Reductive Dehalogenation of Carbon Tetrachloride by Sodium Dithionite

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Addition of sodium dithionite ($Na_2S_2O_4$) to aqueous carbon tetrachloride solutions (~ 650 mg/L) resulted in CCl_4 concentrations lower than 2.5 mg/L after 2.5 h and in undetectable concentrations after 4-5 h of reaction. The main product of the reductive dehalogenation of CCl_4 by $Na_2S_2O_4$ was found to be the trichloromethanesulfinate ($CCl_3SO_2^-$) anion.

Carbon tetrachloride has been widely recognized as a persistent ground-water and air pollutant. Because of its well known properties as a potent hepatotoxin,[1] the search for methods aimed at its safe elimination has become an area of notable interest. A number of reactions aimed at carrying out the reductive dehalogenation of CCl_4 into environmentally friendly compounds have been previously reported.[2] In the present study, $Na_2S_2O_4$ was investigated as a potential reducing agent for CCl_4 because of its reducing power in basic solutions ($E° = -1.12$ V). In fact, dithionite has been previously studied as a reductant for iron in aquifers with iron-bearing clay minerals.[3] It is interesting, however, that the direct reaction between $Na_2S_2O_4$ and CCl_4 has not been previously studied. The present study, to the best of our knowledge, is the first report presenting evidence for the direct reduction of CCl_4 by $Na_2S_2O_4$.

Experiments were conducted in 70 mL threaded-mouth glass reaction vessels equipped with a sidearm Teflon stopcock. Gas tight sealing was achieved with a Teflon Mininert® valve (Alltech). The reductive dehalogenation of CCl_4 was assayed in 65 mL buffered mixtures consisting of aqueous CCl_4 (650 mg/L) and 1.1 mmol of $Na_2S_2O_4$. Aqueous solutions of CCl_4 were prepared by micro syringe addition of 33 μL of CCl_4 to previously degassed 0.10 M phosphate buffer, pH 7.50, through the septum of the Mininert® valve, followed by stirring to achieve dissolution. Reductive dehalogenation was initiated by injection of 1 mL of anaerobic $Na_2S_2O_4$ (1.1 mmol/mL) via the Mininert® valve. The concentration of CCl_4 was monitored by gas chromatography-mass spectrometry (GC-MS). Sampling was performed with a 100 μm polydimethylsiloxane SPME fiber (Solid Phase Micro Extraction fiber; Supelco) and the sample analyzed with a Hewlett Packard GC-MS (HPG 1800A). Chloride concentrations were determined by ion chromatography with a Dionex-100 ion chromatograph. For NMR experiments, reductive dehalogenation was carried out as described above with $^{13}CCl_4$ (99%, Cambridge Isotope Laboratories). At the end of the reaction (5 h), 500 μL of the resultant solution was mixed with 100 μL D_2O to obtain a ^{13}C NMR spectrum with a 400 MHz *Unity Inova* spectrometer.

When $Na_2S_2O_4$ is added to an anaerobic aqueous solution of CCl_4 (650 mg/L), the concentration of the halogenated hydrocarbon gradually decreases to less than 2.5 mg/L after 2 h and to less than 0.5 mg/L after 5 h (Figure 1). Analysis of the reaction mixture by extraction with the polydimethylsiloxane SPME fiber, followed by GC-MS indicates that a small amount of chloroform ($CHCl_3$), less than 9 mg/L, is formed (Figure 1).

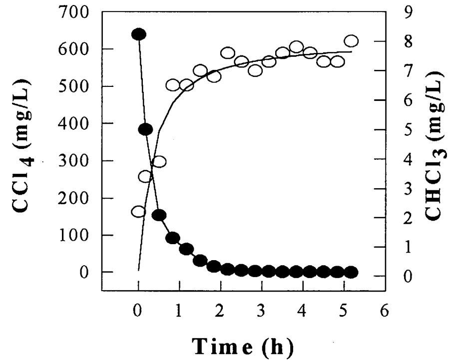

Figure 1. Disappearance of CCl_4 (•) and appearance of traces of $CHCl_3$ (○) in reaction mixtures consisting of 33 μL of CCl_4 and 1.1 mmol of $Na_2S_2O_4$ in 65 mL of phosphate buffer.

Analysis of the volatiles from the reaction mixture was accomplished by sampling the head space of the reaction vessel after acidifying the reaction mixture with 1 mL of 3 M H_2SO_4. Carbon dioxide (CO_2) and sulfur dioxide (SO_2) were detected. Control experiments, however, indicated that CO_2 is due to HCO_3^- formed upon dissolution of atmospheric CO_2 in the phosphate buffer and that CO_2 is not formed from the reaction between CCl_4 and dithionite. SO_2 is formed from SO_3^{2-} and $S_2O_4^{2-}$ upon acidification. The GC-MS analysis of the head space from reaction mixtures in which $^{13}CCl_4$ was reductively dehalogenated with $Na_2S_2O_4$ clearly indicated that ^{13}CO is not formed during the reaction as evidenced by the absence of a peak at $m/z = 29$.

