

Aqueous Phase Oxidation: The Effect of Soil on Oxidation Kinetics

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ABSTRACT

The aqueous phase oxidation of *m*-xylene and tetrachloroethylene has been studied in a batch reactor over a temperature and pressure range of 523 to 563 K and 10.3 to 17.2 MPa, respectively, in the presence of a well-characterized soil. Oxidation rates have been compared to previously measured rates in the absence of soil. The soil has been found to have a serious inhibiting effect on *m*-xylene oxidation, but to have virtually no effect on the rate of tetrachloroethylene disappearance. The *m*-xylene inhibition is interpreted by postulating that the soil serves as a free radical scavenger, thus preventing the concentration of free radicals in solution from reaching the level required for the chain mechanism to become self-propagating. An alternate and substantially slower mechanism then becomes responsible for *m*-xylene oxidation in the presence of soil. In contrast, soil-free tetrachloroethylene oxidation is not thought to proceed by a free radical mechanism. Hence, the addition of the soil has no effect on its oxidation rate.

INTRODUCTION

Waste disposal methods such as landfilling, which were once considered safe, are now recognized as threats to the environment, and in certain cases to human life as well. One problem in particular is contaminated soil associated with abandoned disposal sites or chemical spills. Sites requiring decontamination range in size from a few cubic yards to many cubic miles. At present, the most common method of handling contaminated soils consists of excavation and transportation to "approved" sites for reburial.

Incineration provides a mechanism for true detoxification of contaminated soil, but at a cost which may exceed \$500 per ton of soil (1). Large quantities of energy are required to raise the temperature to the level necessary to support gas phase oxidation. If the contaminated soils are wet, much of the total energy is required to vaporize the large quantities of water present. In addition, there is concern over the formation and discharge of products of incomplete combustion (PICS) which accompany incineration.

Aqueous phase oxidation has been proposed as an alternative and potentially

more economical method for decontaminating soils. Energy requirements are much lower than for incineration because the oxidation temperature is lower and vaporization of water is avoided. The totally oxidized products are the same for both processes, although aqueous phase oxidation may produce some quantities of low molecular weight acids and aldehydes. Though oxidation rates are much slower in the aqueous phase, reduced energy requirements could make aqueous phase oxidation the process of choice in certain soil detoxification applications.

Regeneration of activated carbon is the only example to date in which aqueous phase oxidation has been used in the presence of a solid phase. In carbon regeneration applications the primary objective is to desorb and oxidize organic contaminants without producing major oxidation of the carbon itself. For example, Knopp et al., (2) report greater than 98% removal and oxidation of ethylene dichloride with less than 10% carbon oxidation at 240°C. In the case of soil decontamination greater operating flexibility would exist since there would be no particular need to minimize oxidation of the organic constituents of the soil.

This paper reports preliminary results of the effect of soil on the aqueous phase oxidation kinetics of two organic compounds whose oxidation characteristics without soil have been reported previously (3).

EXPERIMENTAL

The aqueous phase oxidation of both m-xylene and tetrachloroethylene in the presence of soil was studied over a temperature and pressure range of 523 to 563 K and 10.3 to 17.2 MPa, respectively. The experimental apparatus, liquid-phase sampling procedure, and gas chromatographic analysis used have been described previously (3,4). Certain changes in operating procedure which were necessitated by the presence of soil in the reactor are described below.

Five grams of uncontaminated subsoil were added to the 1L reactor with the initial charge of 700 grams of water. As in previous studies, the reactor was heated and pressurized to desired reaction conditions at which time approximately 10^{-4} kg of m-xylene or tetrachloroethylene were flushed into the reactor using 80 mL of distilled water. Although separate addition of the organic and soil does not simulate exactly the situation in which a contaminated soil would be treated, the time required to achieve an equilibrium distribution of organic between aqueous and soil phases was small compared to the oxidation time so that oxidation kinetics should be essentially identical in both cases.

Selected properties of the subsoil, which was obtained near Commerce, Louisiana (East Carroll Parish), are presented in Table I. Because of the small particle size, the soil was well-mixed in the water by the action of the impeller during the experiment. Stirring was stopped for two minutes prior to each sample withdrawal to permit the entrained soil particles to settle to the reactor bottom. This settling time, coupled with the use of a two-micron in-line filter, effectively prevented the entry of solids into the sampling and analysis system. Liquid samples were injected directly into a gas chromatograph using a 1 μ L high-pressure liquid sampling valve. Five mL of sample were flushed through the sample loop prior to each sample injection to insure that each sample was representative of the reactor contents.

