1), less than 1.5% of the mass of these halocarbons would have been lost through partitioning to the volumes of headspace that accumulated. For more volatile hydrocarbon constituents such as ethane ($K_H' = 20.4$ [(mol/L$_{air}$)/(mol/L$_{water}$)]; 22) and ethylene ($K_H' = 8.7$; 22), however, losses could have been more significant, amounting to approximately 20% of the ethane mass and 10% of that of ethylene. Smaller losses would have been anticipated for the other hydrocarbons observed, namely, cis-2-butene ($K_H' = 5.8$ at 24 °C; determined in our lab according to ref 23) and 2-butyne (K_H' estimated as 0.44; 24). Aqueous concentrations reported for all species therefore include a correction for calculated volatilization losses, based on our estimates of the headspace volume that had accumulated at each sampling point.

Detection limits for selected species were calculated from confidence bands around linear calibration curves using the method of Hubaux and Vos (25). For purposes of assessing detection limits, five-point calibration curves were based on low concentration ranges (generally within a factor of 5 of the estimated detection limit) rather than on the full concentration range that was used to quantitate the results of the kinetic experiments.

Due to the coelution of 1,1,1-TCA with one possible reaction product, 1-hexene, verification of 1,1,1-TCA concentrations was made by analyzing hexane extracts via cold on-column injection onto an Rt$_x$-1 GC column (30 m × 0.32 mm i.d. × 5.0 μm film thickness; Restek) followed by detection with a Carlo Erba [63]Ni ECD. The GC/ECD results agreed well with results obtained from the headspace GC/FID analysis technique. Identities of all major reaction products observed were confirmed by headspace injections onto a Hewlett-Packard (HP) 5890 GC equipped with an HP 5970 mass spectrometer detector and a GS-Q PLOT column (30 m × 0.32 mm i.d.) or the Rt$_x$-1 column previously described. Products were identified on the basis of retention time (using authentic compounds as standards) and mass spectra. The mass spectra were recorded under electron impact (EI) ionization by conducting scans in the range of m/e 15−140; a narrower range (m/e 15−40) was used to maximize sensitivity in measuring the spectra of low molecular weight deuterated products (ethane and ethylene) in the experiment with isotopically labeled 1,1,1-TCA.

Mass Spectral Modeling. One of the objectives in the experiments conducted with Cl$_3$C−CD$_3$ was to assess the deuterium content in the reaction products. GC/MS spectra indicated that ethylene and ethane products resulting from reactions of trideuterated 1,1,1-TCA consisted of a mixture of coeluting isotopomers with varying numbers of deuterium atoms. To estimate the retention of the deuterium label among the products, a set of linear programs was developed. Two such programs were developed for ethane and one for ethylene modeling. For unlabeled compounds, model fits were based on mass spectra of gas standards determined on our instrument, while for deuterated compounds, model fits were based on the eight major peaks reported in ref 26. In the first ethane fit, the observed mass spectra were assumed to include contributions from unlabeled ethane; ethane-d$_1$; ethane-1,1-d$_2$; ethane-1,2-d$_2$; and ethane-1,1,1-d$_3$. We were unable to locate mass spectral information for ethane-1,1,2-d$_3$, although we expect its mass spectrum is quite similar to that of ethane-1,1,1-d$_3$. Ponec and Bond (27) note that these

two isotopomers cannot be differentiated by mass spectrometry. In the second ethane fit, the previous program was supplemented with contributions from ethane-1,1,1,2-d$_4$ and ethane-1,1,2,2-d$_4$. The following compounds were included in trying to fit observed spectra of ethylene: unlabeled ethylene, ethylene-d$_1$, ethylene-d$_2$, and ethylene-d$_3$. Because reported mass spectra for the three dideuterated ethylenes are virtually identical, these isomers were lumped together as a single species in our analysis. For ethylene isotopomers, the most abundant ion is always the parent ion. For ethanes, the molecular ion is not the most abundant ion; relative intensities for the parent ion range from 27% to 42%. The most abundant ions for these species are as follows: unlabeled ethane, m/e 28; ethane-d$_1$, m/e 29; ethane-1,1-d$_2$, m/e 29; ethane-1,2-d$_2$, m/e 30; ethane-1,1,1-d$_3$, m/e 30; ethane-1,1,1,2-d$_4$, m/e 31; ethane-1,1,2,2-d$_4$, m/e 31.

A best fit distribution was found by minimizing the objective function:

$$Z = \sum_{i=25}^{36} (U_i + V_i) + L \qquad (1)$$

where the index i denotes the m/e values, subject to the following constraints:

$$\sum_j a_{ij}x_j + U_i - V_i = e_i L \qquad \forall i, i = 25, ..., 36 \quad (2)$$

$$\sum_j a_{ij}x_j \leq L \qquad \forall i \qquad (3)$$

$$\sum_j x_j = 1 \qquad (4)$$

$$0 \leq x_j \leq 1 \qquad \forall j \qquad (5)$$

where the index j refers to the specific isotopomers considered in the mixture. The constant a_{ij} represents the theoretical abundance of m/e i for isotopomer j, and e_i is the experimentally determined abundances for the mixture at each m/e value. The decision variables x_j are the fractions of isotopomer j in the mixture, while U_i and V_i are so-called target-hitting variables. Their function in the linear program is such that minimizing the objective function is equivalent to minimizing the absolute value of the difference between the experimental and calculated mixtures. Through constraints (3), the decision variable L equals the largest calculated m/e abundance and is used to normalize the calculated values to obtain relative intensities.

