REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 31 Dec 2003	3. REPORT TYPE AND DATES COVERED Final Report May 1999-~~Dec 2003~~ 01 31 Jan 04

4. TITLE AND SUBTITLE Kinetics of Chemical Agents Destruction in Supercritical Water	5. FUNDING NUMBERS Contract # DAAD 19-99-1-0211
6. AUTHOR(S) J.W. Tester, P.A. Sullivan, J.M. Ploeger, R.P. Lachance	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Massachusetts Institute of Technology Department of Chemical Engineering and LFEE Cambridge, MA 02139	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER A~~RO Proposal # 39250~~-CH 39250.6-CH

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The work accomplishments during this project consist of five different studies conducted by three current PhD students in the laboratory. An experimental study of methylphosphonic acid (MPA) oxidation has been completed that includes macroscopic modeling of the overall global rate law for MPA oxidation in supercritical water (SCW) and for the major pathways in MPA oxidation. Additionally, an elementary reaction rate model for supercritical water oxidation (SCWO) of MPA has been developed consisting of rate parameters from the available literature and *ab initio* calculations. Urea hydrolysis kinetics have been experimentally measured at sub and supercritical water conditions. Additionally, recent studies in the laboratory include a co-oxidation study of MPA and ethanol kinetics in SCW and a methane SCWO experimental study.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT **UNCLASSIFIED**	18. SECURITY CLASSIFICATION ON THIS PAGE **UNCLASSIFIED**	19. SECURITY CLASSIFICATION OF ABSTRACT **UNCLASSIFIED**	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

Abstract

Our work during this project has focused on obtaining experimental data and developing predictive models for the oxidation and hydrolysis kinetics of three important model compounds in sub- and supercritical water, methylphosphonic acid, urea, and methane.

Methylphosphonic acid (MPA), a model organophosphorus compound, was studied because it is a refractory compound and it is a hydrolysis product of most organophosphorus chemical warfare agents, such as VX, Sarin, and Soman gases. The hydrolysis kinetics of $(NH_2)_2CO$, urea in sub- and supercritical water have also been measured because urea is a major nitrogen-containing component of sewage. In addition, we began MPA and C_2H_5OH, ethanol co-oxidation experiments to determine if the addition of this labile compound can increase the slow MPA oxidation rates that occur at temperatures less than 525 °C. We also began an experimental and modeling study of methane oxidation in supercritical water (SCW).

For the MPA experimental study, the effects of MPA concentration (0.5 to 1.0 mM), oxygen concentration (1.0 to 3.8 mM), temperature (478 to 572 °C) and pressure (138 to 277 bar) on oxidation rates were measured over a residence time range from 3.0 to 9.5 s. The results indicate that the MPA oxidation rate is dependent on both oxygen concentration and pressure (or water density), but is relatively independent of initial MPA concentration. The only detected phosphorus-containing product was phosphoric acid, while the primary carbon-containing products included carbon monoxide, methane, and carbon dioxide. With the experimental data, a global rate law was regressed along with macroscopic rate constants for the major reaction pathways.

Additionally, an elementary reaction rate model was developed to predict MPA oxidation kinetics in SCW. Due to the lack of reliable organophosphorus rate constants in the literature, reaction rates for key MPA oxidation pathways, including H abstraction by OH radicals and unimolecular decomposition of MPA intermediates, have been estimated by molecular level, *ab initio* calculations. Predictions from this newly developed model are in good agreement with MPA conversions and carbon yields and provide insights into new organophosphorus reaction pathways that had been previously ignored.

A kinetic study of the destruction of a model nitrogenous waste compound in sub- and supercritical water began with a hydrolysis study of urea both above and below the critical temperature of water (T_c=374 °C). Urea is labile under hydrothermal conditions resulting in complete conversion after a residence time of 5 s at T>250 °C. Hydrolysis rates were also measured at supercritical temperatures of 450 and 500 °C to determine if the polar/ionic hydrolysis pathway would be impaired by the nonpolar supercritical environment. However, complete conversion of urea was measured after a residence time of 5 s, indicating that urea hydrolysis rates are rapid both in polar and nonpolar environments. The nitrogen-containing hydrolysis product of urea is ammonia, frequently the most refractory intermediate formed in supercritical water oxidation (SCWO) of sewage sludges and other nitrogen-containing chemical wastes. Thus, an SCWO study of ammonia kinetics is planned for next year over a temperature range of 550 to 650°C to complete this study of nitrogenous waste in SCW.

In addition, we began an experimental co-oxidation study of MPA and ethanol in supercritical water. The SCWO kinetics for both MPA and ethanol have recently been studied in this laboratory (Schanzenbacher et al, 2002 and Sullivan et al., 2003). MPA and ethanol oxidation rates in a mixed feed will be compared to the reliable rates from single component kinetics studies to determine if possible co-oxidation effects exist. Due to the increased radical

pool concentrations produced by labile species (ethanol) reactions at lower temperatures one anticipates accelerated oxidation rates for more refractory species (MPA). Kinetic models, including global rate laws and an elementary reaction rate model, are being developed to describe these co-oxidation results.

Additionally, we have begun to re-examine methane hydrolysis and oxidation kinetics in SCW as first measured in our laboratory in 1989 (Webley and Tester, 1991). As evidenced in the recent MPA investigation, methane is an important intermediate product of the oxidative destruction of many carbon-containing wastes. Although several other investigators have explored SCWO kinetics of methane (Hirth and Franck, 1993; Steeper et al, 1996; Savage et al, 1998), their results are contradictory and the scope of each study was limited. Our plan includes experimentally measuring methane oxidation rates in SCW using a more systematic approach, developing a revised global rate law and an elementary reaction model, and exploring methane partial oxidation in supercritical water.

Project Title: Kinetics of Chemical Agents Destruction in Supercritical Water

ARO Proposal #393250 CH

Final Progress Report
Army Research Office

Period: May 1999 to December 2003

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Table of Contents

1. **Objectives**
2. **Summary of Major Scientific Accomplishments**
3. **List of Publications**
4. **People Supported By and/or Active in this Grant**

1. Original Research Objectives:

A. Overall Goal: Our overall objective was to develop new quantitative understanding of how practically-relevant reaction conditions affect the SCWO kinetics of chemical agents and other military hazardous substances. The approach was comprehensive, and included lab-scale measurements under well-defined conditions and interpretive mathematical modeling of conversion and stable products generation from oxidation, hydrolysis, and pyrolysis of simulant compounds and mixtures under hydrothermal conditions.