Only the concentration of the parent organic was measured; no attempt was made to monitor the appearance/disappearance of partially oxidized intermediates or products. Similarly, the oxidation of organic constituents in the soil was not monitored. Although some soil oxidation likely occurred, the amount should be equivalent in both the m-xylene and tetrachloroethylene tests. In addition, the impact of soil oxidation should be small because of the low organic content and the fact that oxygen was always present in great excess of the stoichiometric oxygen demand.

The data were analyzed using a model (3,4) which accounts for vapor-liquid equilibrium as well as the change in liquid and vapor volumes which accompany sampling. Both of these effects may be important. Significant quantities of moderately volatile species may be present in the equilibrium vapor. Sampling the liquid phase alters both the liquid and vapor volumes and results in a concentration change upon reequilibration. While the concentration change

associated with removing a single sample is small, cumulative sampling during an extended run can produce a significant effect.

Table I. Soil Characteristics

Soil Series	Commerce Silt Loam
Classification	(fine-silty, mixed, non-acid, thermic Aeric Fluvaquents)
Source	East Carroll Parish, Louisiana, at a depth of 24-33 inches
Composition	19% Sand 64% Silt 17% Clay (mostly montmorillonite) 0.2% Organic carbon 0.06% Nitrogen
Properties	7.4 pH (H ₂ O) 13.8 cmol ⁺ ·kg ⁻¹ cation exchange capacity (NH ₄ OAc)
Sieve Analysis	1/3 less than 43 microns 1/3 between 43 and 420 microns 1/3 greater than 420 microns

The model was developed for a two-phase system (gas and liquid) and does not account for organic which may be adsorbed on soil surfaces. However, based upon the elevated temperatures and relatively low surface area of the soil, the amount of adsorbed organic is not thought to be significant. Extraction tests were performed on the soil recovered after selected experiments. Only trace quantities of m-xylene and no tetrachloroethylene were recovered in the extract after refluxing for two hours in hexane.

The model also assumes the mass transfer rate between liquid and vapor phases is sufficiently fast that that equilibrium is quickly achieved and pseudo-equilibrium is maintained at all times. The phase equilibrium relationship may be described by Henry's Law. Further assumptions are that the vapor phase is ideal, that reaction is limited to the liquid phase, and that the intrinsic oxidation kinetics are first-order in organic and one-half order in dissolved oxygen concentration. These reaction orders were determined previously (3) for the aqueous phase oxidation of these components in the absence of soil, and confirmed in the present study.

EXPERIMENTAL RESULTS

Experimental results in the form of normalized concentration versus time curves for m-xylene and tetrachloroethylene in the presence of soil are shown in Figures 1 and 2, respectively. Model results are shown by the solid lines and these will be discussed subsequently. The m-xylene results (Figure 1) indicate the level of reproducibility attained from duplicate runs at the same reaction conditions as well as the increased oxidation rate with both temperature and pressure. The temperature effect may be described by the Arrhenius equation as will be shown subsequently, and the pressure effect is due to increased oxygen solubility at higher pressure. The general trends in the tetrachloroethylene experimental results (Figure 2) are also as expected with oxidation rate increasing with both temperature and pressure.

There are, however, significant differences between the m-xylene oxidation rates shown in Figure 1 and previously reported results for m-xylene oxidation in the absence of soil (3). Higher temperatures were required to achieve oxidation in this study. Previous studies in the absence of soil were conducted at or below 498 K. However, in the presence of soil no oxidation was observed at

