

## Note

# Preparation of $^{14}\text{C}_2$ -*cis*-1,2-dichloroethylene from $^{14}\text{C}_2$ -trichloroethylene using a cobalt porphyrin catalyst

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## Summary

A protocol for producing  $^{14}\text{C}_2$ -*cis*-1,2-dichloroethylene ( $^{14}\text{C}_2$ -*cis*-DCE) from  $^{14}\text{C}_2$ -trichloroethylene ( $^{14}\text{C}_2$ -TCE) was developed as an economical alternative to commercial, custom synthesis of  $^{14}\text{C}_2$ -*cis*-DCE. The method uses 5,10,15,20-tetrakis-(4-carboxyphenyl) porphyrin cobalt(II) as a catalyst in the presence of titanium(III) citrate to convert  $^{14}\text{C}_2$ -TCE to  $^{14}\text{C}_2$ -*cis*-DCE as shown in Figure 1. A purge-and-trap technique was used to isolate  $^{14}\text{C}_2$ -*cis*-DCE to provide a methanolic stock solution of high purity (97% *cis*-DCE). The overall  $^{14}\text{C}_2$ -*cis*-DCE yield of the process was approximately 53%. Copyright © 2005 John Wiley & Sons, Ltd.

**Key Words:** trichloroethylene; dichloroethylene; carbon 14; cobalt porphyrin catalyst

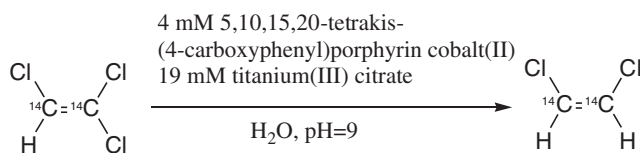
## Introduction

Trichloroethylene (TCE) is a widely occurring pollutant whose fate in the environment has been extensively studied. 1,2-Dichloroethylene (1,2-DCE) isomers are daughter products of TCE that are produced in many environmental situations, but they have not been studied as extensively as TCE. While both *cis* and *trans* isomers of 1,2-DCE have been observed in the environment, *cis*-1,2-DCE is the most prevalent product of TCE biodegradation.<sup>1–4</sup>

$^{14}\text{C}_2$ -TCE has been used as an effective tool to investigate the fate of TCE in environmental systems.<sup>5–7</sup> While  $^{14}\text{C}_2$ -TCE is commercially available,

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Contract/grant sponsor: Minnesota Water Resources Center; contract/grant number: 2004MN48B



**Figure 1.** Conversion of TCE to *cis*-1,2-DCE with a cobalt porphyrin catalyst

$^{14}\text{C}_2$ -DCE must be custom synthesized.<sup>8</sup> The cost of custom synthesis can be considerable, and the resultant product may be a mixture of both *cis* and *trans* isomers.<sup>9,10</sup> We have developed a protocol for converting  $^{14}\text{C}_2$ -TCE to  $^{14}\text{C}_2$ -*cis*-DCE with a yield of approximately 53%. This protocol will provide an economical alternative for synthesis of  $^{14}\text{C}_2$ -DCE for studies concerning the fate of this important pollutant.