B. Specific Approach: Our specific aims and methods were:

(1) To determine rates and extents of conversion of compound classes relevant to chemical agents and other DOD wastes, as well as yields and generation rates of resulting stable products, and selected (i.e., modest lifetime) intermediates of mechanistic importance.

(2) To study effects of independent variations in operating conditions relevant to current or emerging SCWO process equipment, i.e., temperature, residence time, pressure (density), inlet stoichiometry, initial concentration of waste (stimulant) and oxidant, type of oxidant (e.g., O_2 or H_2O_2), waste (stimulant) composition, and fluid mechanical mixing regime, e.g., near plug flow, intensely back-mixed.

(3) To elucidate individual contributions of pyrolysis, "hydrolytic" reactions (i.e., chemical participation by water), and oxidation, to the overall chemistry of waste conversion and destruction.

(4) To investigate effects of solid surfaces on observed destruction chemistries. Reaction materials of construction (e.g., Hastelloy, Inconel) by-product salts (e.g., NaCl, Na_2SO_4, Na_3PO_4), and solids intentionally added to promote desired chemistries (e.g., Na_2CO_3) are of interest.

(5) To develop means to predict the global kinetic behavior of mixtures from knowledge of the global kinetic behavior of their components, e.g., test the strengths and limitations of linear superposition and more elaborate predictive algorithms (e.g., based on interactions among compounds or more probably, their decomposition products).

(6) To interpret the results of (1) through (5) in terms of engineering kinetics models, and more refined molecular kinetic pathways such as (reduced) elementary reaction models, solvent-cognizant models, etc.

2. Summary of Major Scientific Accomplishments 1999-2003

The work accomplishments for the duration of this project consist of five different studies conducted by three current PhD students in the laboratory. An experimental study of MPA oxidation has been completed that includes macroscopic modeling of the overall global rate law for MPA oxidation in supercritical water (SCW) and for the major pathways in MPA oxidation. Additionally, an elementary reaction rate model for supercritical water oxidation (SCWO) of MPA has been developed consisting of rate parameters from the available literature and *ab initio* calculations. Urea hydrolysis kinetics have been experimentally measured at sub and supercritical water conditions. Additionally, our most recent studies in the laboratory include a co-oxidation study of MPA and ethanol kinetics in SCW and a methane SCWO experimental and modeling study.

2.1 MPA Experimental Study

The present study examined the SCWO kinetics of the model compound, MPA ($PO(OH)_2CH_3$) because it is a key, refractory intermediate that limits the complete oxidation of organophosphorus agents. One previous literature study by Bianchetta et al. (1999) focused on high conversion oxidation kinetics, with over half of the experiments having conversions greater than 90% to represent more practical treatment applications. The primary goal of our work was to characterize the oxidation kinetics of MPA in SCW at moderate conversions where derived kinetic parameters are less uncertain and thus yield more quantitative insight into the MPA oxidation mechanism.

Experimental MPA conversions and product yields were measured at varying MPA concentration, fuel equivalence ratio, temperature, residence time, and pressure (or water density). Fuel equivalence ratio (Φ) is defined as:

$$\Phi \equiv \frac{\left({[MPA]}/{[O_2]} \right)_0}{\left({[MPA]}/{[O_2]} \right)_{stoichiometric}} \tag{1}$$

At P=246±1 bar and temperatures between 503 to 571°C, hydrolysis conversions were very low, between 3 to 6% ± 3% were observed, in agreement with previous measurements by Bianchetta et al. (1999). At stoichiometric conditions (Φ=0.98±0.07), P=246±1 bar, and $[MPA]_0$=0.99±0.03 mM, MPA conversion is fairly low (X<30% at a residence time of τ=8.9 s) at $T \leq$ 503°C and conversion is almost complete (X>99%) at τ=7.5 s and T=571°C (Figure 1) [throughout this report, all ± values are to 95% confidence levels]. The carbon yields of the intermediates, CH_4 and CO, and the final carbon containing product, CO_2, are plotted in Figure 2 as a function of temperature at τ=5.8±0.4 s. The carbon yield for species (i) is defined as:

$$\text{Species}(i)\text{ carbon yield} \equiv \frac{\text{Moles of carbon in product}(i)}{\text{Total moles of carbon reacted}} \equiv \frac{[Cproduct]_i}{[MPA]_0 - [MPA]} \tag{2}$$

CO and CO_2 are the major MPA oxidation products, while CH_4 is a minor product whose yield is always less than 20% at our experimental conditions.

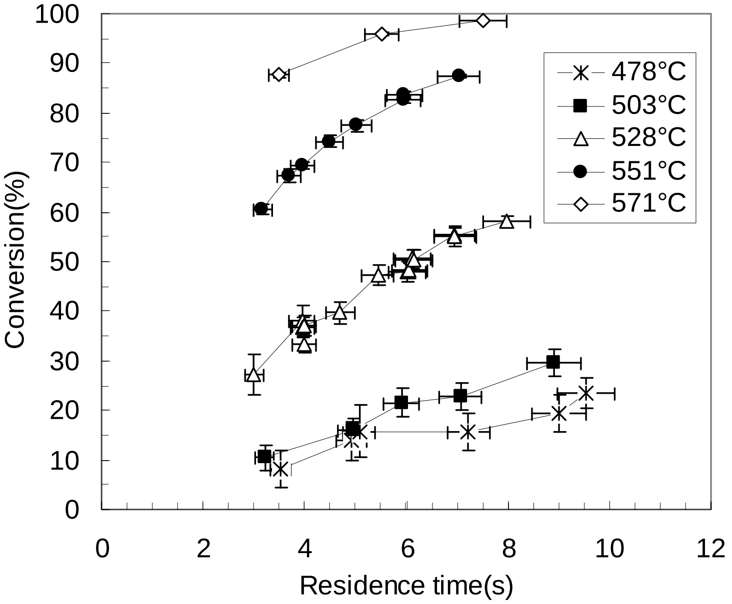


Figure 1: MPA conversion as a function of temperature and residence time at stoichiometric conditions (Φ=0.98±0.07), $[MPA]_0$=0.99±0.03 mM, and P=246±1 bar