Results from the analysis of possible nonpolar extractable products and from analysis of potential volatile products indicated that the carbon-containing product of the reductive dehalogenation may be a water soluble ionic species. To test this hypothesis, the solution resulting from reaction of $^{13}CCl_4$ with $Na_2S_2O_4$ was analyzed by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the reaction mixture (Figure 2) displays only one resonance with a chemical shift of 112 ppm. Since the NMR spectrum was obtained at the end of the reaction when $^{13}CCl_4$ was no longer detectable by GC-MS, it is possible to conclude that this resonance corresponds to the main carbon containing product of the reaction, the minor product being $CHCl_3$. The ^{13}C NMR spectrum was also acquired with the proton decoupler turned off in order to observe the multiplicity for the carbon signal which arises from ^1H-^{13}C coupling. The resulting spectrum was identical to that shown in Figure 2, thus indicating that the observed resonance corresponds to a quaternary carbon. The peak at $\delta = 112$ ppm was assigned to the carbon atom in $CCl_3SO_2^-$ based on the spectrum previously reported for this compound.[4]

Further evidence that the major product of the reaction is the anion $CCl_3SO_2^-$ comes from the amount of chloride formed during the reaction. Chloride concentration analyzed by ion chromatography indicated that 28% ± 2% of the chlorine present as CCl_4 was found as chloride in the final mixture, thus providing

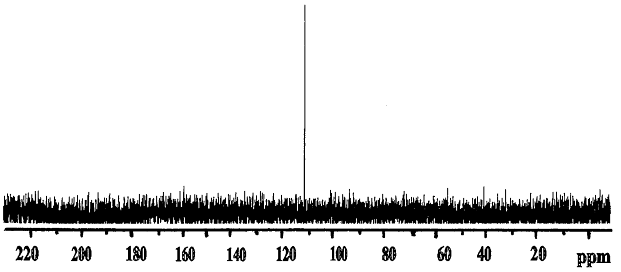

Figure 2. ^{13}C NMR spectrum of the product of the reaction between $Na_2S_2O_4$ and $^{13}CCl_4$.

further evidence for the formation of $CCl_3SO_2^-$.

In alkaline solutions, $S_2O_4^{2-}$ is known to be in equilibrium with the sulfonyl anion radical $SO_2^{\bullet -}$, as indicated by equation 1.[5]

$$2S_2O_4^{2-} \rightleftharpoons 2SO_2^{\bullet -} \tag{1}$$

Because $SO_2^{\bullet -}$ is extremely reactive, the dissociation depicted in equation (1) is believed to be the rate-limiting step in most reactions involving dithionite. It may therefore be possible to propose the following pathway for the reaction between $S_2O_4^{2-}$ and CCl_4.

$$CCl_4 + SO_2^{\bullet -} \rightleftharpoons Cl_3C^{\bullet} + SO_2 + Cl^- \tag{2}$$

$$Cl_3C^{\bullet} + SO_2^{\bullet -} \rightleftharpoons CCl_3SO_2^- \tag{3}$$

The formation of traces of $CHCl_3$ can be explained by reactions 4 and 5.

$$Cl_3C^{\bullet} + SO_2^{\bullet -} \rightleftharpoons Cl_3C{:}^- + SO_2 \tag{4}$$

$$Cl_3C{:}^- + H_2O \rightleftharpoons CHCl_3 + OH^- \tag{5}$$

Recently, an interesting initiator system for the polymerization of methyl methacrylate consisting of N-benzyl quinolinium chloride (BQ^+Cl^-)-$Na_2S_2O_4$-CCl_4 was reported.[6] The polymerization in this system was proposed to occur via the formation of N-benzyl-1,4-dihydroquinoline-4-sulfinate (BQ-sulfinate) upon reaction between BQ^+Cl^- and $Na_2S_2O_4$. BQ-sulfinate is subsequently transferred to the organic phase where it reacts with CCl_4 to form BQ^+ and $Cl_3C^{\bullet}$, which initiates the polymerization.[6] In light of the evidence presented in this report for the direct reaction between CCl_4 and $Na_2S_2O_4$ to produce $Cl_3C^{\bullet}$, this mechanism may be open to reinterpretation.

In summary, this is the first report documenting the reductive dehalogenation of CCl_4 by $S_2O_4^{2-}$ to produce the trichloromethanesulfinate anion, chloride ion and traces of chloroform. Once the trichloromethanesulfinate anion is formed it may be removed from water by an ion exchange process.

Studies currently underway in our laboratory also indicate that dithionite reduces a saturated solution of hexachloroethane to produce non-detectable concentrations of hexachloroethane in 4 h with the accumulation of tetrachloroethylene, which indicates that the later is unaffected by sodium dithionite.

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