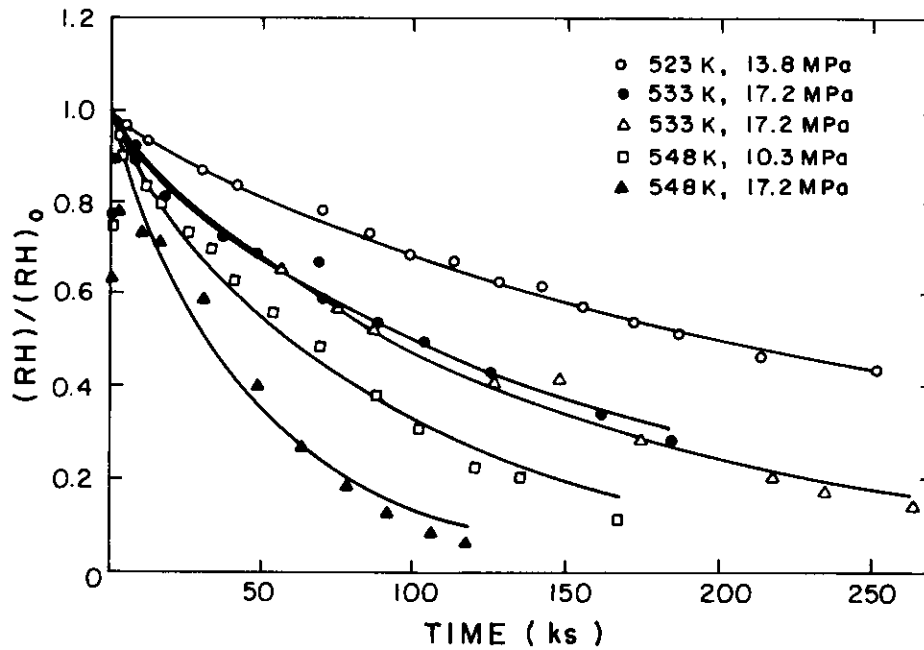


Figure 1: Time-Concentration Results for m-Xylene in the Presence of Soil

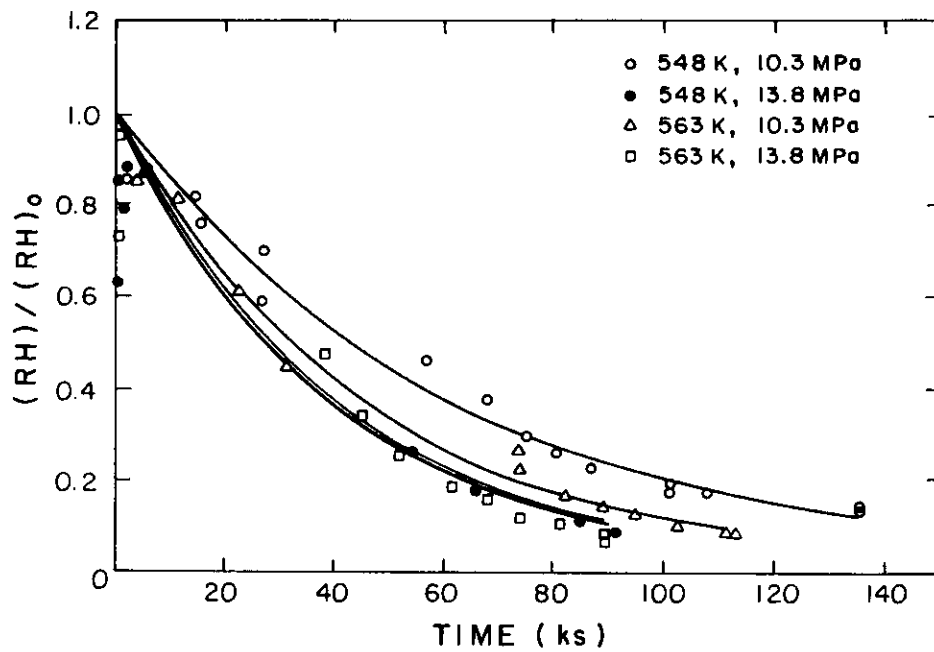


Figure 2: Time-Concentration Results for TCE in the Presence of Soil

temperatures below 523 K. In addition, no induction period was noted in these tests; instead, the m-xylene concentration decreased slowly from time zero. The oxidation rates were also much slower than expected. Extrapolation of the non-soil kinetic results (3) to the temperatures and pressures of this study suggests that the reaction half-life should vary between 36 and 120 seconds. Instead, the observed half-life varied between 4.2×10^4 and 1.8×10^7 seconds.