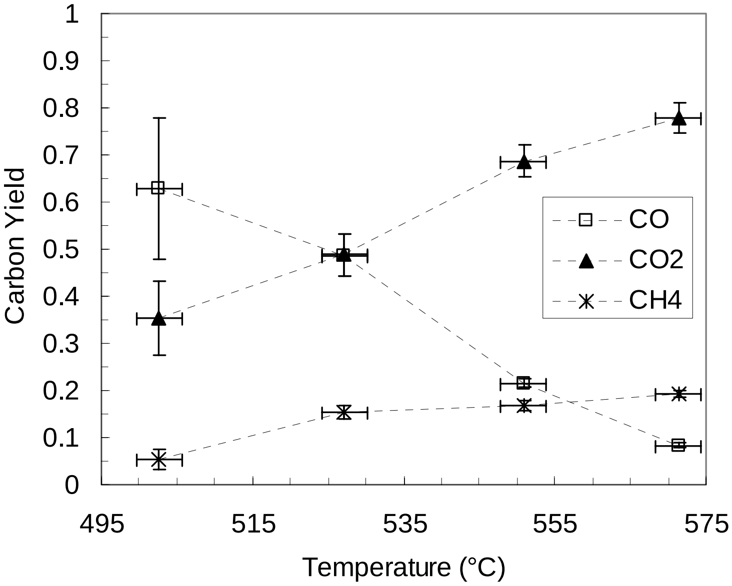


Figure 2: Carbon yields for the carbon-containing intermediates, CO and CH_4, and product, CO_2, as a function of temperature at a constant residence time of 5.8±0.4 s. These data were taken at stoichiometric conditions (Φ=0.97±0.07), $[MPA]_0$=0.99±0.03 mM, and P=246±1 bar.

MPA conversion increases as the oxygen concentration increases from a set of 13 experiments at varying fuel equivalence ratios from Φ=0.5 to 2.0 at temperatures of 503, 528, and 551°C with P=246±1 bar, and $[MPA]_o$=1.00±0.03 mM. Additionally, MPA conversion also increases as pressure (or water density) increases from a subcritical pressure of 138 bar to a supercritical pressure of 277 bar at T=528 and 551°C, Φ=1.01±0.05 and $[MPA]_0$=1.00±0.03 mM for a set of 15 experiments. However, MPA conversion was found to be independent of initial MPA concentration at Φ=1.00±.06, P=246±1 bar, and T=528±3°C. For example, decreasing $[\mathrm{MPA}]_0$ by 50% caused a minimal decrease in MPA conversion: at τ=3 s, the conversion decreased from 27±4 to 24±2%, at τ=4s, from 37±2 to 31±2%, and at τ=6.2 s, from 50±2 to 45±3%.

A global rate law was developed as a convenient means to predict MPA oxidation as a function of temperature, residence time, and MPA, O_2, and water concentrations. The MPA global rate law was regressed from 67 data points to yield:

$$\frac{-d\left[\mathrm{MPA}\right]}{dt}=10^{14.0\pm1.6}\exp\left(\frac{-\left(228\pm22\right)\mathrm{x}10^{3}}{RT}\right)\left[\mathrm{MPA}\right]\left[\mathrm{O}_2\right]^{0.30\pm0.18}\left[\mathrm{H}_2\mathrm{O}\right]^{1.17\pm0.30} \tag{3}$$

The activation energy of $228\pm22\mathrm{x}10^3$ is in J/mol and all concentrations are in mol/L. A first-order dependence for MPA was assumed since the experimental data indicate first-order behavior. Experimental and predicted conversions are compared in the parity plot of Figure 3. The dotted lines represent ±5% conversion to illustrate the accuracy of the predicted conversions. These results were presented at the Annual AIChE Conference in Indianapolis, IN in November, 2002 and are being published in the *AIChE Journal* in March 2004 (Sullivan et al, 2002 and Sullivan et al, 2004).

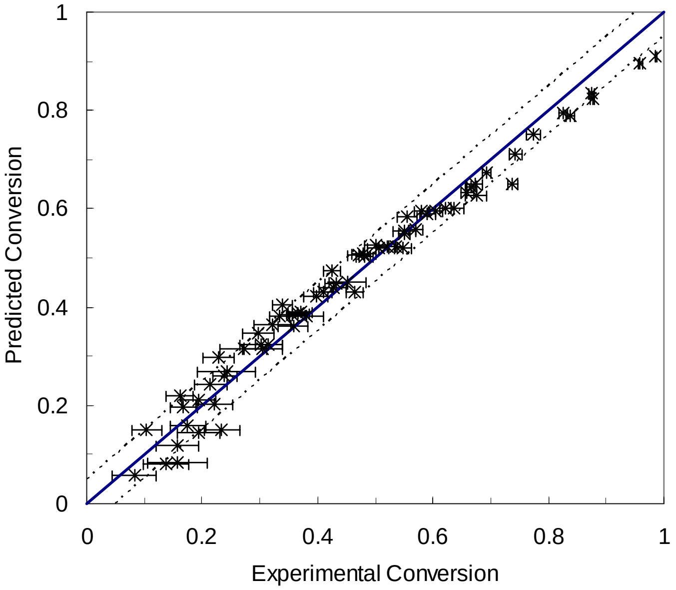


Figure 3: Predicted conversions vs experimental conversions for all MPA oxidation data from the global rate law given in Eq. 3

2.2 MPA Predictive Modeling Study

To gain a more fundamental understanding of the free radical chemistry in SCW and to predict the experimental conversion and product yields, an elementary reaction model for MPA oxidation has been developed. Elementary reaction mechanisms for SCWO are typically taken from combustion mechanisms operable at higher temperatures and lower pressures. Overall mechanisms have been validated for pressures from near or below ambient to about 20 atm, all well below the critical pressure of water. Normally, we apply corrections to these mechanisms to account for the higher pressures and lower temperatures of SCW conditions. Since the organophosphorus combustion models in the literature contain only estimated reaction rates and appear to be missing key reaction pathways that could occur during MPA oxidation, important MPA oxidation reaction rates were calculated using high-level *ab initio* methods in conjunction with Dr. Sumathy Raman and Prof. William Green.