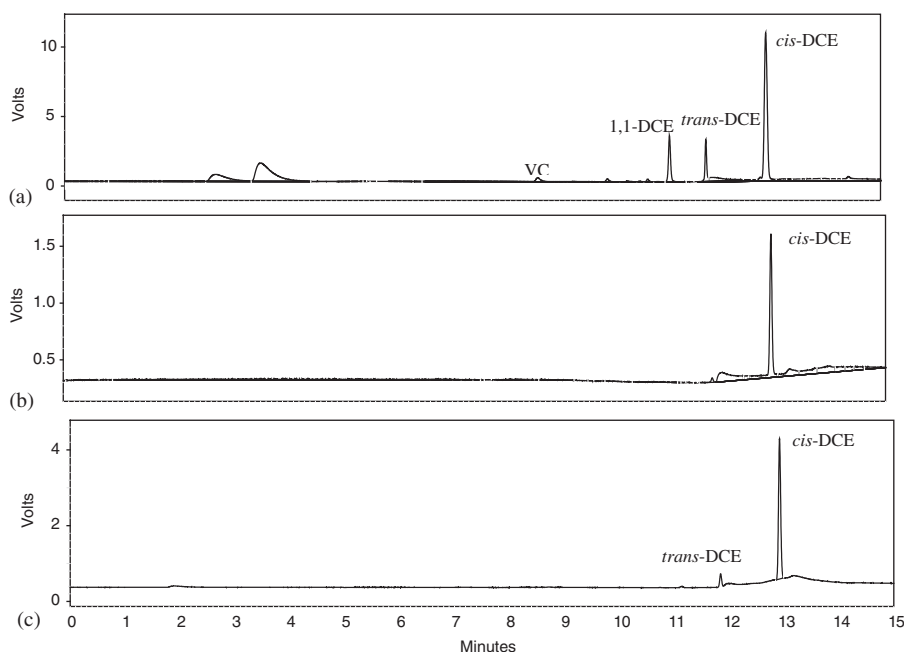
### Results and discussion

The preparation of  $^{14}\text{C}_2$ -*cis*-DCE was performed through aqueous-phase reductive dechlorination (hydrogenolysis) of  $^{14}\text{C}_2$ -TCE by Ti(III) citrate mediated by a water-soluble catalyst, 5,10,15,20-tetrakis-(4-carboxyphenyl) porphyrin cobalt (II), as depicted in Figure 1. The reaction reached completion in approximately 19 h, resulting in the production of 4.1  $\mu\text{mol}$  of *cis*-1,2-DCE, 0.2  $\mu\text{mol}$  of 1,1-DCE, 0.2  $\mu\text{mol}$  of *trans*-1,2-DCE, and 7 nmol of vinyl chloride (Figure 2(a)). Minor amounts of acetylene and ethylene were also produced. The *cis*-1,2-DCE yield of the reaction was 67%.

After purging, *cis*-1,2-DCE (0.3  $\mu\text{mol}$ ) was the only detectable product remaining in the reactor (Figure 2(b)). The radioactivity recovery for the experiment was 77% (Table 1), with 52% of the radiolabel being recovered from the cold trap. Analysis of the contents of the cold trap indicated that *cis*-1,2-DCE (3.2  $\mu\text{mol}$ ) was the dominant compound in the trap, and was accompanied by 98 nmol of *trans*-1,2-DCE (Figure 2(c)). The overall *cis*-1,2-DCE yield of the procedure was 53%, and the total carbon recovery was 58% (Table 2).

### Experimental

Reactions were conducted in 40 ml borosilicate serum bottles. Serum bottles were assembled in an anaerobic glove bag (93%  $\text{N}_2$ , 7%  $\text{H}_2$ , Coy Laboratory Products, Grass Lake, MI) and contained 25 ml of deoxygenated nanopure water, 4 mM 5,10,15,20-tetrakis-(4-carboxyphenyl) porphyrin cobalt (II) catalyst (Porphyrin Systems, Lübeck, Germany), and 19.2 mM Ti(III) citrate. The pH of the solution was then adjusted to 9 using deoxygenated 1 M potassium hydroxide solution. The bottles were then capped and sealed with PTFE septa, removed from the glove bag, and spiked with a mixture of cold TCE (3.0  $\mu\text{mol}$ ) and  $^{14}\text{C}_2$ -TCE (17.66  $\mu\text{Ci}$ , Sigma-Aldrich, Milwaukee, WI).



**Figure 2.** FID chromatograms for product distributions: (a) in serum bottle upon completion of reaction, (b) in serum bottle after 75 min of purging with argon, and (c) in methanol from the cold trap

**Table 1.** Radioactivity balance for conversion of  $^{14}\text{C}_2\text{-TCE}$  to  $^{14}\text{C}_2\text{-cis-1,2-DCE}$

	Activity ( $\mu\text{Ci}$ )	Percentage of initial activity (%)
Residual activity in reactor	4.19	24
Activity in cold trap (MeOH)	9.28	52
Activity in front carbon bed	0.125	0.7
Activity in rear carbon bed	0.023	0.1
Total activity recovered	13.53	77
Initial activity	17.66	100

