

OXIDATION OF CHLORINATED SOLVENTS BY PERMANGANATE

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INTRODUCTION

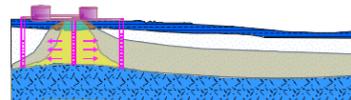
Both laboratory and field experiments have shown that potassium permanganate is able to oxidize common chlorinated ethylene like trichloroethylene (TCE) and tetrachloroethylene (PCE). Most of these experiments can be considered as a proof-of-concept that demonstrates the efficacy of the remedial concept rather than reaction pathways and kinetics. The goal of this study is to provide a detailed process-level understanding of the oxidative destruction of chlorinated ethylene by permanganate.

Objectives

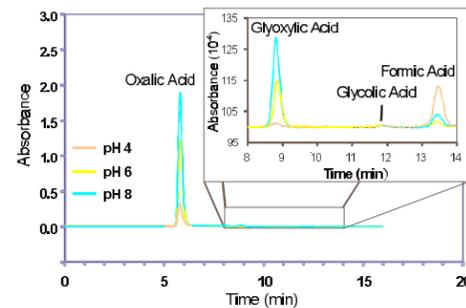
- ◆ Degradation Rate
- ◆ Products
- ◆ Dechlorination
- ◆ Reaction pathways and pH effect

Permanganate

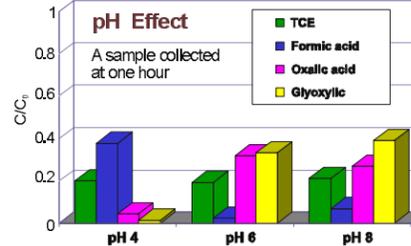
- ◆ Powerful to oxidize many organic compounds
- ◆ Not reactive with carbonate/bicarbonate
- ◆ Inexpensive \$3/kg
- ◆ Easy to implement



Chromatogram



REACTION PRODUCTS



Products

Four carboxylic acids, formic, oxalic, glyoxylic, and glycolic acids, were identified in the system as intermediate products. The final product is CO_2 .

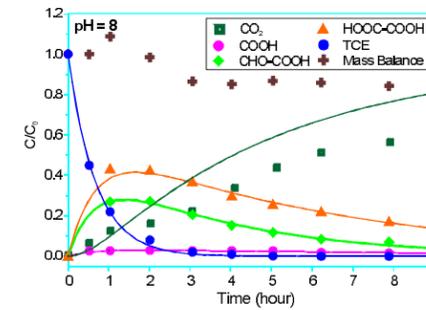
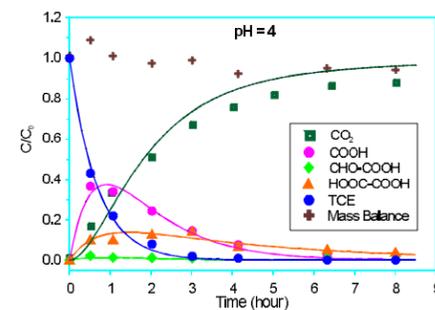
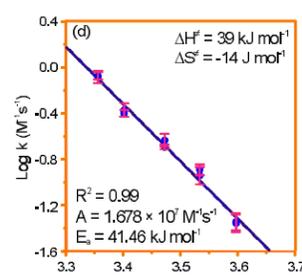
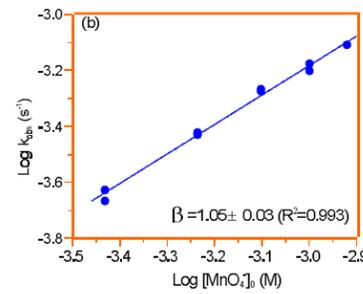
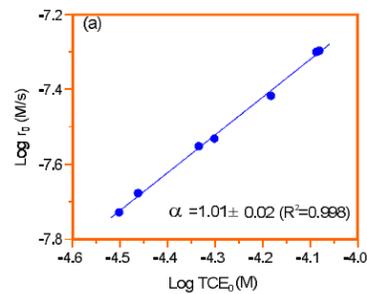
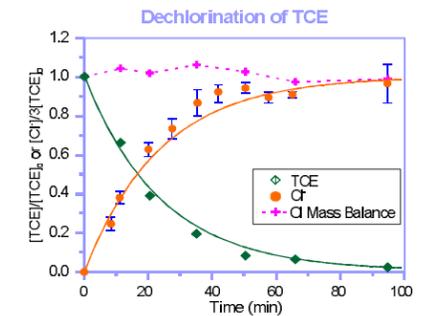
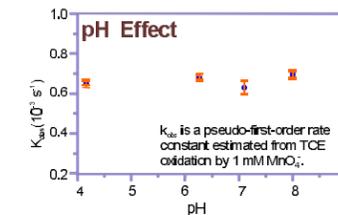
pH Effect

The pseudo-first-order rate constant (k_{obs}) has no strong correlation with pH. The TCE degradation is independent of pH.

