Electronic Supporting Information

Dechlorination of chlorinated ethylenes by a photochemically generated iron(0) complex

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Kinetic data fitting (MATLAB).

Chlorinated ethylene growth and decay. Growth and decay k values were determined by globally fitting GC-MS or NMR data to kinetic models in MATLAB. The equations (E1-E3) that describe the kinetic behavior of the chlorinated ethylenes are based on the kinetic model in Scheme 3.

$$[TCE]_t = [TCE]_0 e^{-(k_1+k_2)t} \quad \text{(Equation E1)}$$

$$[cDCE]_t = \frac{k_1[TCE]_0}{k_3-k_1-k_2}\left(e^{-(k_1+k_2)t} - e^{-k_3 t}\right) \quad \text{(Equation E2)}$$

$$[tDCE]_t = \frac{k_2[TCE]_0}{k_4-k_1-k_2}\left(e^{-(k_1+k_2)t} - e^{-k_4 t}\right) \quad \text{(Equation E3)}$$

Matrix approach to ascertaining D incorporation. In order to determine the deuterium incorporation present in photoproducts, a matrix approach was chosen to convert ion intensities into the number of deuterium atoms present. Based on the ion intensities of the parent ion fragment of the species of interest, a theoretical matrix (A) was generated. This matrix was calculated by extrapolating the relative ion intensities of the fragment without deuterium to relative ion intensities of the fragment with a defined number of deuterium atoms (Tables E1 and E2). It is reasonable to use the same isotope pattern, shifted by one mass unit, for each deuterated analog, since the intensity pattern is set almost entirely by $^{12}C/^{13}C$ and $^{35}Cl/^{37}Cl$ abundances.

Table E1. Theoretical matrix (A1) containing relative ion intensities for the mass spectrum fragment 96 of DCE, which can contain up to two deuterium atoms. The fragment without deuterium consists of masses m/z 96 (100%), 97 (2.2%), and 98 (64.8%).

		number of D atoms		
		0 D	1 D	2 D
masses (m/z)	96	1	0	0
	97	0.022	1	0
	98	0.648	0.022	1
	99	0.014	0.648	0.022
	100	0.105	0.014	0.648
	101	0.002	0.105	0.014
	102	0	0.002	0.105
	103	0	0	0.002

Table E2. Theoretical matrix (A2) containing relative ion intensities for the mass spectrum fragment 62 of VC, which can contain up to three deuterium atoms. The fragment without deuterium consists of masses m/z 62 (100%), 63 (2.2%), 64 (32.4%), and 65 (0.7%).

		number of D atoms			
		0 D	1 D	2 D	3 D
masses (m/z)	62	1	0	0	0
	63	0.022	1	0	0
	64	0.324	0.022	1	0
	65	0.007	0.324	0.022	1
	66	0	0.007	0.324	0.022
	67	0	0	0.007	0.324
	68	0	0	0	0.007

For each deuterated product generated during a photolysis experiment, the integrated peak area for each m/z value in the parent ion fragment was extracted. The extracted area integrations were normalized to the highest mass to generate a “photolysis column vector” (B).

Table E3. "Photolysis column vector" (B1) containing relative ion intensities extracted from the mass spectrum for deuterated cDCE as a product of the reaction between **1-D_2** and TCE at 1 min.

	reaction product
masses (m/z)	relative peak areas
96	0.172
97	1
98	0.129
99	0.638
100	0.0170
101	0.0889
102	0
103	0

The number of deuterium atoms contained in the product is then calculated by weighting the theoretical matrix (A) so that it gives the vector with the extracted relative ion intensities of the mass fragment of the product (B); that is, the theoretical matrix (A) multiplied with a weighting vector (X) gives the photolysis column vector (B).

theoretical matrix (A) × weighting vector (X) = photolysis column vector (B)

$$AX = B$$

The weighting vector (X) can be calculated with the mldivide (\) function in MATLAB.

$$X = A \setminus B$$

The weighting vector (X) is the least-squares solution to the overdetermined system of equations AX = B. From the resulting weighting vector (X), the values were normalized to total 100%.

