SUPPORTING INFORMATION

Oxidation of Chlorinated Ethenes by Heat Activated Persulfate: Kinetics and Products

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Contents

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Figure S1

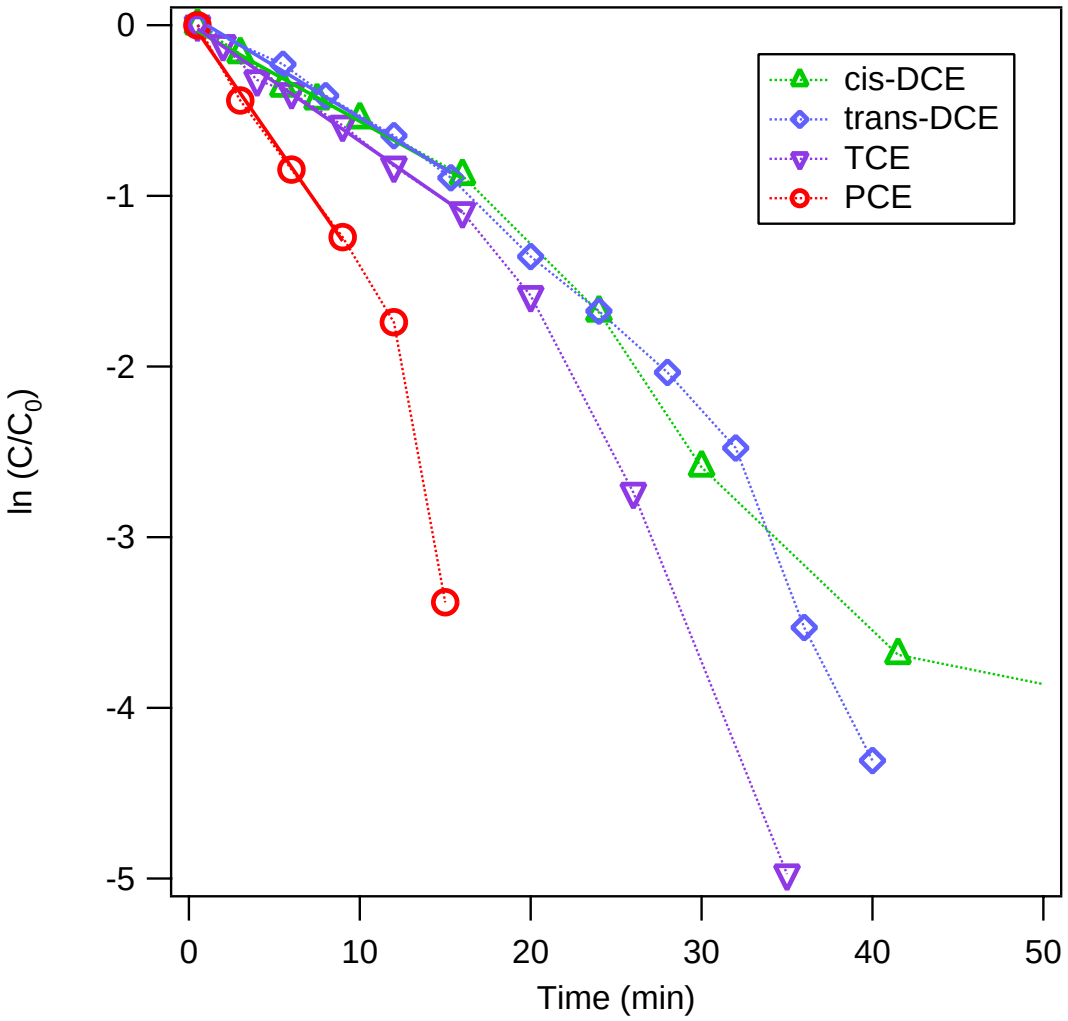

Figure S1: Concentration over extended time periods, showing non-pseudo first-order behavior at longer experimental times. Experimental conditions: Unbuffered DI water, 70 ^{o}C, 10:1 molar ratio of $Na_2S_2O_8$ and chlorinated ethenes, concentration of PCE = 0.0014 M, concentration of the other chlorinated ethenes = 0.002 M.