For the *ab initio* rate calculations, reactant and transition state geometries and energies were calculated using the CBS-Q method in Gaussian 98. Reaction rates were then calculated using transition state theory. The important MPA reaction rates estimated are shown below.

$$PO(OH)_2CH_3 \rightarrow [TS_1]^{\dagger} \rightarrow PO_2CH_3 + H_2O \tag{R1}$$

$$PO(OH)_2CH_3 \rightarrow [TS_2]^{\dagger} \rightarrow PO_2OH + CH_4 \tag{R2}$$

$$PO(OH)_2CH_3 \rightarrow [TS_3]^{\dagger} \rightarrow PO(OH)CH_2 + H_2O \tag{R3}$$

$$PO(OH)_2CH_3 \rightarrow [TS_4]^{\dagger} \rightarrow PO(OH) + CH_3OH \tag{R4}$$

$$PO(OH)_2CH_3 + OH^{\bullet} \rightarrow [TS_5]^{\dagger} \rightarrow PO(OH)_2CH_2^{\bullet} + H_2O \tag{R5}$$

$$PO(OH)_2CH_3 + OH^{\bullet} \rightarrow [TS_6]^{\dagger} \rightarrow PO(O^{\bullet})OHCH_3 + H_2O \tag{R6}$$

$$PO(OH)_2CH_3 + OH^{\bullet} \rightarrow [TS_7]^{\dagger} \rightarrow PO^{\bullet}(OH)_3CH_3 \tag{R7}$$

$$PO^{\bullet}(OH)_3CH_3 \rightarrow [TS_8]^{\dagger} \rightarrow PO(OH)_3 + CH_3^{\bullet} \tag{R8}$$

$$PO(OH)_3 \rightarrow [TS_9] \rightarrow PO_2OH + H_2O \tag{R9}$$

$$PO(OH)_3 + H^{\bullet} \rightarrow [TS_{10}]^{\dagger} \rightarrow P^{\bullet}O(OH)_2 + H_2O \tag{R10}$$

$$PO(OH)_3 + H^{\bullet} \rightarrow [TS_{11}]^{\dagger} \rightarrow P^{\bullet}(OH)_4 \tag{R11}$$

$$P^{\bullet}(OH)_4 \rightarrow [TS_{12}]^{\dagger} \rightarrow P^{\bullet}O(OH)_2 + H_2O \tag{R12}$$

$$PO_2OH + H^{\bullet} \rightarrow [TS_{13}]^{\dagger} \rightarrow P^{\bullet}O(OH)_2 \tag{R13}$$

$$P^{\bullet}O(OH)_2 + O_2 \rightarrow [TS_{14}]^{\dagger} \rightarrow PO_2OH + HO_2^{\bullet} \tag{R14}$$

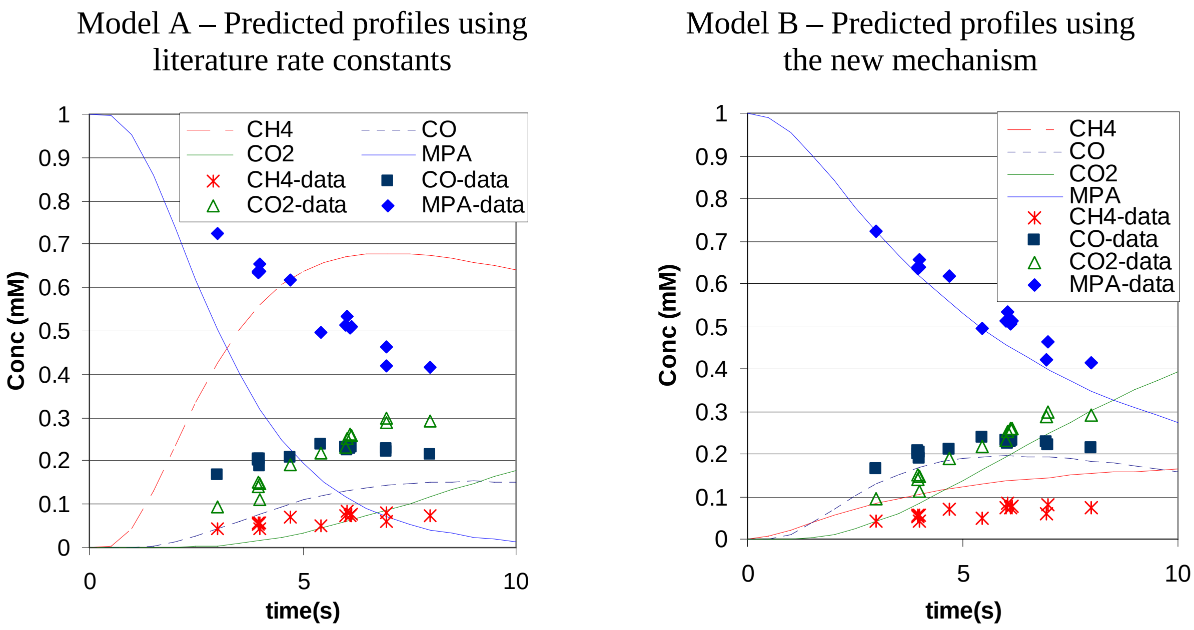
Our calculations reveal that the reaction rate for H-abstraction from the CH_3 group (reaction R5) is a dominant reaction pathway for MPA oxidation. This is an important finding since there are no previous reports of the R5 pathway and the related reaction kinetics for the intermediate product, $PO(OH)_2CH_2$.

An elementary reaction rate model has been developed with 41 species and 242 reaction rates. The H_2/O_2 chemistry was taken from a recent SCWO model for benzene that accounts for the pressure dependence for these reaction rates (DiNaro et al., 2000). The C-1 chemistry in the model was taken from the University of Leeds methane mechanism (Hughes et al, 2001) and modified to include pressure dependence and the species, CH_3OO and CH_3OH, which are important at supercritical conditions. All organophosphorus rate constants in the mechanism were either calculated by *ab initio* methods or estimated from similar carbon chemistry available in the literature.

The modeling results are shown below for MPA carbon fractions at T=528°C, P=246 bar, Φ=1.00, and $[MPA]_0$=1.00 mM in Figure 4. The results for model A contain only the three available reaction rates from literature for the organophosphorus chemistry:

$$PO(OH)_2CH_3 = PO_2CH_3 + H_2O \tag{R1}$$
$$PO(OH)_2CH_3 = PO_2OH + CH_4 \tag{R2}$$
$$PO(OH)_2CH_3 + OH = CH_3 + PO(OH)_3 \tag{R15}$$

The results for model B are the model predictions from the mechanism that was developed in this work. From these results, model A with the previous literature rates overestimates the MPA oxidation rate and predicts that most of the reacted carbon forms methane since CH_3 reacts primarily with water to form methane at these conditions. With the newly developed mechanism, the MPA oxidation rate is correctly predicted and the predicted CH_4, CO, and CO_2 concentration histories are all in much closer agreement with experimental results. Such agreement is encouraging, suggesting that we have correctly identified the dominant elementary reaction pathways for MPA oxidation.