Table E4. Weighting vector (X) calculated for deuterated cDCE as a product of the reaction between **1-D_2** and TCE, containing the percentage of the cDCE products containing a certain number of deuterium atoms.

	number of deuterium atoms		
	0 D	1 D	2 D
%	15.1	85.9	0

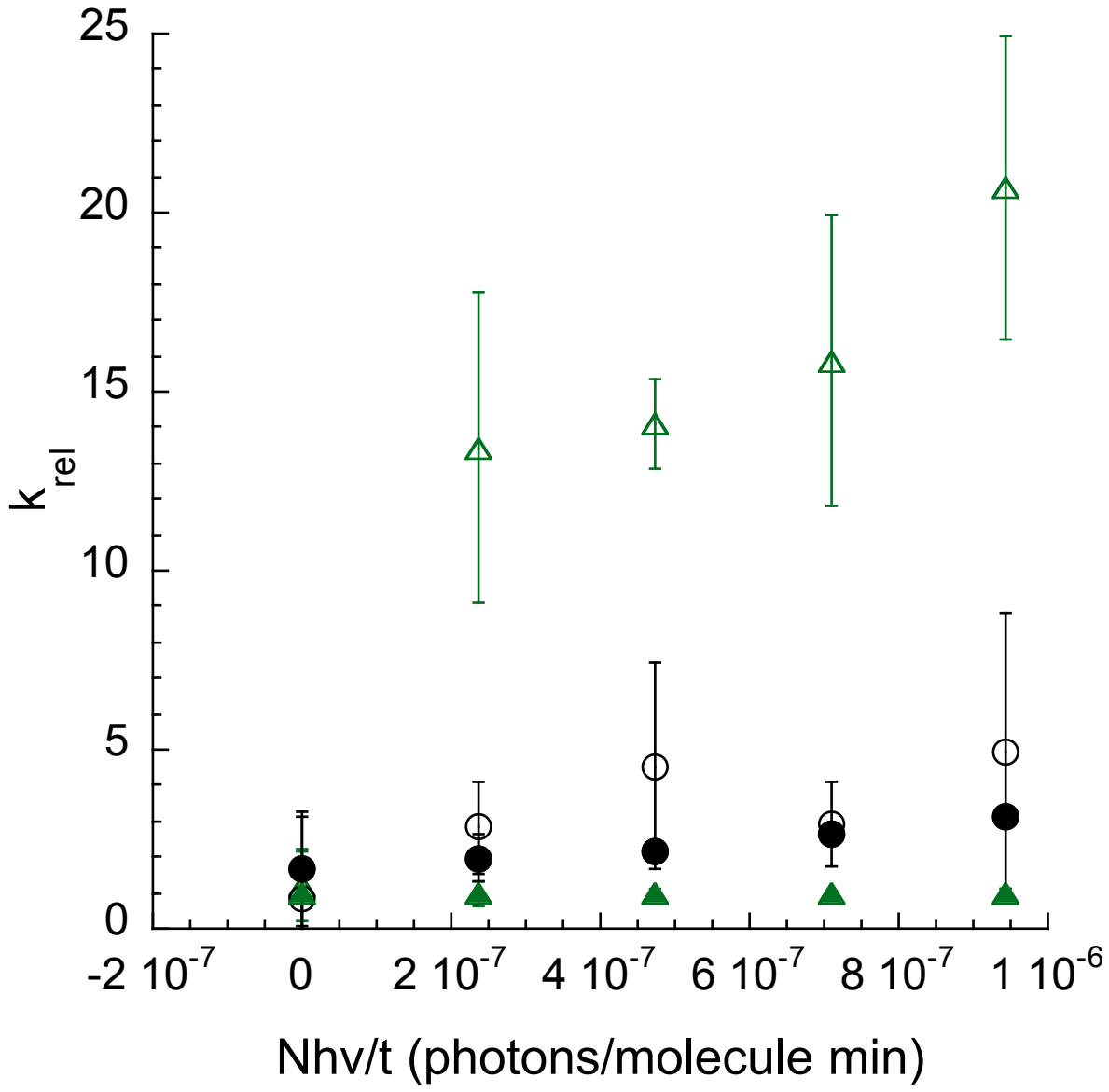

Figure E1. Dependence of k values, relative to k_3, of k_1 (Δ), k_2 (°), k_3 (▲), and