Figure S2

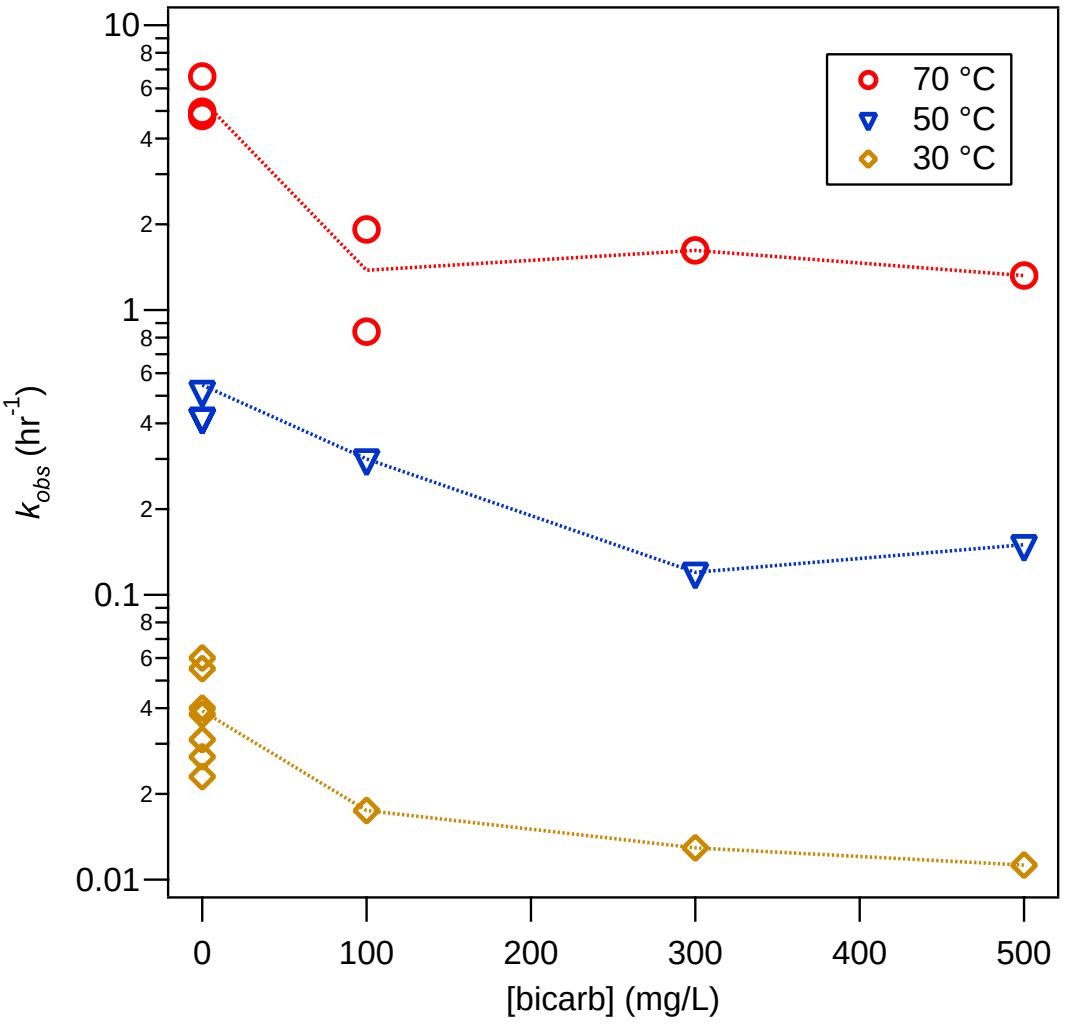

Figure S2. Effect of bicarbonate concentration on k_{obs} for PCE oxidation by persulfate activated at three temperatures. Conditions: 4.5×10^{-5} M PCE, 4.5×10^{-4} M $Na_2S_2O_8$.