Model A – Predicted profiles using literature rate constants

Model B – Predicted profiles using the new mechanism

Figure 4: Modeling results using literature rate constants (Model A) and with the new mechanism developed in this study (Model B). Results are for T=528°C, P=246 bar, $[MPA]_0$=1.0 mM, Φ=1.0

2.3 Urea Hydrolysis Study

Urea was selected as a model compound because it is a major nitrogen-containing component of sewage and other organic feeds that contain bound nitrogen. The destruction of the nitrogenous waste in a closed-loop SCWO system is of great interest for waste disposal and water recovery in any isolated environment.

The urea hydrolysis study was conducted in our Inconel 30 cm³ batch cell reactor system at P=250 bar. A 100 microliter sample of concentrated urea at room temperature was rapidly injected into the autoclave reactor filled with de-aerated water and maintained at specific temperatures. Upon reaching the desired residence time for analysis, the entire sample was vented into a volumetric flask. Ammonia was the only identified stable product at significant concentrations. Over a low temperature range (T=135-200 °C) the hydrolysis activation energy was 23.2±3.4 kcal/mol, shown in Figure 5. However, at T> 250 °C, urea hydrolysis was complete before the minimum residence time of 5 s was reached, both at polar subcritical and nonpolar supercritical conditions. Given these results, urea will hydrolyze completely to ammonia regardless of injection method, either cold injection into water held at supercritical temperatures in our batch cell reactor or by preheating to supercritical temperatures in our plug flow, tubular reactor.

The next step for this study of SCWO kinetics of nitrogenous waste will be to accurately measure ammonia oxidation rates in a temperature range of 550 to 650 °C given its refractory behavior (Webley et al., 1991).

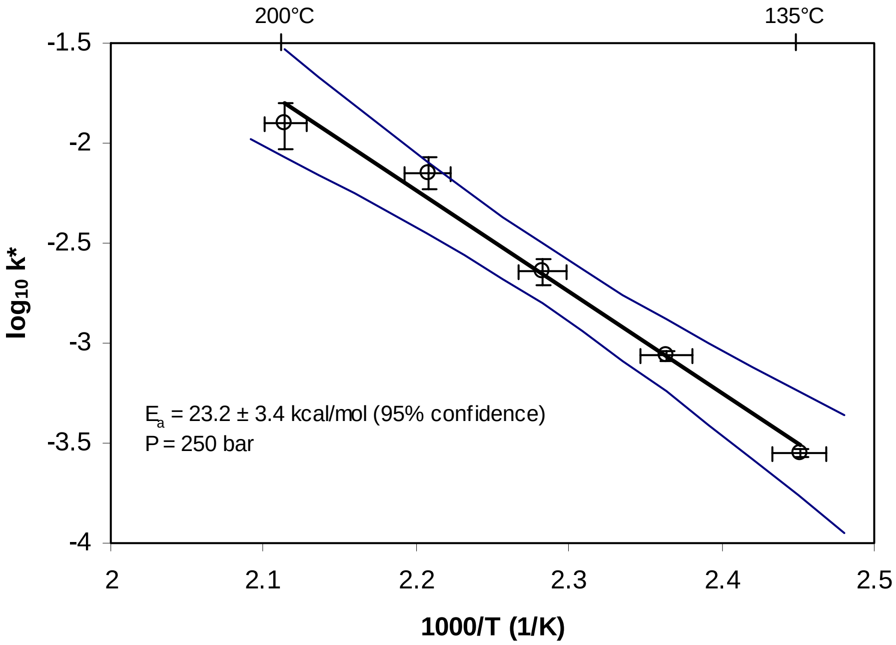


Figure 5: Urea hydrolysis assumed first order rate constants as a function of temperature. Error bars are at the 95% confidence limit and lines represent the 95% confidence interval of the linear regression.

2.4 MPA and Ethanol Co-Oxidation Study

In practice, the destruction of chemical warfare agents will yield both MPA and small hydrocarbons as intermediates. It has been observed (Hong, 1987) that the oxidation of labile compounds can accelerate the oxidation of refractory compounds. To model a more realistic, mixed waste stream, we choose ethanol as our labile co-oxidant. This compound has the dual advantages of having been recently studied experimentally in our group (Schanzenbacher) and in Chemkin simulations by Rice (2001) and Marinov (1999). Beyond producing a model of the behavior of MPA in a mixed waste stream, we hope that this study is this first step towards a more comprehensive and deeper understanding of co-oxidation in general.

Based on the strength of the existing Sullivan (2003) model for MPA and Marinov (1999) model for ethanol, we have taken a different plan of attack for the co-oxidation study. Initially a short series of scoping runs probed the range of concentrations and temperatures of interest. This was followed by a modeling study that sought to elucidate the linkages between the two oxidation networks that produced the acceleration in MPA oxidation in the presence of ethanol. Once the pathways were found, a set of experiments were planned to attempt to confirm the co-oxidation mechanism predicted by the model.

All experiments were conducted at 473°C and 246 bar in the plug flow reactor using a mixed organic feed of MPA and ethanol. At supercritical conditions the concentrations ranged from 0.1 to 1.0 mM for MPA and 0.1 to 3.0 mM for ethanol. Oxygen was fed into the reactor as a stream of hydrogen peroxide sufficient to allow complete combustion of both MPA and ethanol to phosphoric acid and carbon dioxide. Conversion of MPA for a range of initial ethanol concentrations is shown below. For low concentrations of ethanol, there is no discernible effect, but once an equimolar ratio of ethanol to MPA is reached, conversion is doubled.

