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QUARTERLY TECHNICAL PROGRESS REPORT

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DOE Grant Number DE-FG22-92PC92536
Project Title: Oxidation of Phenolics in Supercritical Water
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Our work during this quarter has focused on gaining experience with computational quantum chemistry programs and on improving the statistical analysis of our existing data. This emphasis on computing and analysis was forced upon us when the HPLC system that we rely on for reaction product analysis ceased to function properly. Lacking an HPLC forced us to postpone experimental work. We used MOPAC for the computational quantum chemistry work and our statistical analysis employed SimuSolv, which is different from the software package we had been using. SimuSolv offered advantages in that it could weight the experimental data to account for the error in each point and it provided the complete variance-covariance matrix, which is required to estimate the uncertainty in the parameter estimates.

MOPAC

We have begun to explore the applicability of MOPAC for performing computational quantum chemistry calculations to provide reactivity indices. We used the software package Cerius² to graphically input the compound structure, optimize the bond lengths, and perform the MOPAC calculations. After MOPAC again optimized the intermolecular distances, it calculates the final heat of formation, total energy, electronic energy, core-core repulsion, and ionization potential for the molecule. As seen in Table 1, we compared the values that MOPAC calculated for the heat of formation with literature values found in Reid, Prausnitz, and Sherwood's "The Properties of Gasses and Liquids". The heat of formation values we obtained differed from the literature values, but MOPAC will allow us to calculate values for compounds and ions for which empirical heats of formation are not present in the literature. Some potential reactivity

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indices, including proton affinity and adiabatic ionization potential, require the calculation of the properties of intermediate ions. These values are not easily found in the literature but can be calculated with MOPAC.

Table 1, Heat of Formation of Cresols (in kcal)

	MOPAC Calculation	Literature Value
<i>o</i> -cresol	-25.48	-30.74
<i>m</i> -cresol	-26.56	-31.63
<i>p</i> -cresol	-26.50	-29.97

SimuSolv

We decided to re-analyze all of the kinetics data using SimuSolv for two reasons. One is that our earlier analyses using SYSTAT implicitly assumed that all of the data points possessed equal absolute errors. This assumption is often made in fitting data, but we did not believe it was necessarily true for our experimental data. SimuSolv, which is a more powerful package than SYSTAT, relieves the user of the task of specifying the error pattern in the data. Rather, SimuSolv determines how the data should be weighted by examining the residuals as it tries to fit the data to the model (below) with different weightings.

$$\left[(1-X)^{1-a} - 1\right] = (a-1)10^k[\text{organic}]^{a-1}[O_2]^b \tau$$

The type of error pattern that SimuSolv detects is reflected in the numerical value of the heteroscedasticity, which the program reports.

A second motivation for using SimuSolv is that this program provides the complete variance-covariance matrix in the output. With this information one can use the equations that describe the propagation of errors to estimate the uncertainty in calculated reaction rates from the uncertainties in the rate law parameters. Having covariances is essential in this case because all of the estimated parameters were correlated rather than being independent.

Table 2, below, provides the new rate law parameters and their associated 95% confidence intervals for each of the compounds we have studied so far. The 95% confidence interval was calculated in the standard manner for normally distributed error, the product of the standard deviation and the *t* statistic. We also provide a sample SimuSolv output file so that the reader can see the detailed statistical information that is available.