Figure S3

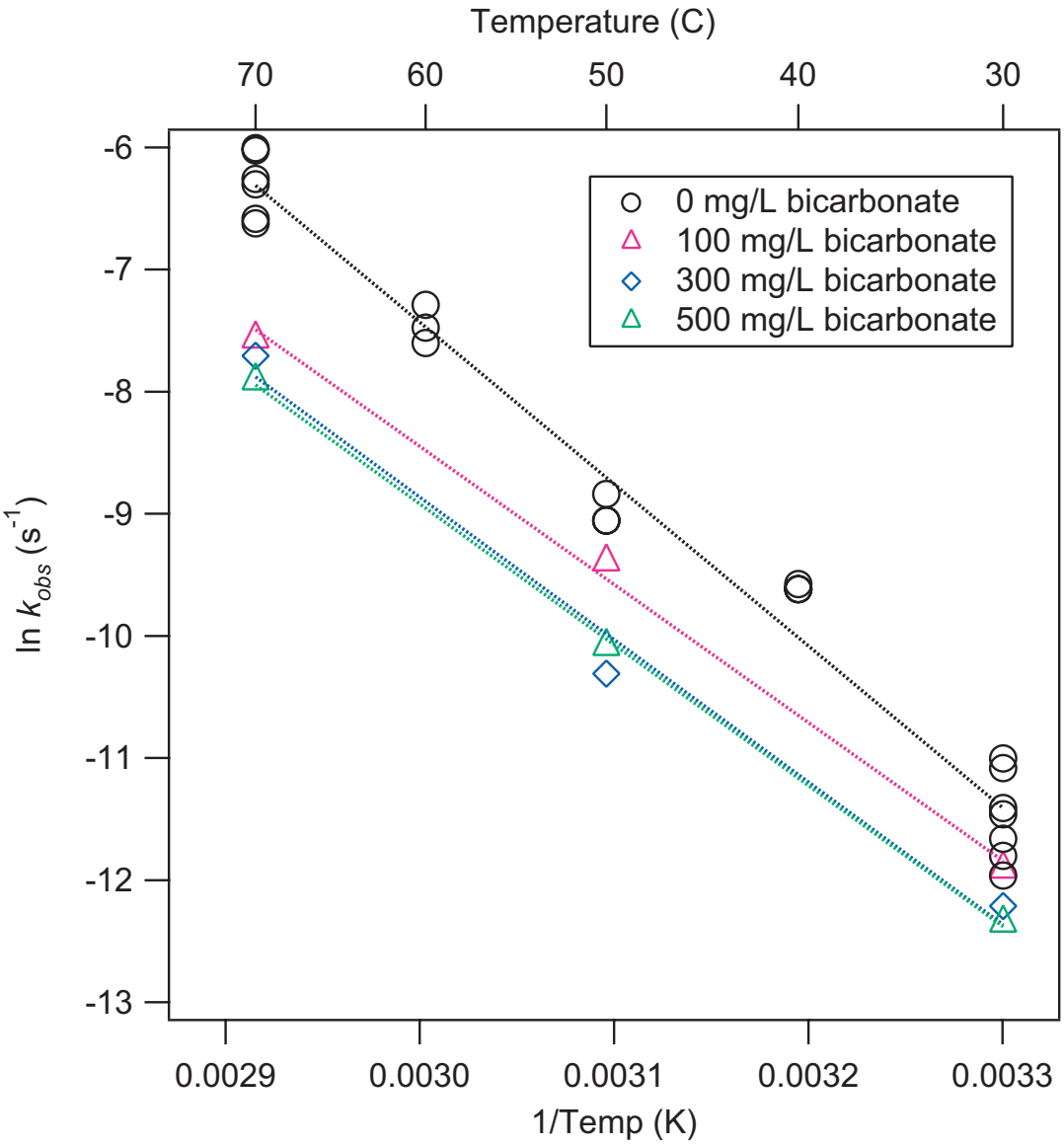

Figure S3: Arrhenius plots of the oxidation of PCE by persulfate in the presence of various concentrations of bicarbonate. Experimental conditions: 4.5×10^{-5} M PCE, 4.5×10^{-4} M $Na_2S_2O_8$. The data for 0 mg/L bicarbonate are the same as the data in Figure 2 in the text. Values for the data shown here are in Table S2.