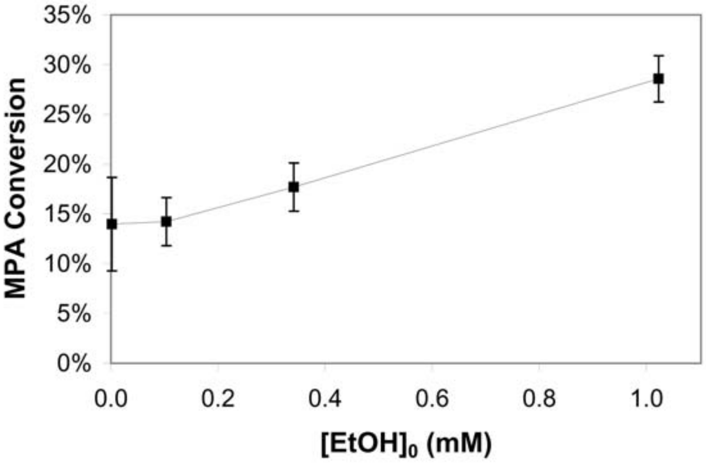


Figure 6: MPA conversion as a function of initial ethanol concentration.
T = 473°C, P = 246 bar, τ = 9 s, $[MPA]_0$ = 1 mM with stoichiometric oxygen

In order to provide stoichiometric oxygen for both compounds, the oxygen concentration was increased in proportion to the increasing ethanol concentration. Where the stoichiometric ratio for MPA is 2:1, for ethanol it is 3:1, which means that in the 1.0 mM $[EtOH]_0$ case the $[O_2]_0$ is 5 mM, compared to 2 mM for the zero ethanol case. To confirm the acceleration effect due to the increased oxygen, a 0.1 mM $[MPA]_0$ feed solution was reacted first with 0.2 mM $[O_2]_0$, second with 1.0 mM $[EtOH]_0$ and 3.2 mM $[O_2]_0$, and finally with 3.2 mM $[O_2]_0$. The first two cases were conducted under stoichiometric oxygen, the final under excess stoichiometric oxygen by a factor of 16. The figure below shows that the majority of the increase in conversion is due to the introduction of ethanol.

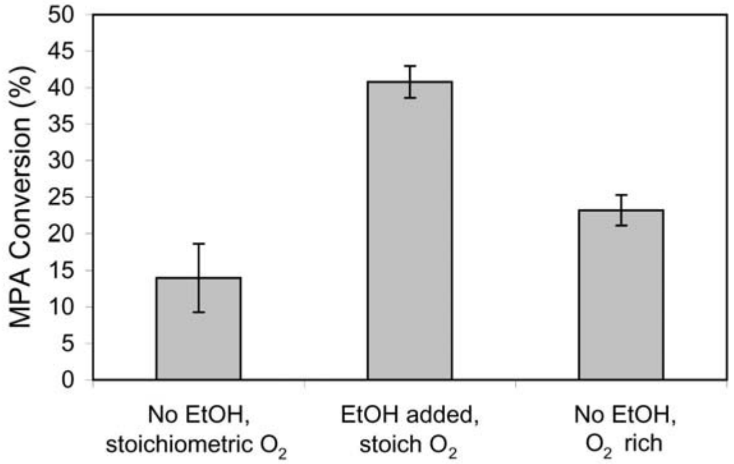


Figure 7: MPA conversion after 9 s for two cases of increased oxygen concentrations, one with and one without ethanol.

Having identified a co-oxidation effect of significant interest, the Marinov model for ethanol was appended to our model for MPA and C_1 chemistry (Sullivan, et al., 2003 and Marinov, 1999). Although the model overpredicts the conversion of MPA in the mixed feed stream case, it does provide qualitative insight into the mechanism. Rather than simply increasing the concentration of the hydroxyl (OH•) species, the increase in concentration of the hydroperoxy (HO_2•) radical has the greater effect in co-oxidation of MPA. As seen in the figure below, the hydrogen abstraction by OH• forms an equilibrium. The acceleration in MPA destruction happens when an increase in [HO_2•] increases the flux through the $PO(OH)_2CH_2O$• - generating pathway.

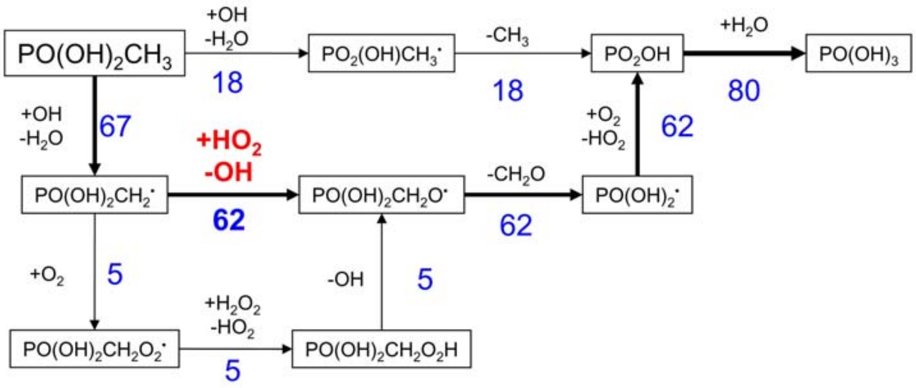


Figure 8: Reaction mechanism for 1 mM $[MPA]_0$ and no ethanol at 473 °C and stoichiometric oxygen. Numbers reflect the average flux over the first 10 s of residence time in nmol/cm^3s. The thickness of each arrow is proportional to the flux through that pathway.

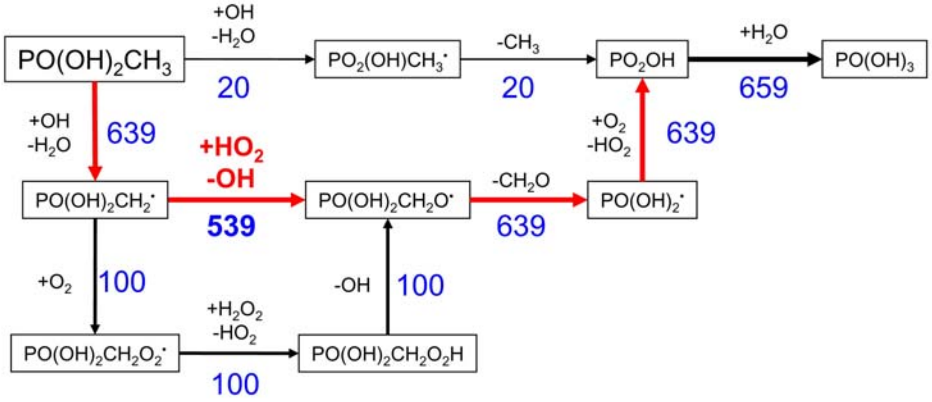


Figure 9: Reaction mechanism for 1 mM $[MPA]_0$ and $[EtOH]_0$ at 473 °C and stoichiometric oxygen. Numbers reflect the average flux over the first 10 s of residence time in nmol/cm^3s. The thickness of each arrow is proportional to the flux through that pathway.

