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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

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ABSTRACT

A number of possible Diels-Alder reactive systems involving anthracene (diene) in supercritical solvent were proposed at the outset of research. Scouting experiments designed to select out the optimum reactive system from among the candidate dienophiles and solvents have been completed. The nitrogen bearing compound 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) has demonstrated superior reactivity and sensitivity to cosolvent additions and has been selected as dienophile. A convenient half-life of reaction between PTAD and anthracene is obtained at temperatures in the neighborhood of 50 C. Carbon dioxide has been selected as the solvent because of its convenient critical properties, and also to optimize the safety of the experiments. In the process of completing these scouting experiments, the experimental apparatus that will be used to obtain kinetic data for calculation of partial molar volumes of the reaction transition state has also been optimized.

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OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

KINETIC MEASUREMENTS

The fluorescence spectroscopic equipment which is to be employed in the supercritical phase of the project was used to obtain kinetic and thermodynamic data for the Diels-Alder reaction of anthracene and PTAD in liquid acetonitrile. Results of selected runs are presented as Figure 1 in the Appendix. The observed first order rate constant for this system normalized to 25 C was obtained using these data, and was found to be 0.35 1/Ms. A. I. Konvalov (1979) measured the kinetics of the identical chemical system using UV spectroscopy and obtained an observed first order rate constant of 0.32 1/Ms. This agreement validates our fluorescence equipment and methods for this task.

As mentioned in a previous report, some preliminary measurements of the kinetics of anthracene and PTAD in supercritical CO2 have been completed. Results confirmed that this reaction does run in the supercritical phase, and that the reaction has a conveniently short half-life, but that the solubility of PTAD in supercritical CO2 is low. This low solubility necessitates the acquisition of accurate solubility data for the temperatures and pressures at which the reaction will be run. Once accurate solubility values have been determined, the supercritical phase of the project will begin. PTAD will be introduced into the reaction cell in quantities well below its solubility limit in order to avoid possible distortion of results that could occur if the experiments are performed with excess solid PTAD in the bottom of the reaction cell.

There are two paths by which distortion of results could occur in response to the presence of excess solid PTAD. The first is by possible solubility enhancement in the presence of anthracene. Solubility limits will be measured for PTAD in CO_2 with no anthracene present. If solid PTAD is present in the cell during an actual reaction the concentration of PTAD in the reaction mixture should then be the saturation value. But it is possible that under actual reaction conditions the saturation solubility of PTAD in CO_2

could be enhanced by the presence of anthracene. In this case, the actual saturation concentration of PTAD in the reaction mixture would be greater than that measured using the solubility apparatus. This would lead to incorrect values of the observed first order rate constant for that reaction, and this in turn would lead to incorrect values for partial molar volumes of the transition state.

The second path by which distortion of results could occur in response to the presence of excess solid PTAD involves the possibility of reaction at the solid-CO_2 interface. In this case, the disappearance of anthracene - which produces the measured signal in fluorescence spectroscopy - would proceed by a complex mechanism involving both supercritcal phase kinetics and solid kinetics. This event would also have the effect of distorting the measured value of the observed first order rate constant.

Apparatus for measuring the solubility of solids in pure and mixed supercritical solvents has been assembled. The design follows that of K. P. Johnston (1987). The solubility equipment has been calibrated and is ready for use in determining saturation solubilities for PTAD in supercritical CO2 at the temperatures and pressures that will be needed for the analysis of partial molar volumes in the transition state.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

We shall use the new solubility equipment to obtain data for the solubility of PTAD in supercritical CO2 over an appropriate range of temperatures and pressures.

We shall complete collection of kinetic data for the system PTAD with anthracene in supercritical CO_2. Kinetic data will be collected at various pressures along at least one isotherm for the reaction in pure CO2. The data will be correlated with respect to the following equation:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT}$$

If the quantification of partial molar volumes in pure CO2 proceeds smoothly, it may be possible to begin gathering kinetic data for the PTAD/anthracene system in cosolvent modified CO_2. A set of scouting experiments will be designed to select among candidate cosolvents for those which provide optimum enhancement of PTAD/anthracene reaction kinetics.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F}\left(\frac{V^F v^S}{V^S}\right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P}\right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T}\right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