Figure S4

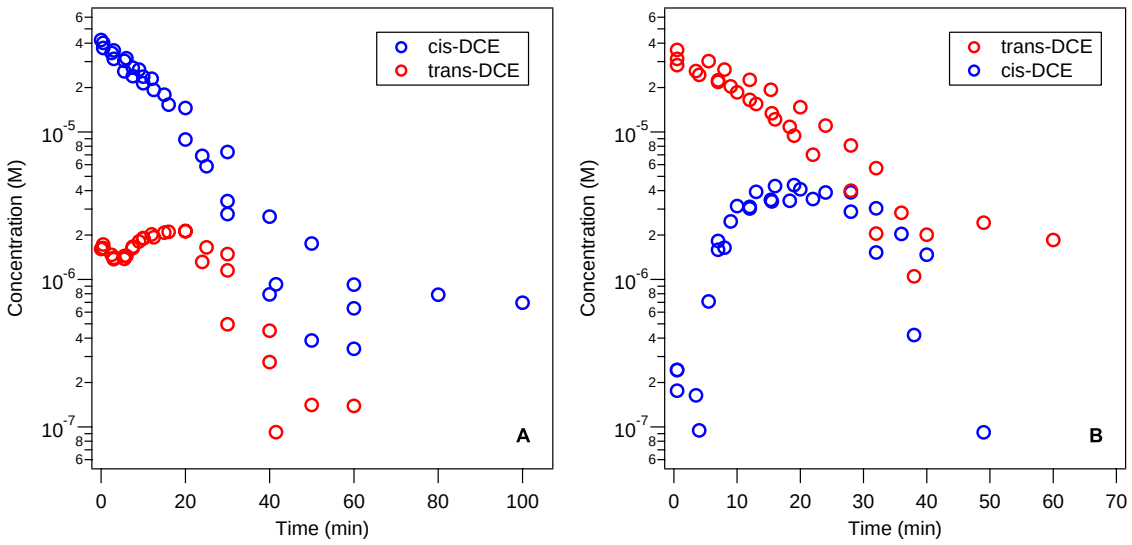

Figure S4: Concentration of cis-DCE and trans-DCE vs. time for A) the reaction of cis-DCE with persulfate and B) the reaction of trans-DCE with persulfate. Experimental conditions: unbuffered, triplicate experiments, 0.002 M dichloroethenes, 0.02 M $Na_2S_2O_8$, 70 ^oC.