Results

Reaction of 1,1,1-TCA and 1,1-DCA with Zn. 1,1,1-TCA reacts rapidly with zinc to form ethane and 1,1-DCA (Figure 1). A model fit to the first five data points for 1,1,1-TCA shows a reasonable adherence to exponential decay, with some evidence that the reaction slows down toward the end of the experiment (Figure 1). Pseudo-first-order k_{obs} values obtained from initial rates and rate constants normalized to metal surface area loading (k_{SA}; 9) are shown in Table 1.

Ethane is the more abundant product observed, with a lesser amount of 1,1-DCA formed. The yield of 1,1-DCA was calculated as

$$\frac{(1,1\text{-DCA})_t}{(1,1,1\text{-TCA})_o - (1,1,1\text{-TCA})_t}$$

where the subscript t denotes concentrations measured at all but the initial time point and (1,1,1-TCA)$_o$ is the model-fit initial TCA concentration. Results indicated a 1,1-DCA yield
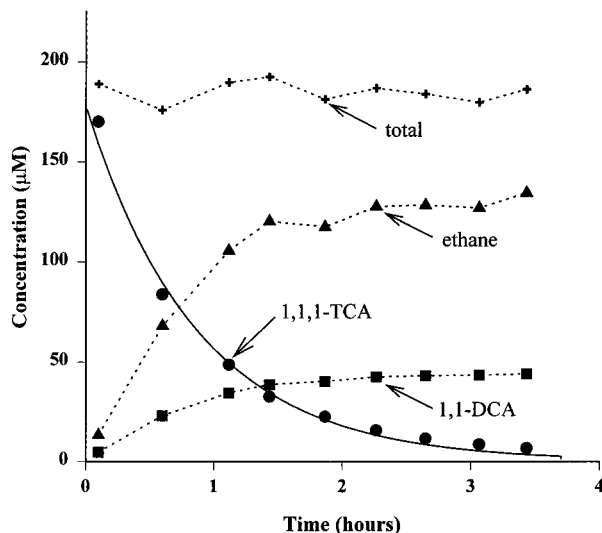
FIGURE 1. Reduction of 1,1,1-TCA in 0.1 M NaCl/0.05 M Tris buffer (pH 7.5) by Zn(0). Solid line reflects exponential decay fit to initial 1,1,1-TCA data.

TABLE 1. Summary of Rate Data Obtained for Reactions of 1,1,1-TCA with Zero-Valent Metals and Bimetallic Reductants in NaCl/Tris Buffer, pH 7.5[a]

reductant	metal mass (g)	k_{obs} (h^{-1})	k_{SA} (L m^{-2} h^{-1})
zinc	0.5	1.15 ± 0.18	10.0
iron	1.0	0.48 ± 0.06	0.46
nickel/iron	1.0	1.86 ± 0.20	1.77
copper/iron	1.0	1.35 ± 0.04	1.29

[a] Metal loading represents mass of metal per 150 mL of buffer solution in reactor. Uncertainties on k_{obs} values represent 95% confidence limits obtained from an exponential fit to the first five data points.

of 25.8 ($\pm$ 0.5)%, where the stated uncertainty reflects 95% confidence limits. Replicate experiments indicated that product distributions determined for reaction of 1,1,1-TCA with zinc (as well as with iron; see below) were reproducible within 5−10%. No organic products were observed in blank experiments conducted with zinc (or iron or the bimetallic reductants employed) plus NaCl/Tris buffer in the absence of 1,1,1-TCA either in the presence or absence of methanol at the concentration employed as a carrier in the 1,1,1-TCA spike.

The carbon mass balance at the end of the experiment (calculated as the sum of all organic species measured) was approximately 93% of the calculated spiked 1,1,1-TCA concentration (based on the volume of water in the reactor and the concentration of the 1,1,1-TCA in the methanol stock). We suspect that minor losses may have occurred during spiking through the stopcocks, as no other organic products were observed, and mass balances throughout the time course agree well with initial 1,1,1-TCA measurements. Lacking authentic standards of 2,2,3,3-tetrachlorobutane and cis- and trans-2,3-dichloro-2-butene, however, we cannot rule out the possibility that these could have been missed by the analytical techniques employed. Also, the headspace analytical technique is not optimal for products such as acetaldehyde or ethanol, which have low Henry's law constants. The detection limit for acetaldehyde was approximately 9.2 μM (more than an order of magnitude higher than for the volatile organic products reported herein), and that for ethanol was greater than 200 μM. The high detection limit for the latter compound may be in part attributable to the GC column employed, which is not well-suited to quantitative analysis of alcohols.
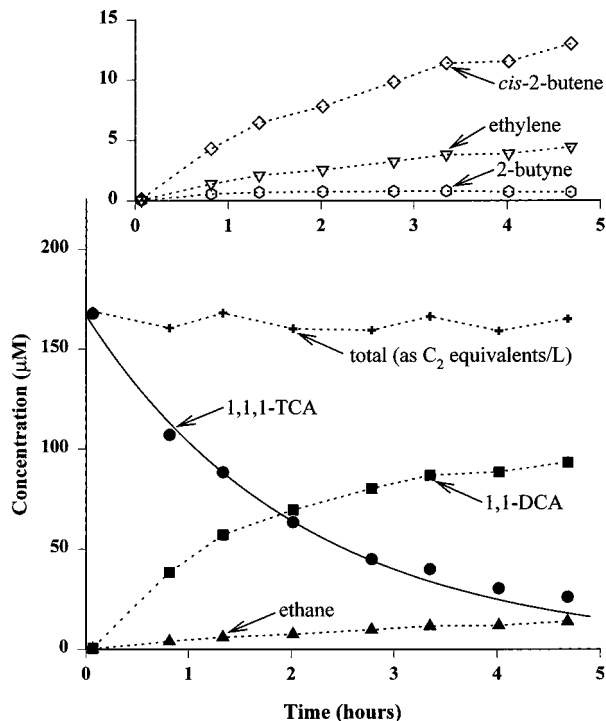