The bottles were then placed on a magnetic stir plate. Headspace samples (100  $\mu\text{l}$ ) were collected using a gastight syringe and analyzed using a ThermoQuest Trace GC gas chromatograph equipped with a GS Gas-Pro column and flame ionization detector (FID). Upon completion of the reaction, the serum bottles were purged with argon gas for 75 min. The purged gas was passed through a U-tube apparatus immersed in a bath of dry ice and isopropanol ( $T = -78^\circ\text{C}$ ), followed by an activated carbon filter. Upon completion of purging, methanol (1 ml) was added to the U-tube and the apparatus was inverted to facilitate mixing. The methanol solution was then

**Table 2. Carbon balance for conversion of  $^{14}\text{C}_2$ -TCE to  $^{14}\text{C}_2$ -*cis*-1,2-DCE**

	Amount ( $\mu\text{mol}$ )	Percentage of initial TCE (%)
<i>Pre-reaction</i>		
TCE	6.08	100
<i>cis</i> -1,2-DCE	0	0
<i>Post-reaction</i>		
TCE	0	0
<i>cis</i> -1,2-DCE	4.1	67
<i>trans</i> -1,2-DCE	0.23	3.8
1,1-DCE	0.17	2.8
Vinyl chloride	0.007	0.1
<i>Post-purge</i>		
TCE (aq)	0	0
<i>cis</i> -1,2-DCE (aq)	0.3	4.9
TCE (MeOH)	0	0
<i>cis</i> -1,2-DCE (MeOH)	3.2	53
<i>trans</i> -1,2-DCE (MeOH)	0.098	1.6

removed from the U-tube, placed in a 1.5 ml autosampler vial and capped with a PTFE septum.

An aqueous sample (1 ml) was collected from the serum bottle, added to scintillation cocktail, and analyzed for residual radioactivity using a Packard T2100 liquid scintillation counter (LSC). A sample of the methanol solution (10  $\mu\text{l}$ ) was added to a sealed vial (1.5 ml) containing 500  $\mu\text{l}$  nanopure water. A headspace sample from the vial (100  $\mu\text{l}$ ) was analyzed via GC-FID to identify trapped products. A 10  $\mu\text{l}$  sample of the methanol solution was added to scintillation cocktail and analyzed via LSC. The activated carbon trap was extracted overnight using hexane (15 ml). Samples of the hexane extraction solution were analyzed via LSC.

Standards (0–500  $\mu\text{M}$ ) for verification of retention times and quantification of TCE, 1,1-DCE, *trans*-1,2-DCE and *cis*-1,2-DCE via GC-FID were constructed in 40 ml serum bottles containing 25 ml nanopure water. *cis*-1,2-DCE standards (0–10  $\mu\text{M}$ ) were also prepared in methanol and diluted in 500  $\mu\text{l}$  nanopure water for verification of retention times and quantification of trapped products.

## Conclusion

While the *cis*-1,2-DCE carbon yield (53%) corresponded well with the radioactivity recovered from the cold trap (52%), the overall carbon recovery (58%) was much lower than the radioactivity balance (77%). This difference appeared in the serum bottle after purging, which contained 24% of the radioactivity, whereas only 4.9% of the carbon was detected by FID. A portion of the carbon (and, hence, radioactivity) may have been bound to the

catalyst due to exhaustion of the reductant. Although bound carbon compounds would be nonvolatile and undetectable via FID, bound radioactivity would still be detected via LSC. While the identity of the catalyst-bound species is unknown, other research has provided evidence for a reductive dechlorination pathway involving cobalt-bound species.<sup>11</sup> We have also observed the formation of a bound monochlorinated species in similar systems.<sup>12</sup>

The favorable yield (53%) of the process described herein and the purity of its resultant product make it an attractive alternative to commercial synthesis. This protocol can serve as a cost-effective route to  $^{14}\text{C}_2\text{-cis-1,2-DCE}$ , thus making fate studies concerning this important environmental pollutant more economically feasible.

### Acknowledgements

This work was supported by Grant 2004MN48B from the United States Geological Survey through the Minnesota Water Resources Center.

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