Figure S5

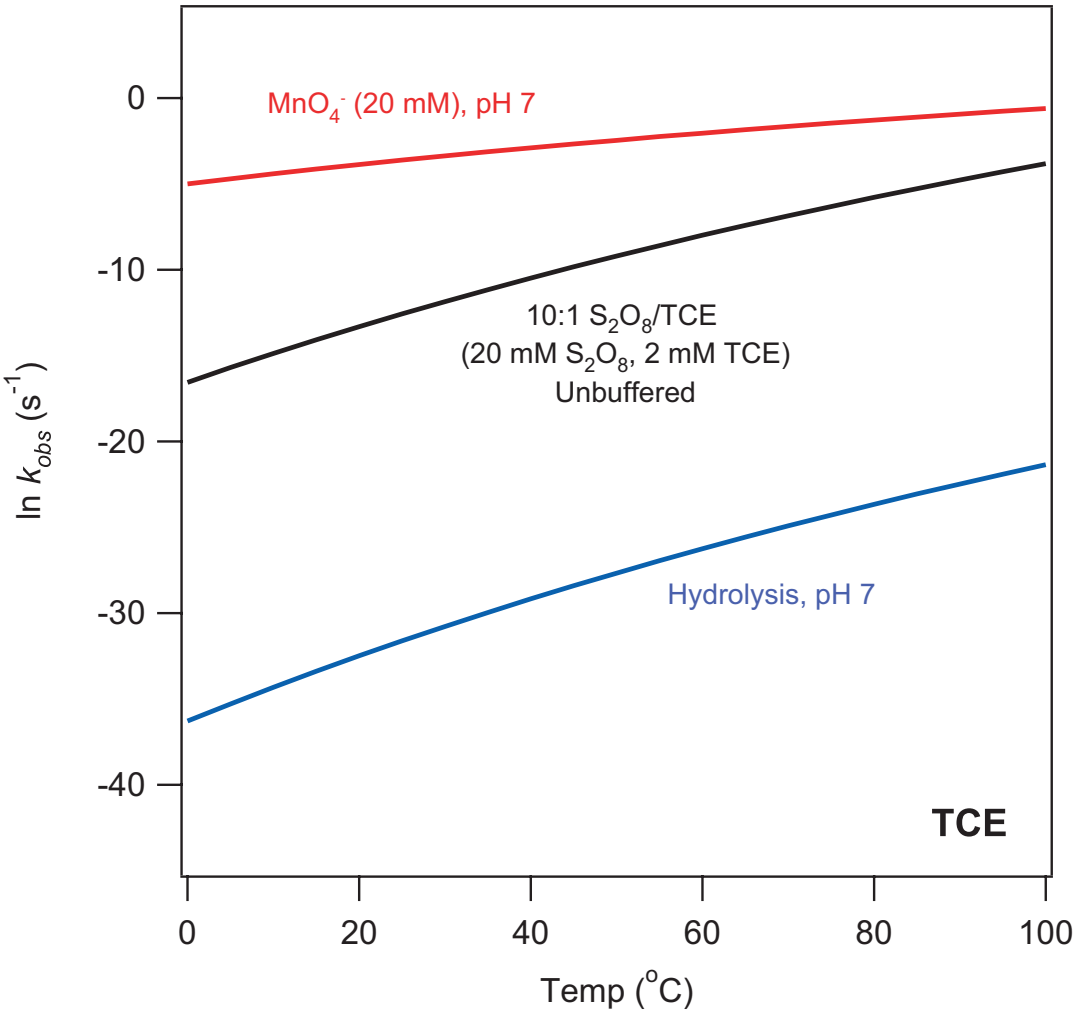

Figure S5: Comparison of three degradation processes as a function of temperature for TCE. The hydrolysis band was calculated using Arrhenius parameters obtained from (36). The permanganate band was calculated using Arrhenius parameters obtained from (35). The persulfate band was calculated using Arrhenius parameters obtained from experiments with 20 mM $Na_2S_2O_8$ and 2 mM TCE.