Of intermediate products transformed from TCE, formic acid predominated at low pH, and Oxalic and glyoxylic acids at high pH.

Dechlorination

A complete dechlorination was achieved rapidly in oxidation of TCE (0.06 mM) by 1 mM MnO_4^- .



Reaction Order

$$r = -\frac{1}{\alpha} \frac{d[C_2Cl_nH_{4-n}]}{dt} = k[C_2Cl_nH_{4-n}]^\alpha [MnO_4^-]^\beta$$

(a) Initial rate versus initial TCE of 0.031-0.083 mM oxidized by 1mM MnO_4^- . The reaction order, α , with respect to TCE is unity.

(b) k_{obs} ($=k[MnO_4^-]^\beta$) versus initial MnO_4^- of 0.37-1.2 mM reacting with 0.078 mM TCE. The reaction order, β , is also unity.

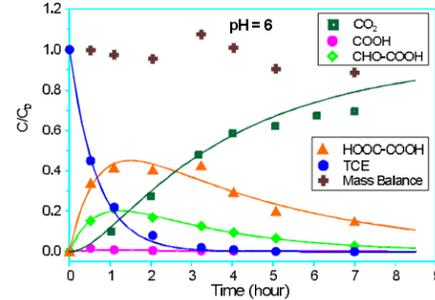
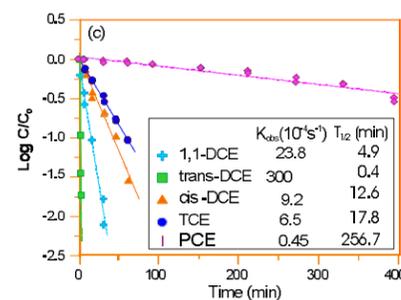
KINETICS

Degradation Rate

(c) Degradation of chlorinated ethylenes by 1 mM MnO_4^- .

Temperature Dependence

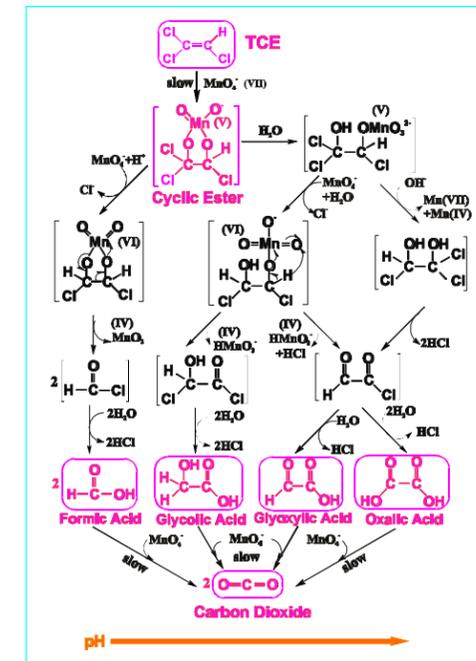
(d) Arrhenius plot for the oxidation TCE (0.06 mM) by MnO_4^- (1mM). Error bars are standard deviation for each 2nd-order rate constant k.



REACTION PATHWAYS

The TCE oxidation process involves three reaction steps: (1) the destruction of TCE to form an organometallic compound (hypomanganate ester), (2) the decomposition of the ester to various carboxylic acids, and (3) eventually the oxidation to the final product, CO_2 .

The initial reaction step is a rate-limiting step, which control the destruction rate of TCE. The fast reactions involved in the second step determine the nature of products.



CONCLUSIONS

- Chlorinated ethylenes can be rapidly degraded and the rate is inversely proportional to the number of chlorine substituents.
- TCE oxidation is a second-order reaction.
- The major intermediate products in TCE oxidation are formic, oxalic, and glyoxylic acids and final product is CO_2 .
- Oxidation process mainly involves three reaction steps. The destruction of TCE to cyclic complex is a rate-limiting step and independent of pH. The fast decomposition of cyclic complex involved in the second step determines the nature of intermediate products and is pH dependent. The final step controls the formation of CO_2 at a relatively slow rate.
- Chlorine was liberated immediately and completely after the formation of the complex.

ACKNOWLEDGEMENTS

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