FIGURE 2. Reduction of 1,1,1-TCA in 0.1 M NaCl/0.05 M Tris buffer (pH 7.5) by Fe(0). Solid line reflects exponential decay fit to initial 1,1,1-TCA data. Inset shows minor products not observed in reaction with Zn.

1,1-DCA represents a two-electron reduction product, and ethane is a six-electron reduction product. We do not, however, believe that 1,1-DCA is an intermediate in ethane formation. Both reaction products appeared simultaneously, and both persisted throughout the 3.5 h course of the experiment. Independent experiments demonstrated that 1,1-DCA reacts slowly with zinc to produce ethane, with a half-life of approximately 14 days at a 5-fold higher loading of zinc. This slow rate of reaction precludes 1,1-DCA as an intermediate in the formation of ethane from 1,1,1-TCA.

Reaction of 1,1,1-TCA and 1,1-DCA with Fe. Somewhat different products were obtained with iron (Figure 2). With this reductant, 1,1,1-TCA reacted to form mainly 1,1-DCA as a major product (67 ± 2% yield) along with lesser amounts of ethane, cis-2-butene, ethylene, and a trace of 2-butyne.

Final mass balances on carbon were approximately 84% relative to the calculated spiked concentration. We do not believe that sorption to the iron metal or impurities therein (as observed by Burris et al.; 28) is responsible for the imperfect mass balance. Unlike the cast iron employed by Burris, the Fisher electrolytic iron used in the present study has a very low carbon content (29); furthermore, we have not observed any losses in aqueous concentration that could be attributed to sorption of chlorinated ethenes to either Fisher electrolytic iron or to zinc (15). Note that the total mass balance throughout the time course coincides closely with the initial 1,1,1-TCA measurement; if reaction to relatively polar products were significant, mass balances would have decayed over time. As with zinc, reactions initially followed pseudo-first-order decay with an apparent slowing at later times. Initial rate constants are shown in Table 1.

Complementary experiments with 1,1-DCA again indicate that even though this chlorocarbon reacts to form ethylene and ethane as major products, reaction with iron is too slow (with a half-life of approximately 25 days at a loading of 5.0 g of Fe) for 1,1-DCA to represent an intermediate in the
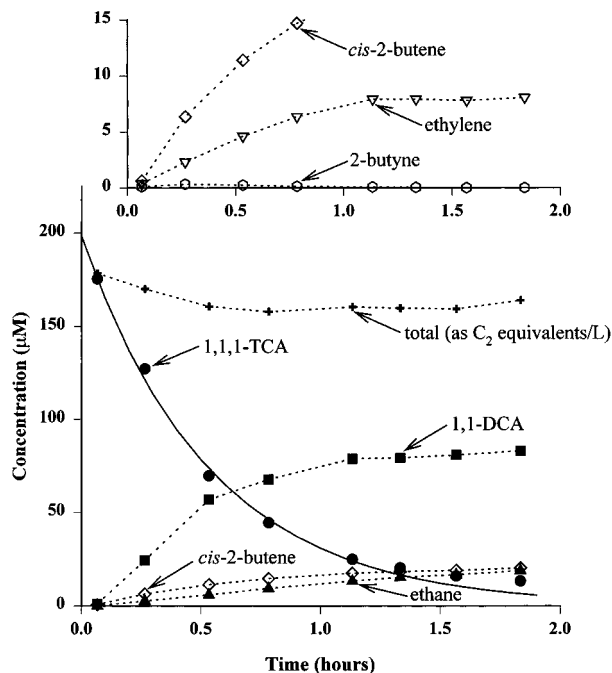
FIGURE 3. Reduction of 1,1,1-TCA by bimetallic (Ni-plated Fe) reductant in 0.1 M NaCl/0.05 M Tris buffer (pH 7.5). Solid line reflects exponential decay fit to initial 1,1,1-TCA data. Inset shows minor products not observed in reaction with Zn.

FIGURE 4. Reaction of 1,1,1-TCA with bimetallic (Cu-plated Fe) reductant in 0.1 M NaCl/0.05 M Tris buffer (pH 7.5). Solid line reflects exponential decay fit to initial 1,1,1-TCA data. Inset shows minor products not observed in reaction with Zn.

formation of ethane or ethylene. Nor is ethylene (a four-electron reduction product of 1,1,1-TCA) an intermediate in ethane formation, as independent experiments conducted in our laboratory demonstrate that ethylene reacts too slowly for such a reaction to account for the amount of ethane observed in reduction of 1,1,1-TCA (*15*). Further evidence that suggests neither 1,1-DCA nor ethylene is an intermediate in ethane formation comes from the observation that yields of 1,1-DCA, ethylene, and ethane were independent of time. These three products must therefore originate from parallel and not consecutive reactions.