In contrast, soil does not have this adverse effect on the rate of tetrachloroethylene oxidation. The concentration-time results shown in Figure 2 are quite similar to the previously reported soil-free results (3). At 548 K and 13.7 MPa (reaction conditions which were duplicated in the soil and soil-free tests) the observed reaction half-life was approximately 2.7×10^4 seconds in both cases. No induction period was noted in either case.

Reaction rate constants for each of the experimental tests were determined using the reaction-phase equilibrium model (3,4). The length of the induction period was set equal to zero, and best values of the rate constants were determined by regression. The data of Himmelblau (5) were used to calculate dissolved oxygen concentrations at reaction conditions. Results of this modeling are shown by the solid lines in Figures 1 and 2. The level of agreement between experimental results and model correlation is comparable to that reported in previous non-soil tests.

The substantial effect of soil on m-xylene oxidation is emphasized in Figure 3, an Arrhenius plot of the correlated rate constant as a function of temperature. The upper line represents the previously reported rate constant (3) for m-xylene reacting alone, and the results of this study with soil are shown by the lower line. There is approximately three orders of magnitude reduction in the rate constant. The activation energy for the m-xylene/soil system was determined from the slope to be 157 ± 36 kJ/mol (confidence limits are at the 95% level), significantly higher than the value of 90 ± 9 kJ/mol for the reaction in the absence of soil.

Figure 4 is an Arrhenius plot which further substantiates the observation that soil has a negligible influence on tetrachloroethylene oxidation kinetics. The combined soil and non-soil results can be described by a single Arrhenius line having an activation energy of 89 ± 23 kJ/mol, not significantly different from the activation energy of 97 kJ/mol previously determined from limited data on the oxidation of tetrachloroethylene alone.

It is significant to note that at comparable reaction temperature and pressure in the presence of soil, tetrachloroethylene is oxidized more rapidly than m-xylene, while without soil the m-xylene oxidation rate is faster.

INTERPRETATION OF RESULTS

Previous experimental results for m-xylene oxidation without soil were interpreted on the basis of a free radical reaction mechanism. During the induction period when the net rate of disappearance of m-xylene is negligible, the concentration of free radicals gradually increases to a critical level required for the reaction to become self-propagating. In the presence of soil, we may presume that the interaction of radicals in solution with soil provides an additional chain termination step, thus preventing the concentration of radicals from reaching that critical level. It is not clear from these tests whether chain termination can be attributed to a particular component of the soil, or whether the same response would be observed with any finely divided solid in suspension. The elimination of the induction period and the greatly reduced oxidation rate, coupled with the significant change in activation energy, suggests that a substantially different oxidation mechanism is responsible for m-xylene disappearance in the presence of soil. This alternate mechanism would presumably be present in the absence of soil as well, but would not be noticed in competition with the faster free-radical reaction.

This interpretation is also consistent with the fact that the rate of tetrachloroethylene oxidation is not affected by the addition of soil. Evidence, including the absence of an induction period, suggests that the reaction proceeds