Figure S6

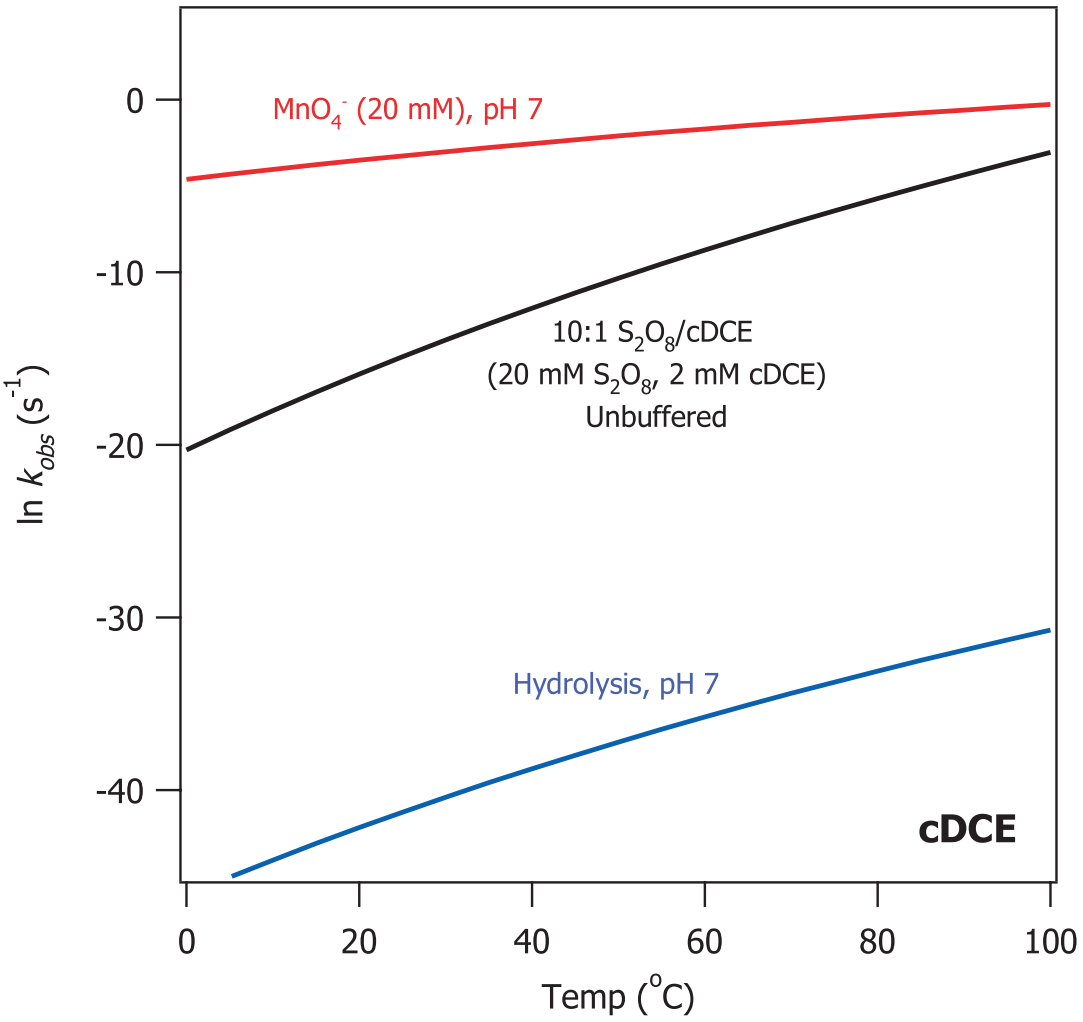

Figure S6: Comparison of three degradation processes as a function of temperature for cis-DCE. The hydrolysis band was calculated using Arrhenius parameters obtained from (36). The permanganate band was calculated using Arrhenius parameters obtained from (35). The persulfate band was calculated using Arrhenius parameters obtained from experiments with 20 mM $Na_2S_2O_8$ and 2 mM cis-DCE.

Figure S7

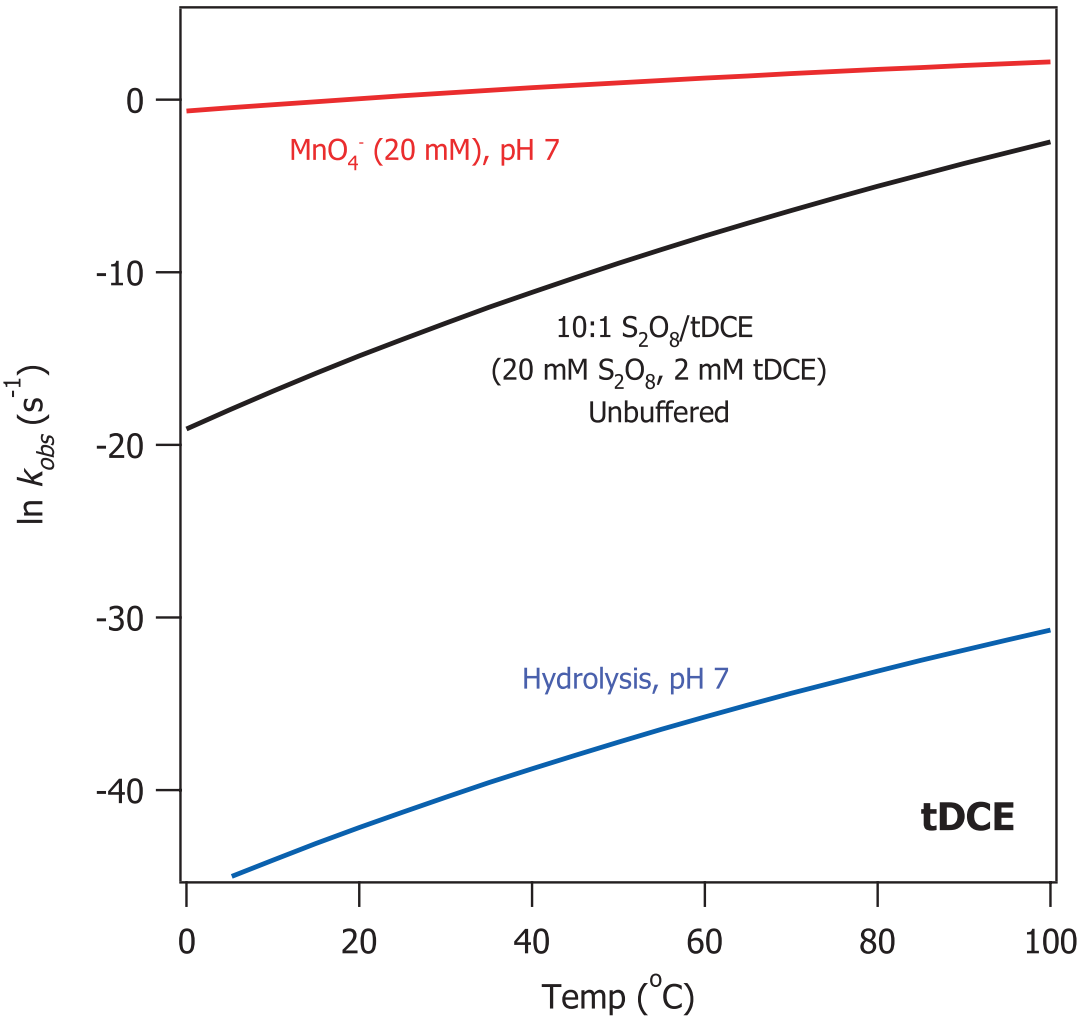

Figure S7: Comparison of three degradation processes as a function of temperature for trans-DCE. The hydrolysis band was calculated using Arrhenius parameters obtained from (36). The permanganate band was calculated using Arrhenius parameters obtained from (35). The persulfate band was calculated using Arrhenius parameters obtained from experiments with 20 mM $Na_2S_2O_8$ and 2 mM trans-DCE.