Reaction of 1,1,1-TCA and 1,1-DCA with Bimetallic Reductants. 1,1,1-TCA reacted with nickel/iron (Figure 3) at a significantly faster rate than with iron (Table 1). This enhanced reactivity of Ni/Fe accords with observations by other researchers for reactions of chlorinated ethylenes (*30, 31*). The increased rate of reaction was accompanied by a small change in the product distribution: a slightly higher yield of *cis*-2-butene and ethylene was obtained and a lower yield (43 ± 4%) of 1,1-DCA. As with iron, only a trace of 2-butyne was detected. The carbon mass balance at the end of the experiment was approximately 83% of the calculated spiked concentration. 1,1-DCA again reacts slowly with nickel/iron, with a half-life of approximately 9 days at a loading of 5.0 g of Ni/Fe.

A more dramatic change in product distribution was found in the copper/iron system (Figure 4). A substantial increase in yield was observed for ethylene, while a decrease in 1,1-DCA (30 ± 1% yield) and *cis*-2-butene formation was obtained relative to nickel/iron. A significant concentration of 2-butyne was also measured; this product exhibited accumulation and subsequent disappearance indicative of a reaction intermediate. In addition, a trace of 1,1-dichloroethylene (1,1-DCE; detection limit 0.03 μM) was observed, a product confirmed by GC/MS. Final mass balances on carbon were approximately 76% relative to calculated spiked concentration. Once more, kinetic arguments indicate that 1,1-DCA cannot represent an intermediate in ethane or ethylene formation.
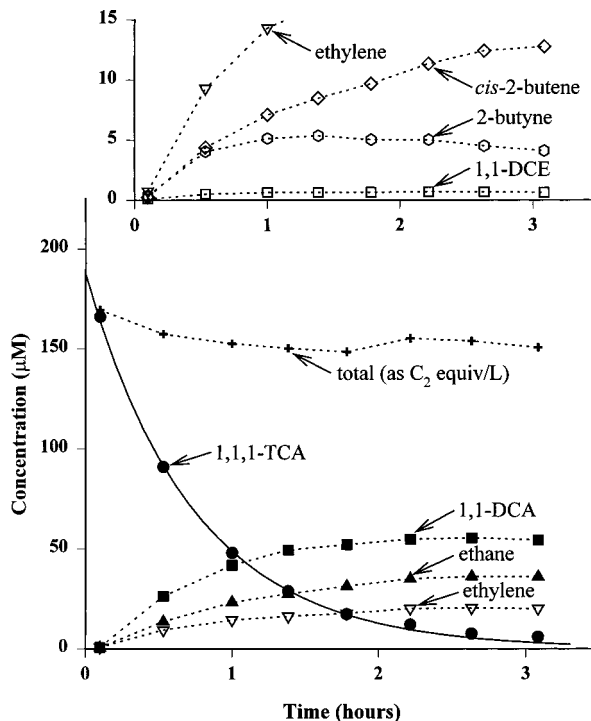
Reduction of 2-Butyne. Reactions of 2-butyne with iron and bimetallic reductants also were examined to assess whether this species could represent an intermediate in *cis*-2-butene formation. With iron and the two bimetallic reductants studied, the major reaction product observed was *cis*-2-butene, with only traces of *trans*-2-butene and 1-butene formed. Preliminary modeling studies based on a simple pseudo-first-order approach suggested, however, that the measured rate of 2-butyne reaction was insufficient to account for all of the *cis*-2-butene observed in 1,1,1-TCA experiments. This may indicate limitations of a pseudo-first-order approach; alternatively, some additional pathway may be responsible for *cis*-2-butene formation.

In summary, these experiments with 1,1,1-TCA show no evidence that the dehydrohalogenation reported with Al(0) (*14*) takes place with zero-valent zinc or iron. The expected dehydrohalogenation product (1,1-DCE) is observed only with copper/iron and only in trace concentrations (less than 2% yield). The major reaction products (1,1-DCA and ethane) are consistent with reductive dehalogenation. A simple stepwise reduction from 1,1,1-TCA to 1,1-DCA to chloroethane to ethane does not however appear to be involved.

Discussion

Reaction Pathways. One potential scheme that could account for all of the products observed in our experiments with Fe(0) or reported in the literature is indicated in Figure 5. According to this scheme, ethane is formed via a sequence that involves successive one-electron reduction steps to form radicals and carbenoids, analogous to the pathway involved in reduction of 1,1,1-TCA by Cr(II) in aqueous solution (*32*).

The first step in the sequence involves a one-electron dissociative electron-transfer step to result in the 1,1-dichloroethyl radical:

$$H_3C-CCl_3 + e^- \longrightarrow [H_3C-CCl_3]^{\cdot-} \longrightarrow H_3\overset{\cdot}{C}-CCl_2 + Cl^-$$
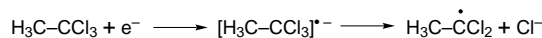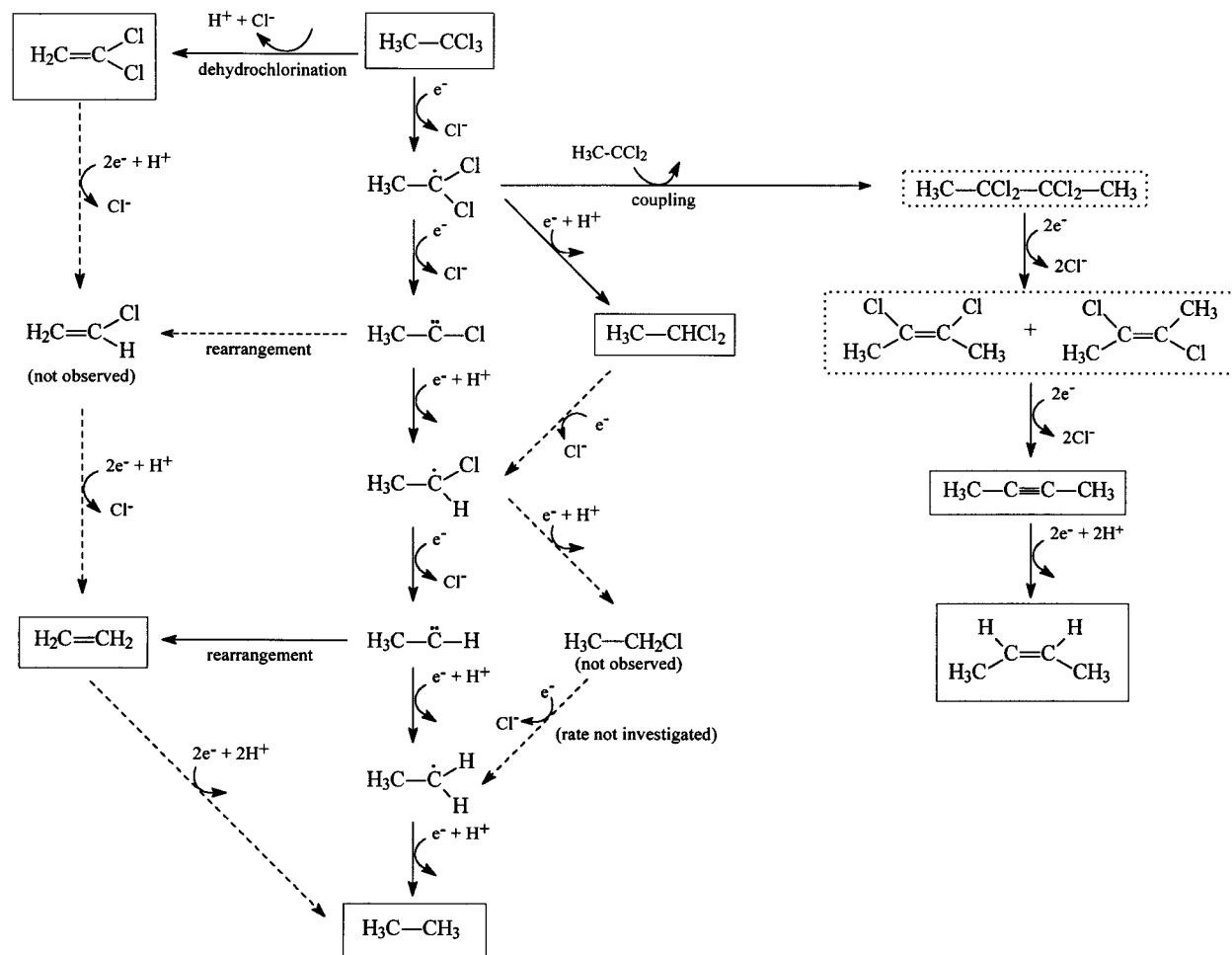
FIGURE 5. Proposed scheme for reaction of 1,1,1-TCA with Fe(0). Boxes indicate reaction products identified in this study; dashed boxes indicate products previously reported in the literature (14). Dashed arrows reflect potential pathways that are too slow to explain the observed distribution of reaction products, as shown by this study or by unpublished data from our laboratory (15). Note that intermediates shown for simplicity as free carbenes are in fact more likely to occur as carbenoids. Not shown: potential coupling of chloroethyl radicals or of carbenoid species to C4 compounds.

This radical could couple with other dichloroethyl radicals to form 2,2,3,3-tetrachlorobutane (which could undergo two successive reductive β-elimination reactions to form 2,3-dichloro-2-butenes and hence 2-butyne, which in turn was observed to undergo reduction to cis-2-butene). The importance of such coupling reactions would be expected to be dependent on the concentrations of the parent compound, as higher initial 1,1,1-TCA concentrations should give rise to higher steady-state concentrations of radicals.

Alternatively, the dichloroethyl radical could undergo a second one-electron reduction to form the dichloroethyl carbanion, either free or complexed as an organometallic species. This carbanion could undergo protonation (to yield 1,1-dichloroethane) or else could undergo α-elimination to form the $H_3C-\ddot{C}-Cl$ carbene (or carbenoid). Carbanions are known to be stabilized by halogen substituents (33), which could favor the competition between protonation vs α-elimination to a carbene; the extra stabilization energy provided by two halogens may explain why 1,1-dichloroethane was observed but not chloroethane (which would be expected to result from protonation of a chloro-ethyl carbanion). We note that our detection limit for chloroethane is approximately 0.24 μM. Assuming that (as with 1,1-dichloroethane) chloroethane is reduced slowly by the zero-valent metals investigated, even a chloroethane yield less than 0.2% should have resulted in

detectable accumulation of this product.