Table 2, Rate law parameters determined with SimuSolv

	k	a	b
<i>m</i> -cresol	-1.43±0.48	0.65±0.09	0.61±0.23
<i>p</i> -cresol	-1.55±0.40	0.60±0.07	0.54±0.17
<i>m</i> -nitrophenol	-0.61±1.05	0.73±0.23	0.45±0.37
<i>p</i> -nitrophenol	2.86±0.76	1.30±0.11	0.95±0.24
resorcinol	-2.89±0.92	0.57±0.12	-0.49±0.37

Figure 1, Sample SimuSolv output for the SCWO of *p*-cresol

DESCRIPTION		PARAMETER ESTIMATES		STANDARD
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		INITIAL	FINAL	
LOG LIKELIHOOD FUNCTION		1.8628	41.695	
	K	-2.0000	-1.5532	0.193
	A	0.60000	0.60312	3.148E-02
	B	0.53000	0.53686	8.401E-02

N	X OBSERVED	X PREDICTED	% ERROR	STANDARDIZED RESIDUAL	RESIDUAL PLOT
1.000	0.1847	0.2557	-38.42	-1.67	*****
2.000	0.1744	0.2557	-46.60	-1.91	*****
3.000	0.4401	0.5010	-13.83	-1.43	*****
4.000	0.4377	0.5010	-14.46	-1.49	*****
5.000	0.2241	0.1792	20.05	1.06	*****
6.000	0.2226	0.1792	19.52	1.02	****
7.000	0.4242	0.3705	12.65	1.26	*****
8.000	0.4275	0.3705	13.33	1.34	*****
9.000	0.2906	0.2766	4.82	0.329	*
10.00	0.2991	0.2766	7.52	0.528	**
11.00	0.3222	0.3086	4.22	0.319	*
12.00	0.3251	0.3086	5.07	0.387	**
13.00	0.3756	0.4211	-12.10	-1.07	*****
14.00	0.3879	0.4211	-8.55	-0.779	***
15.00	0.4008	0.3823	4.61	0.434	**
16.00	0.4074	0.3823	6.16	0.589	***
17.00	0.4199	0.3692	12.08	1.19	*****
18.00	0.4261	0.3692	13.36	1.34	*****
19.00	0.4173	0.4074	2.38	0.233	*
20.00	0.4286	0.4074	4.96	0.499	**
21.00	0.5034	0.5412	-7.51	-0.888	****
22.00	0.5158	0.5412	-4.93	-0.597	***
23.00	0.5823	0.5682	2.42	0.331	*
24.00	0.5827	0.5682	2.48	0.340	*

STATISTICAL SUMMARY

	MAXIMIZED LOG LIKELIHOOD FUNCTION	WT RESID SUM OF SQUARES	WEIGHTED RESIDUAL SUM	STANDARD ERROR OF ESTIMATE	PERCENTAGE VARIATION EXPLAINED	PERCENTAGE WEIGHTING PARAMETER
X	41.69	4.353E-02	5.830E-02	4.553E-02	84.756	0.00

CORRELATION MATRIX

	K	A	B
K	1.000		
A	0.4248	1.000	
B	0.7605	-0.2620	1.000

VARIANCE-COVARIANCE MATRIX

	K	A	B
K	3.7203E-02		
A	2.5788E-03	9.9071E-04	
B	1.2323E-02	-6.9273E-04	7.0570E-03

OPTIMIZATION METHOD: GENERALIZED REDUCED GRADIENT

CAUSE OF TERMINATION: NO IMPROVEMENT IN LINE SEARCH ---
ALL REMEDIES HAVE FAILED TO FIND A BETTER POINT

FUNCTION EVALUATIONS FOR OPTIMIZATION = 207
FUNCTION EVALUATIONS FOR STATISTICS = 5
NUMBER OF LINE SEARCHES = 17
OPTIMIZE TIME = 2.417 SECONDS

PLANS FOR THE NEXT QUARTER

Our plans for the next quarter are to get back into the lab and conduct more SCWO experiments. We will focus on obtaining quantitative information about the product yields from the SCWO of *m*- and *p*-cresol, and then performing SCWO experiments with *o*-, *m*-, and *p*-hydroxybenzaldehydes, which are the major primary products from SCWO of the cresols. This work will improve our understanding of the reaction pathways and kinetics for the SCWO of phenolics and it will also give us new data that can be used in working toward quantitative structure-reactivity correlations

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