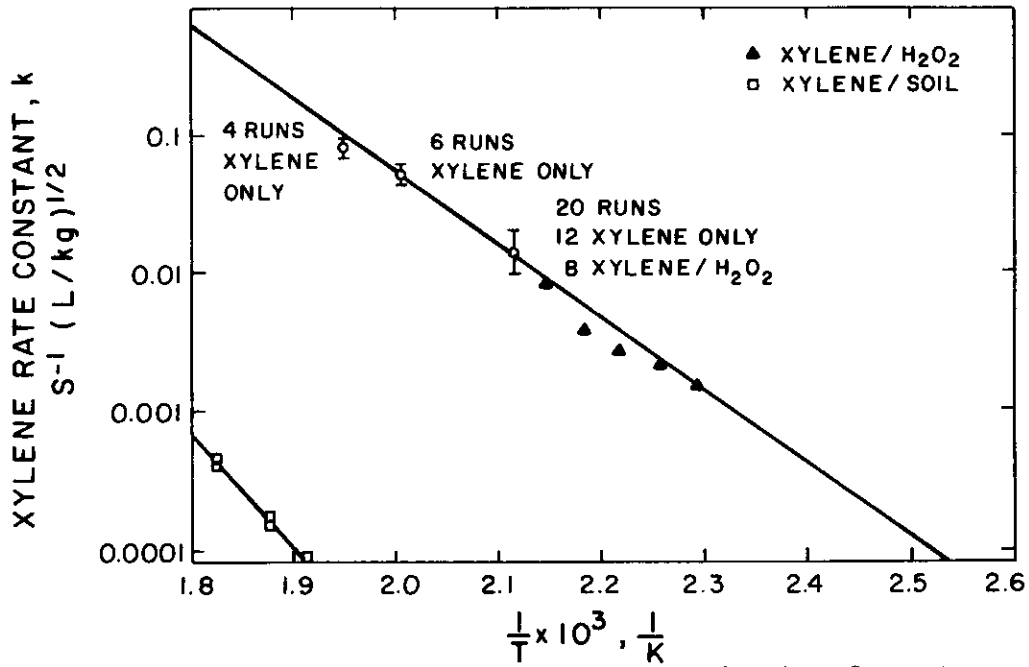


Figure 3: Arrhenius Analysis of the m-Xylene Rate Constant

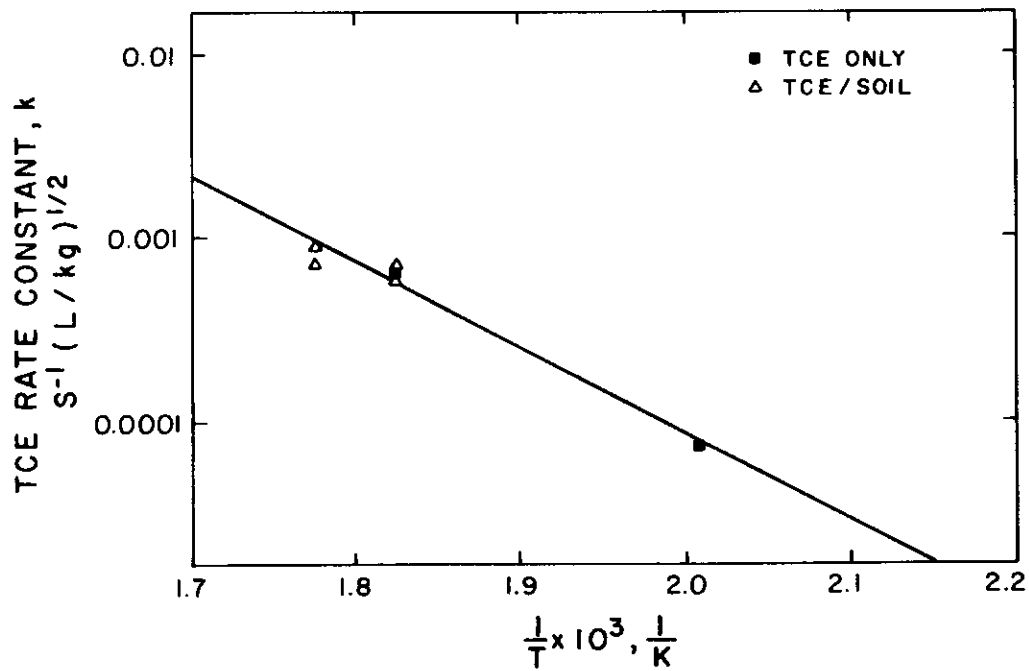


Figure 4: Arrhenius Analysis of the TCE Rate Constant

via some mechanism other than by the free-radical chain mechanism. This alternate but slower mechanism remains accessible when soil is present.

With or without soil, aqueous phase oxidation of tetrachloroethylene does not appear to be feasible because of the intrinsically low oxidation rate. Further, the direct oxidation of soil contaminated with materials like m-xylene which react via a free radical mechanism does not appear feasible unless the chain termination reactions attributed to the presence of soil can be avoided. We suggest that this might be accomplished using a two-stage process. The first stage would extract the organic from the soil into the aqueous phase. The feasibility of this step has been shown in this study by the fact that only trace quantities of organic were extracted from the soil using hexane following the reaction. The aqueous extract would then be routed to the reactor where oxidation would occur at the more rapid intrinsic rate, or, by adding easily oxidizable components such as phenol at a still faster synergized rate (6). Water would be continuously circulated between the extraction unit and the reactor, thereby minimizing energy requirements and reducing the quantity of aqueous effluent which may contain low molecular weight organic species such as acids and aldehydes.

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