We suspect that $H_3C-\ddot{C}-Cl$ exists as a carbenoid (e.g., as a carbene—metal complex or α-haloorganometallic compound; 33) rather than as a free carbene. A free carbene might be expected to undergo a significant amount of trapping by the solvent, which would be expected to result in the formation of acetaldehyde in the case of $H_3C-\ddot{C}-Cl$. There is precedent in the chemical literature for carbenoids as intermediates of polyhaloalkane reduction by zero-valent metals in organic solvents. For example, in the Simmons—Smith synthesis of cyclopropanes through reaction of olefins with CH_2 (34), it is believed that the methylene (generated through the reduction of CH_2I_2 by the zinc—copper couple in ether) exists in the form of iodomethylzinc iodide, which is in equilibrium with the dialkylzinc species ($ICH_2)_2Zn \cdot ZnI_2$ (35, 36). Although the iodomethylzinc iodide intermediate is sufficiently stable in ether to be isolable (35), the presence of water could have an enormous impact on the stability of organometallic intermediates, which may only possess only a fleeting existence as reactive intermediates in the present system.

Further reduction of $H_3C-\ddot{C}-Cl$, accompanied by proton transfer, would result in formation of the chloroethyl radical. This radical could undergo reduction to the $H_3C-\ddot{C}-H$ carbenoid. One of the characteristic reactions of alkylcarbenes is rearrangement (37), with migration of hydrogen:
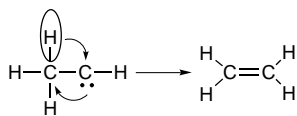
Such a rearrangement could explain the ethylene observed. A similar rearrangement of $H_3C-\ddot{C}-Cl$ does not appear to be taking place to any significant extent, as no vinyl chloride (detection limit 0.19 μM) was observed. This may serve as further indication that $H_3C-\ddot{C}-Cl$ occurs as a carbenoid rather than as a free carbene.

Finally, $H_3C-\ddot{C}-H$ could undergo two successive one-electron reduction steps (accompanied by protonation) to generate the ethyl radical and finally ethane. The latter product also results from reduction of ethylene, albeit at rate that is too slow to account for its formation from 1,1,1-TCA reduction (15).

As with the dichloroethyl radical, the chloroethyl radical and the ethyl radical could potentially undergo self-coupling, forming *meso-* and D,L-2,3-dichlorobutane (in the case of the chloroethyl radical) and *n*-butane (from the ethyl radical). We have previously found that *erythro-* and *threo*-2,3-dibromopentane display a high degree of stereospecificity in their reductive elimination by zero-valent metals, reacting almost exclusively to *trans-* and *cis*-2-pentene, respectively (38, 39). Even if the reaction of 2,3-dichlorobutanes were to be less stereospecific than reactions of the brominated analogues, we would expect if anything that an excess of *trans*-2-butene (as the more stable isomer) over the cis isomer should result from reduction of a racemic mixture of 2,3-dichlorobutanes. Our data indicate that *trans*-2-butene is not formed in appreciable amounts; it did not accumulate above detection limits (0.07 μM), nor was its likely reduction product (butane) ever observed. Unless the coupling of radicals at the metal surface were to result somehow in a substantial excess of D,L-2,3-dichlorobutane over the meso isomer, the apparent lack of *trans*-2-butene production would argue against the coupling of chloroethyl radicals. The absence of butane formation is evidence that coupling of ethyl radicals is not a significant process. The lack of apparent coupling by the chloroethyl and ethyl radicals may reflect the decreased stability of these less highly substituted species (33), resulting in lower steady-state concentrations and thus diminished probability of an encounter with one another.

The possibility that carbenes (or carbenoids) could couple should also be considered. Some authorities (40) have suggested that carbenes can couple to give rise to olefins. Other researchers (33) argue that because of their very high reactivity, it is unlikely that a free carbene could encounter another before reacting in some other manner, such as by rapid intramolecular rearrangement or reaction with the solvent; alternative explanations should therefore be sought for such apparent "dimerization" reactions. Although coupling of free carbenes in homogeneous solution may indeed be an extremely remote occurrence, the formation of organometallic carbenoids, either as dialkyl species or as monoalkyl species at locally elevated concentrations at the solid−water interface, might increase the probability of coupling. Blanchard and Simmons (35) have studied the formation of ethylene as a side product of methylene iodide reaction with the zinc−copper couple. Their evidence suggests that ethylene formation occurs through two simultaneous reactions of an organozinc carbenoid intermediate: (i) reaction of $(ICH_2)_2Zn \cdot ZnI_2$ with unreacted CH_2I_2 to form diiodoethane, which subsequently undergoes reductive elimination to ethylene; (ii) reaction of $(ICH_2)_2Zn \cdot ZnI_2$ to ICH_2-CH_2ZnI, which in turn reacts to ethylene.

For $H_3C-\ddot{C}-Cl$, the resulting coupling products would be *cis-* and *trans*-2,3-dichloro-2-butenes (which could un-
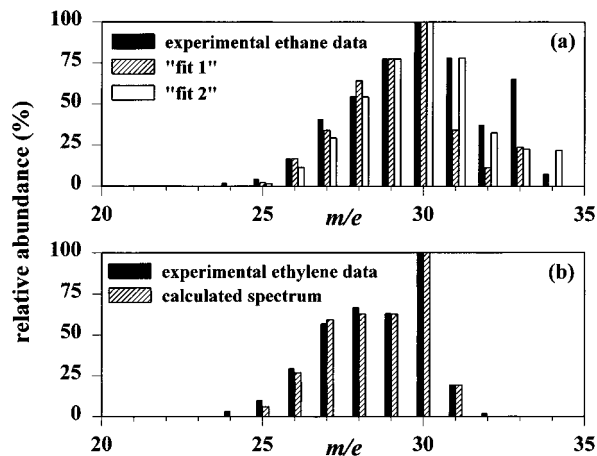
FIGURE 6. Comparison of experimental with calculated GC/MS spectra for reaction of isotopically labeled 1,1,1-TCA-*2,2,2-d₃* with iron: (a) experimental ethane mixture (solid bars); best-fit mass spectrum assuming a mixture of unlabeled, mono-, di-, and trideuterated ethane isotopomers (fit 1, patterned bars); and best-fit mass spectrum based on a mixture of unlabeled through tetra-deuterated ethanes (fit 2, open bars); (b) experimental ethylene mixture (solid bars) and best-fit mass spectrum based on a mixture of unlabeled through trideuterated ethylene isotopomers (patterned bars).