Since hydrogen abstraction by OH• is the first step in this and many other SCWO mechanisms, it is often assumed that the co-oxidizing effect must center on that radical. By studying the ethanol oxidation mechanism, we found that the oxidation of the acetaldehyde and formaldehyde intermediates yielded HO_2•, however the OH• radicals were changed to a much lesser extent. The figures below show that the dramatic increases in [HO_2•] do not translate to increases in [OH•].

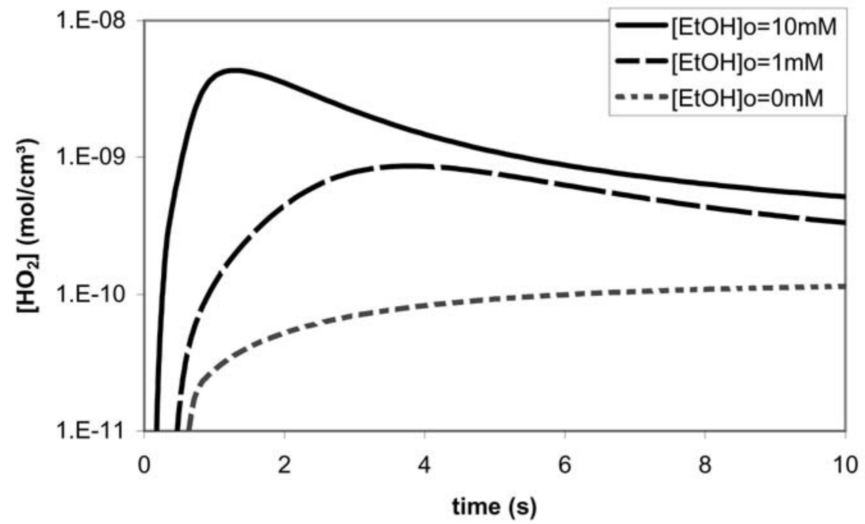


Figure 10: HO_2• concentration profile for varying initial ethanol concentrations. T=473°C, $[MPA]_0$ = 1 mM, stoichiometric oxygen.

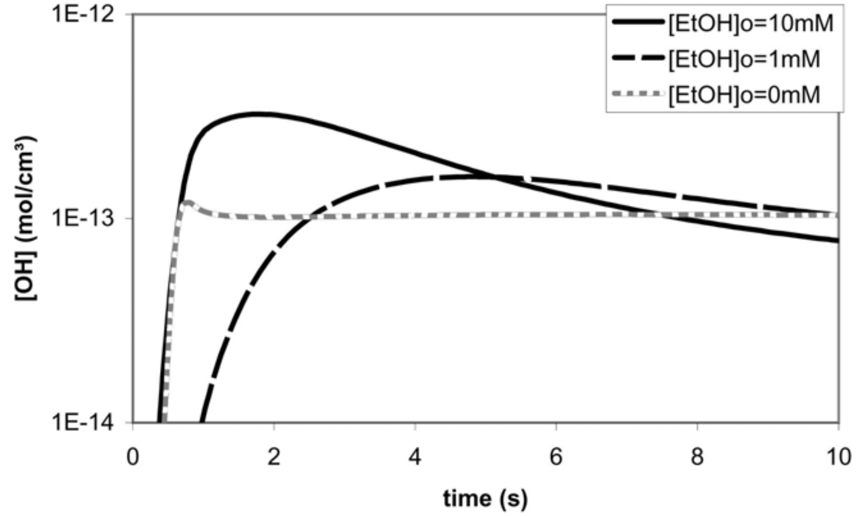


Figure 11: OH• concentration profile for varying initial ethanol concentrations. T=473°C, $[MPA]_0$ = 1 mM, stoichiometric oxygen.

A large increase in [HO_2•] but a small increase in [OH•] is somewhat unexpected. OH• radicals are produced in this mechanism by hydrogen peroxide, which in turn is produced by the collision of two HO_2• radicals. The gain in [OH•] should increase with the square of [HO_2•].

$$HO_2\bullet + HO_2\bullet \Rightarrow H_2O_2 + O_2 \qquad \text{(R13)}$$
$$H_2O_2 \Rightarrow 2\ OH\bullet \qquad \text{(R14)}$$

Due to the increased concentrations of hydrogen peroxide in the co-oxidizing environment, a third decomposition reaction becomes important for hydrogen peroxide.

$$H_2O_2 + OH\bullet \Rightarrow HO_2\bullet + H_2O \qquad \text{(R15)}$$

Reaction R15 is effectively a chain-terminating reaction and causes diminishing returns in the production of OH• radicals by ethanol oxidation. That conclusion based on model predictions requires some kind of experimental evidence, of course. Attempting to match the predicted conversions to experimental values does not work because small errors in rates, especially reaction R15 above, propagate to large errors in the final conversion. Branching ratios, on the other hand, are much more reliable because the errors tend to cancel each other out. Returning to the reaction network for MPA, we see that the only pathway that produces the methyl radical CH_3• is the top pathway involving an OH• hydrogen abstraction and a unimolecular decomposition. Methane is produced when the methyl radical abstracts a hydrogen atom off a water molecule. Therefore, the production of methane is entirely controlled by the concentration of OH• radicals. If the conversion of MPA increases without increasing the carbon fraction of methane, then the increase in [HO_2•] dominates over the increase in [OH•].

In order to observe the methane produced, we had to abandon the use of ethanol as a co-oxidant, as it produces methane during its own oxidation. Since the bulk of the radicals generated by ethanol are generated by formaldehyde and its decomposition products, and formaldehyde itself cannot generate methane, we use formaldehyde as a co-oxidant under the same conditions as the ethanol experiments: T = 473°C, P = 246 bar, $[MPA]_0$ = 1 mM, and equimolar oxygen. As seen in the plot below for data taken at $\tau = 6$, as the concentration of formaldehyde increases, the conversion of MPA increases more than three-fold, but the increase in methane fraction is less than 50%. This shows that the increase in [OH•] is much less than the increase in [HO_2•].