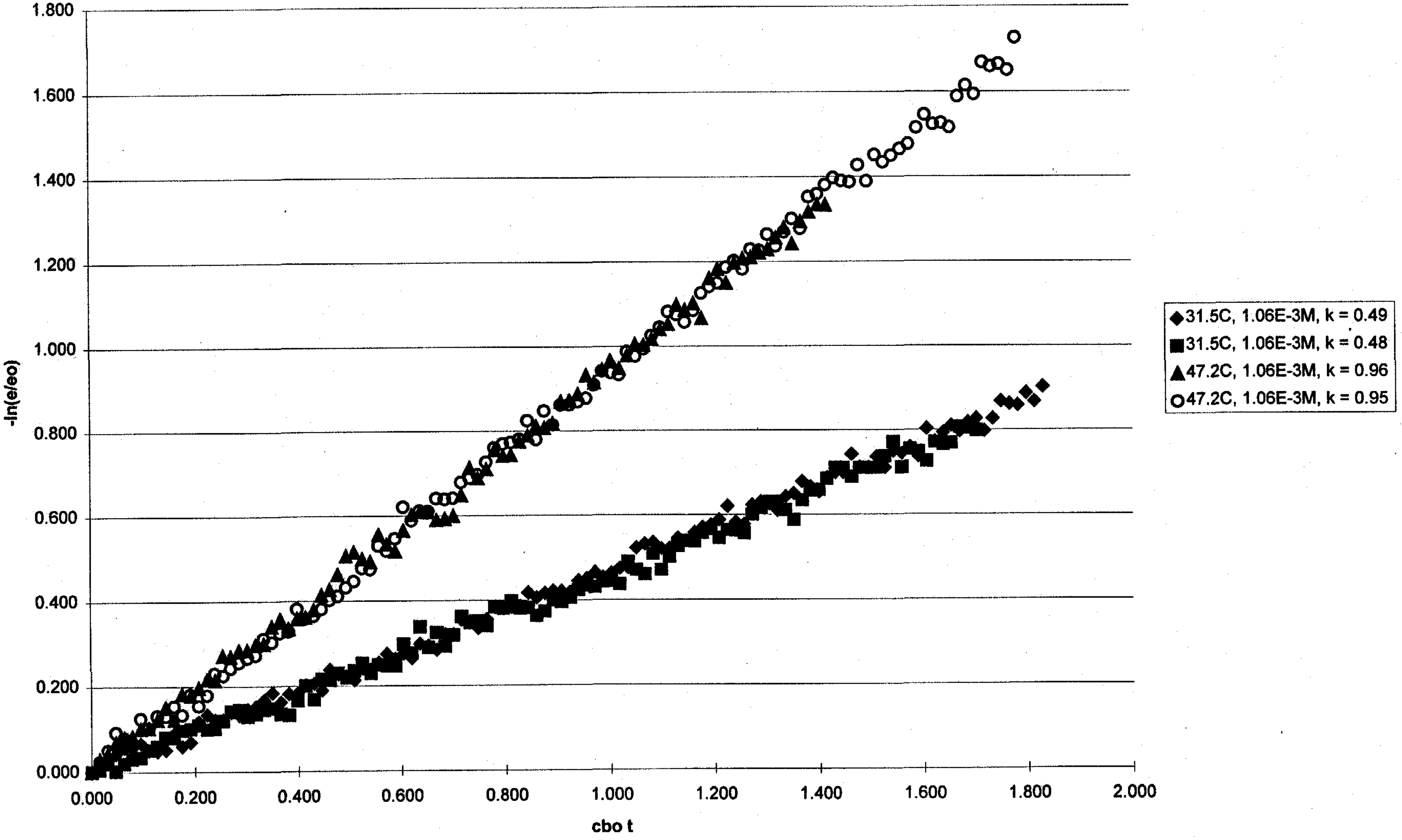
Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

SUMMARY

We have completed the liquid phase work of the reaction of several dienophiles with anthracene in acetonitrile. Our fluorescence spectroscopic techniques were used to obtain the kinetic data for PTAD with anthracene, and the values obtained for observed first order rate constant closely match those reported by A. I. Konvalov (1979). We have constructed equipment necessary for the measurement of the solubility of PTAD in supercritical CO2, and have completed calibration of the equipment. Solubility measurements will be made during the coming quarter. When the solubility measurements have been completed, the collection of kinetic data for the PTAD/anthracene system in supercritical CO2 will begin in earnest. It is reasonable to expect that at least one isotherm of kinetic data can be completed during this quarter.

Appendix

Figure 1. PTAD w/ Anthracene in Liquid Acetonitrile
k=.35 1/Ms at 25C, +/-4%



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