dergo reductive elimination to 2-butyne and then be reduced to *cis*-2-butene); from $H_3C-\ddot{C}-H$, *cis-* and/or *trans*-2-butene would be expected. Once again, unless carbenoid coupling occurs in a highly stereospecific manner, the apparent lack of *trans*-2-butene formation would seem to rule out the possibility that $H_3C-\ddot{C}-H$ species couple. Further assessment of the likelihood of carbenoid coupling must await a more detailed examination of the natures of these intermediates.

Experiments with Trideuterated 1,1,1-TCA. Additional evidence concerning reaction pathways was obtained by conducting experiments using trideuterated 1,1,1-TCA. GC/MS studies of products obtained from reaction of this compound with zero-valent iron, nickel/iron, and copper/iron showed that ethylene and ethane reaction products are partially deuterated. According to the scheme shown in Figure 5, we would predict that the ethane should consist of ethane-*1,1,1-d₃* and that the ethylene should also be trideuterated. The observed spectra did not match library spectra of pure ethane-*1,1,1-d₃* or trideuterated ethylene (26) but rather appeared to represent mixtures of isotopomers exhibiting varying degrees of deuterium label retention. A set of linear programs, described in the Experimental Section, provided estimates of the distribution of isotopomers in each case.

Experimental and optimized results are shown in Figure 6a for ethane and Figure 6b for ethylene. The optimal distribution for the first ethane fit (from zero to three deuterium atoms) consisted of 16% unlabeled ethane, 34% ethane-*d₁*, and 50% ethane-*1,1,1-d₃*. The calculated spectrum does not match the measured spectra well for the higher molecular weight ions. Improved fit is obtained by allowing ethane-*1,1,1,2-d₄* and ethane-*1,1,2,2-d₄* to be present (Figure 6a, fit 2), but the abundance of the *m/e* 33 value is still underestimated. The resulting optimized distribution consisted of 6% unlabeled ethane, 32% ethane-*d₁*, 31% ethane-*1,1,1-d₃*, and 31% ethane-*1,1,2,2-d₄*. Incorporation of higher molecular weight isotopomers (pentadeuterated or hexadeuterated ethane) into the model did not result in any substantial improvement in fit between predicted and measured spectra.

The imperfect agreement between measured and predicted ethane spectra may reflect limitations of our model

and/or the resolution of our mass spectrometric analysis (e.g., limits to instrumental accuracy; variability in background noise leading to imperfect background corrections; or, perhaps most likely, reliance on published spectra rather than on spectra for partially deuterated ethane isotopomers determined on our instrument). We feel that other possibilities for the imperfect match between predicted and measured spectra, such as that some other product coelutes with the ethane, are unlikely. When experiments were run using unlabeled 1,1,1-TCA, the peak obtained for ethane was readily resolved from all other nearby peaks on the GC column employed, and the mass spectrum was identical to that of an authentic ethane standard. Mass spectrometric analysis of the isotopically labeled 1,1,1-TCA failed to reveal significant levels of impurities (such as 1,1,1-trichloroethane-2,2-d_2) that might have led to production of dideuterated or lower molecular weight ethane or ethylene isotopomers. No ethane or ethylene accumulation was detected in the absence of 1,1,1-TCA, as previously discussed.

The best-fit distribution of labeled and unlabeled products in the ethylene mixture was 6% ethylene, 11% ethylene-d_1, 70% ethylene-d_2 (mixture of all three possible dideuterated isomers), and 14% ethylene-1,1,2-d_3. In this case, the simulated spectrum matched the experimental spectrum well, as shown in Figure 6b.

The deviations from the expected deuterium label retention in the ethane and ethylene products suggest that the actual reaction mechanism is more complex than the scheme illustrated in Figure 5. It is possible that H−D exchange could occur either in the reactive intermediates or in the final products ethane or ethylene. Some of the deuterium lost could persist at the surface of the metal, thereby accounting for the variable deuterium retention. Such metal-catalyzed H−D exchange of alkanes and olefins has received intensive scrutiny in the field of metal catalysis (27). According to the generally accepted model, the reaction involves a sequence of steps: (a) adsorption of the hydrocarbon to the metal surface, followed by activation of the C−H (or C−D) bond; (b) dissociation of the carbon−hydrogen bond to yield a metal-bound radical; (c) coupling of the radical with metal-bound atomic H (or D). Most of the prior research, however, pertains to gas-phase reactions, and it is difficult to assess without additional experiments whether such exchange would also occur under the conditions employed in the present study. Certainly no evidence of D−H exchange could be detected in the mass spectrum of 1,1,1-TCA-d_3 over several half-lives of reaction with iron. Furthermore, no significant deuterium label loss was apparent in the 2-butyne-1,1,1,4,4,4-d_6 or the 1,1-dichloroethane-2,2,2-d_3 products observed (see below). This indicates that H−D exchange, if it occurs under the present reaction conditions, is not invariably a facile process.