k_4 (•) on amount of irradiation at 360 nm. Initial concentrations of TCE were 2.3-2.7 mM, 3.2-3.5 mM for cDCE, and 2.9-6.3 mM for tDCE. Initial concentration of **1** was 54 mM.

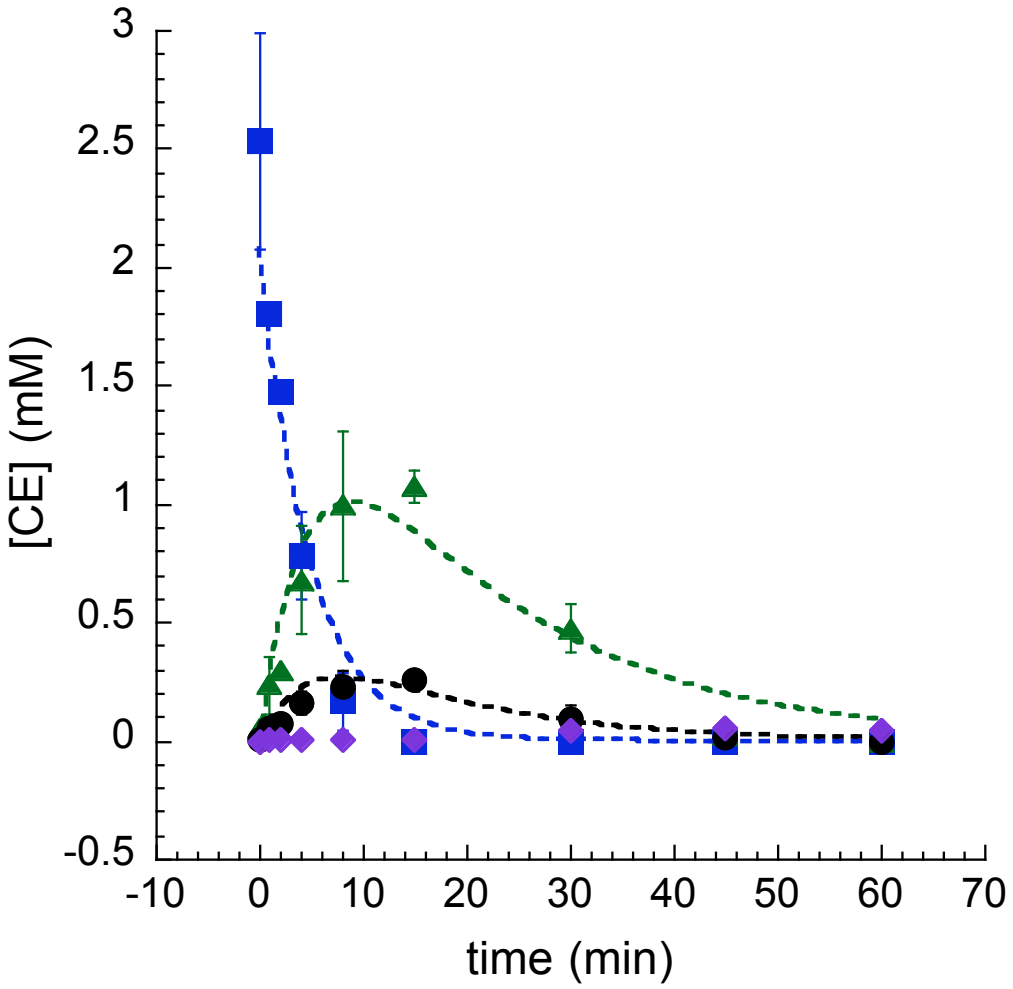

Figure E2a. Decay of TCE (■) upon photolysis at 360 nm with **1** (52.3 mM) and 30 mL added H_2. The observed photoproducts are cDCE (▲) and tDCE (•), which both decay to VC (◆).