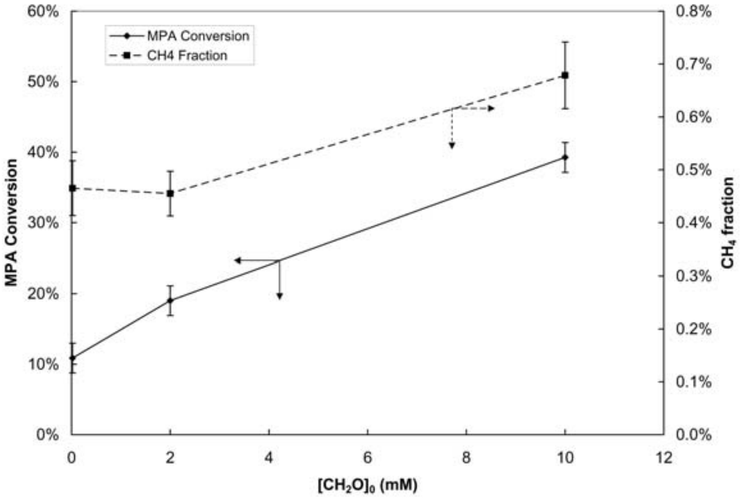


Figure 12: Conversion of MPA and methane carbon fraction for varying initial formaldehyde concentrations. T = 473°C, $[MPA]_0$ = 1mM, stoichiometric oxygen.

This finding indicates that the potential use for co-oxidation to promote complete oxidation at lower temperatures may be hindered, as the oxidation of CO to CO_2 is dependent on the OH• radical. However, there is significant utility of this kind of study for understanding how changes in the feed stream will affect performance. Also, the introduction of a co-oxidant can be used in kinetic studies to determine the effect of increasing the free radical pool independently of temperature or pressure.

Ongoing co-oxidation work will include a study of the ammonia-ethanol system. Due to the slow rate of oxidation of pure ammonia, experiments will be conducted in a batch reactor. Within the expected temperature range of interest (550-600°C), the characteristic reaction time for ammonia oxidation is expected to be on the order of minutes at 250 bar.

For these experiments the batch reactor will be charged with a solution of hydrogen peroxide, and the beginning of the reaction will be marked with the cold injection of a known volume of ammonia or ammonia-ethanol stock solution into the heated reactor. When the desired residence time is reached, the entire contents of the reactor will be vented through an ice bath into a flask for collection and analysis. A gas separation unit will be used in some experiments to determine whether or not nitrous oxide (N_2O) is being formed, but since the gas phase cannot be sampled quantitatively, the focus will be on measuring ammonia disappearance in the liquid phase.

2.5 Methane SCWO Study

In the summer of 2003, we began a detailed re-examination of SCWO kinetics for methane. Methane consistently appears as a stable intermediate in the oxidation of carbon-containing compounds. Therefore, a thorough understanding of the fate of methane in supercritical water is essential to SCWO studies of carbonaceous material. Due to the lack of reliable methane kinetic data in the literature and given the importance of methane in the oxidation of many carbon-containing species, we feel a reliable, comprehensive methane oxidation study is needed. We plan to utilize several of our bench-scale reactor systems that have been significantly improved in recent years (Marrone, 1998 and Phenix, 1998).

Previous methane SCWO studies have measured reaction rates and product distribution at different τ, T, P, and Φ with limited variation of the individual variables. For example, oxidation rates were determined at 5 different residence times at a fixed temperature, pressure, and fuel equivalence ratio. With well-defined experimental conditions in a more systematic approach using our improved experimental apparatus, we can determine a reliable data set that could be used as a benchmark to support all SCWO kinetic experimental and modeling studies. Specifically, we plan to measure oxidation kinetics at T=500 to 600 ^{o}C, τ=2 to 120 s, and Φ=1 to 2 to develop a data set that can be quantitatively used to evaluate the quality of existing methane kinetic data and replace and extend these data where appropriate.

As part of our re-examination of SCWO of methane, we will also develop a predictive, elementary reaction rate model. Previous elementary reaction rate models have had limited success in correctly predicting the methane SCWO data (Webley and Tester, 1991, Dagaut et al, 1996, Savage et al, 1998). These efforts were also hindered by the lack of reliable methane data in the literature. As part of our newly developed MPA elementary reaction rate model, we have re-examined C-1 chemistry in SCWO and have included updated kinetic and thermochemical data in that model. We will use the improvements that have been made in the MPA model as a starting point for a new methane elementary reaction rate model. With better quality kinetic data for methane conversion, we can then determine the ability of this model to accurately predict methane oxidation rates. An accurate methane model will help to improve many SCWO elementary reaction rate models that also include C-1 chemistry.

Additionally, we plan on studying the partial oxidation of methane in SCW. Supercritical water partial oxidation may serve as a convenient means of converting methane to a more practical, distributed liquid fuels and to hydrogen. In addition, measuring methane oxidation rates at lower oxygen concentrations and residence times can improve our overall understanding of the methane oxidation mechanism in SCW. This portion of our methane study will examine the effects of varying temperature, pressure, water density, residence time, and catalyst type and concentration on overall methane conversion and selectivity to specific oxygenates. As part of this study, we may also investigate the use of hydrothermal flames to convert methane.

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3. List of Publications:

Sullivan, P.A. and Tester, J.W., “Organophosphorus Chemistry in Supercritical Water - Determination of Methylphosphonic Acid Oxidation Kinetics”, presented at the 2002 Annual AIChE Conference, Indiana Convention Center, Indianapolis, IN Nov 3-8, 2002.

Sullivan, P.A. et al, “Mechanistic Underpinnings of Organophosphorus Oxidation Kinetics in Supercritical Water”, presented at the 2003 Annual AIChE Conference, San Fransico, CA Nov 15-17, 2003.

Green, W.H., P.A. Sullivan, J. Ploeger, and J.W. Tester, "Supercritical water oxidation (SCWO) kinetics." presented at the International Bunsen Discussion "Dynamics of Molecular Phenomena in Supercritical Fluids", Evangelische Akademie Tutzing, Bavaria, Germany, Sept. 1-5, 2003.

Sullivan, PA and Tester, JW (2004) “Methylphosphonic acid oxidation kinetics in supercritical water.” *AIChE*, 50(3).

Sullivan, P.A., R. Sumathi, W.H. Green, and J.W. Tester, "Ab initio modeling of organophosphorus combustion chemistry." to be submitted to Phys. Chem. Chem. Phys, 2004.

Sullivan, P.A., W.H. Green, and J.W. Tester, "Elementary reaction rate model for MPA oxidation in supercritical water." to be submitted to Phys. Chem. Chem. Phys., 2004.

4. People Supported By and/or Active in this Grant

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