The other reaction products (1,1-dichloroethane, 2-butyne, and cis-2-butene) were found to consist of 1,1-dichloroethane-2,2,2-d_3 (Figure 7a), 2-butyne-1,1,1,4,4,4-d_6 (Figure 7b), and cis-2-butene-d_6, shown in Figure 7c. Note that because of the tendency of hydrocarbons to exhibit a scrambling of hydrogen atoms under electron impact ionization (41, 42), the positions of the deuterium atoms within the cis-2-butene cannot be determined from the mass spectrum. The presence of six deuterium atoms in the C$_4$ products is consistent with their origin via coupling of radicals (or possibly $D_3C-\ddot{C}-Cl$ carbenoids) that then undergo reductive elimination and reduction to 2-butyne and cis-2-butene. Retention of six deuterium atoms would not have been anticipated if C$_4$ products were to originate from reduction of aqueous carbonate (43) or from reaction of carbide impurities within the metal (29).

Relevance of Results. In summary, our results confirm Gillham's (5) and Schreier's (13) observations that 1,1,1-TCA
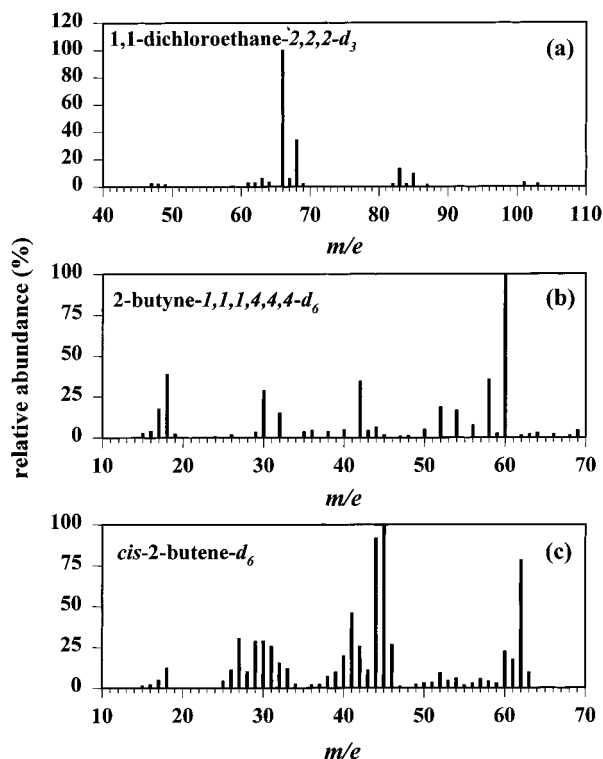

FIGURE 7. GC/MS spectra of (a) 1,1-dichloroethane-2,2,2-d_3; (b) 2-butyne-1,1,1,4,4,4-d_6; and (c) cis-2-butene-d_6 obtained in reaction of 1,1,1-TCA-2,2,2-d_3 with iron.

reacts rapidly with Fe(0). Kinetic analyses and product studies indicate that the reaction does not, however, proceed exclusively through stepwise replacement of halogen by hydrogen, as has been previously proposed as a paradigm for reaction of organohalides with metals. Rather, the data for iron and iron-based bimetallic reductants are consistent with a sequence involving reduction to radicals and carbenoids, resulting in products that reflect reductive α-elimination and coupling in competition with hydrogenolysis. To determine if reaction with zinc also involves free radical intermediates requires additional study. Certainly, none of the coupling products that are often characteristic of free radical reactions and that were observed for reaction with iron, Ni/Fe, and Cu/Fe were detected with zinc.

The data reveal interesting differences in the distribution of products obtained with the various reductants employed. A lower yield of 1,1-DCA, for example, was obtained with zinc than with iron or with either of the two bimetallic reductants. In all cases, the reaction of 1,1-DCA was shown by independent experiments to be sufficiently slow as to preclude major differences between the reactivity of the various reductants as an explanation. It seems that the metal serves a role that goes beyond that of a simple source of electrons: specific chemical interactions between (potentially partially oxidized) metal species present at the solid−water interface and the organohalide (or reactive intermediates resulting therefrom) are likely to be involved in dictating reactivity and reaction product distribution. Boronina et al. (7) have also found that the identity of the metal plays a part in the distribution of products obtained in the reduction of organohalides: reaction of CCl$_4$ with zinc led to dechlorination to methane, while reaction with Sn(0) led to CO$_2$ and chloroform as major products. A complete explanation for such differences in reactivity and reaction product distributions displayed by various metals and bimetallic reductants is bound to involve a multitude of factors, many of which are still imperfectly understood. Even for reactions as well-studied as metal-promoted H−D exchange in alkanes, Ponec

and Bond (27) note "It is still quite unclear why adjacent metals can behave so differently as catalysts... Unfortunately the chemical rules governing metals' behavior have not yet been elucidated... Much work remains to be performed in this field." These statements can be echoed for metal-promoted reductive dehalogenation reactions. Nevertheless, the strong influence that the metal identity exerts on reaction product distribution suggests that it may be feasible to develop a reductant through which the generation of undesirable byproducts could be minimized.

Although the pathways outlined herein for iron are complex, they do make it possible to formulate a reaction scheme that can account for all of the observed reaction products (including the inability of 1,1-DCA and ethylene to represent reaction intermediates). This should facilitate the development of process models that could be used for the design of subsurface iron-based treatment walls for 1,1,1-TCA. Additional studies will be required to assess whether reaction with zinc (which does not appear to give rise to coupling products) also proceeds through similar pathways.

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