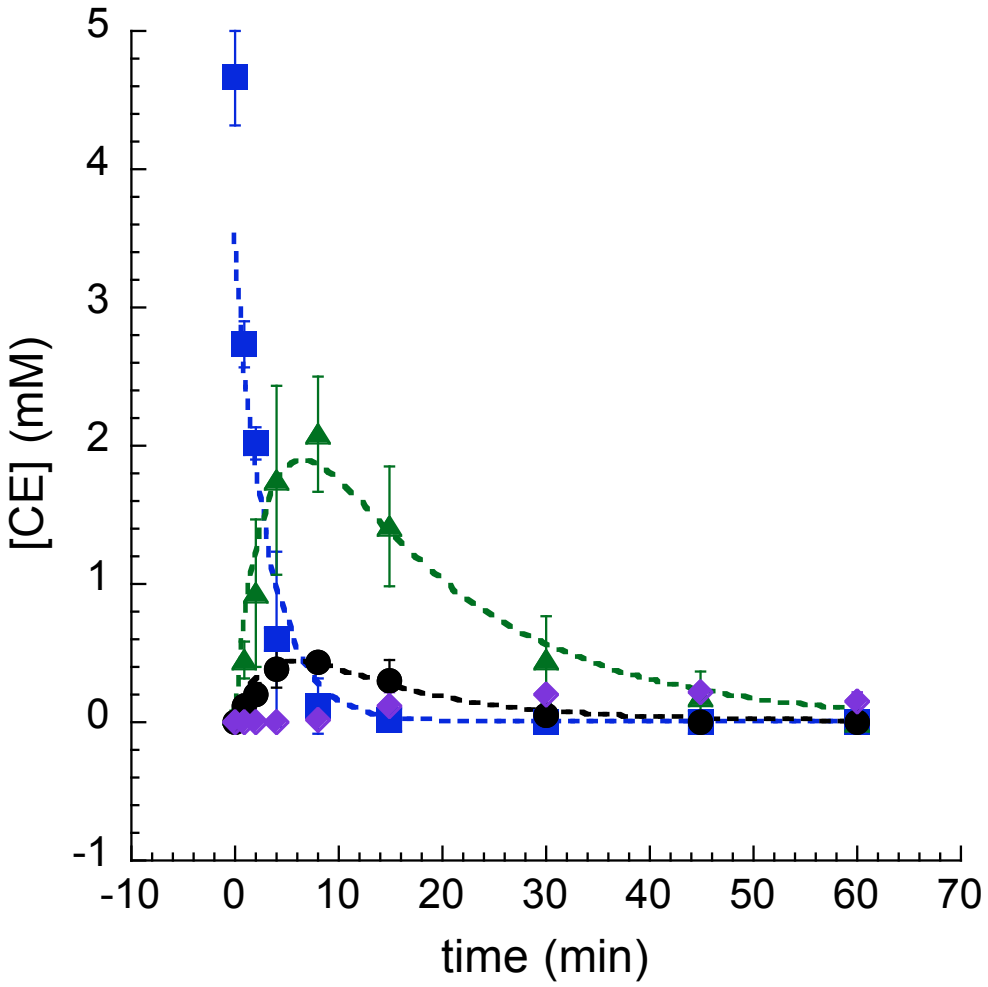

Figure E2b. Decay of TCE (■) upon photolysis at 360 nm with **1** (52.3 mM) and 28 mL added D_2. The observed photoproducts are cDCE (▲) and tDCE (•), which both decay to VC (◆).