Table S1. k_{obs} and corresponding activation parameters for all 4 chlorinated ethenes

Compound	30°C		40 °C		50 °C		60 °C		70 °C		ln *A* (s^{-1})	E_A ($kJmol^{-1}$)
0.045 mM PCE	0.023 hr^{-1}	0.95	0.24 hr^{-1}	0.99	0.0087 min^{-1}	0.94	0.041 min^{-1}	0.98	0.11 min^{-1}	0.97	29 ± 2	101 ± 4
	0.027 hr^{-1}	0.97	0.25 hr^{-1}	0.96	0.0070 min^{-1}	0.91	0.030 min^{-1}	0.98	0.080 min^{-1}	0.99		
	0.031 hr^{-1}	0.97	0.24 hr^{-1}	0.96	0.0070 min^{-1}	0.97	0.034 min^{-1}	0.94	0.083 min^{-1}	0.97		
	0.060 hr^{-1}	0.99	----		----		----		----			
	0.055 hr^{-1}	0.99	----		----		----		----			
0.0014 M PCE	0.038 hr^{-1}	0.99	----		----		----		0.148 min^{-1}	0.99		
	0.040 hr^{-1}	0.99	----		----		----		0.145 min^{-1}	0.98		
	----		----		----		----		0.115 min^{-1}	0.98		
0.002 M TCE	0.027 hr^{-1}	0.98	0.073 hr^{-1}	0.94	0.0046 min^{-1}	0.96	0.0211 min^{-1}	0.99	0.061 min^{-1}	0.99	31 ± 1	108 ± 3
	0.031 hr^{-1}	0.97	0.087 hr^{-1}	0.97	0.0045 min^{-1}	0.97	0.0184 min^{-1}	0.99	0.067 min^{-1}	0.99		
	0.026 hr^{-1}	0.99	0.076 hr^{-1}	0.93	0.0051 min^{-1}	0.96	0.0179 min^{-1}	0.99	0.069 min^{-1}	0.9		
0.002 M cis-DCE	0.0033 hr^{-1}	0.93	0.023 hr^{-1}	0.96	0.0017 min^{-1}	0.94	0.008 min^{-1}	0.91	0.056 min^{-1}	0.99	43 ± 2	144 ± 5
	0.0034 hr^{-1}	0.96	0.022 hr^{-1}	0.99	0.0016 min^{-1}	0.98	0.0054 min^{-1}	0.99	0.068 min^{-1}	0.98		
	0.0032 hr^{-1}	0.95	0.026 hr^{-1}	0.99	----		0.005 min^{-1}	0.80	0.057 min^{-1}	0.99		
0.002 M trans-DCE	0.0048 hr^{-1}	0.97	0.033 hr^{-1}	0.99	0.0030 min^{-1}	0.98	0.018 min^{-1}	0.98	0.050 min^{-1}	0.99	43 ± 1	141 ± 2
	0.0060 hr^{-1}	0.96	0.038 hr^{-1}	0.99	0.0030 min^{-1}	0.99	0.017 min^{-1}	0.98	0.058 min^{-1}	0.99		
	0.0056 hr^{-1}	0.97	0.032 hr^{-1}	0.97	----		0.017 min^{-1}	0.97	0.059 min^{-1}	0.98		

The R^2 values given after each rate constant are for linear regression on the ln concentration vs. time data for each experiment.

Table S2: k_{obs} and corresponding activation parameters for PCE with different concentrations of bicarbonate

Bicarbonate (mg L^{-1})	30°C	50°C	70°C	ln A (s^{-1})	E_A (kJ mol^{-1})
0	See Table S1	See Table S1	See Table S1	29 ± 2	101 ± 4
100	0.018	0.30	0.84	25 ± 2	94 ± 5
300	0.013	0.12	1.62	26 ± 5	97 ± 12
500	0.011	0.15	1.32	26 ± 1	96 ± 2