Supercritical Fluid Reactions for Coal Processing

**Quarterly Report
April 1 - June 30, 1997**

**By:
Charles A. Eckert**

Work Performed Under Contract No.: DE-FG22-94PC94206

For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Georgia Institute of Technology
School of Chemical Engineering
778 Atlanta Avenue
Atlanta, Georgia 30332-0100

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The Diels – Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was chosen as the model system and was investigated in supercritical carbon dioxide.

Kinetic data have been previously collected for pure CO₂ at 40°C and pressures between the critical pressure of CO₂ (73.8 bar) and 216 bar. These data support the theory of local density enhancements suggested in the literature. Data taken at 50°C and pressures ranging from 70 bar to 195 bar are currently reported; they do not exhibit the molecular clustering evident closer to the critical temperature.

The data taken at 40°C are now being used to construct mathematical forms which can model these pressure-induced kinetic changes. One promising avenue of investigation involves treating the supercritical medium as a dense gas, which allows a kinetic model based on high reference pressure fugacity coefficients to be derived.

TABLE OF CONTENTS

Executive Summary	1
Introduction	2
Background	4
Procedures	10
Results and Discussion	17
Conclusion	23
References	24

LIST OF GRAPHICAL MATERIALS

Figure 1. An overview of the high pressure fluorescence apparatus used for kinetic measurements.....	11
Figure 2. An overview of the optical cell and the apparatus used for the injection of cosolvents.....	16
Figure 3. Rate constants for the reaction of PTAD with anthracene in pure CO ₂ at 40°C.	18
Figure 4. Rate constants less than 51/mol s for the reaction of PTAD with anthracene in pure CO ₂ at 40°C.	19
Figure 5. Rate constants for the reaction of PTAD with anthracene in pure CO ₂ at 50°C.	22

EXECUTIVE SUMMARY

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The Diels - Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was chosen as the model system and was investigated in supercritical carbon dioxide.

Kinetic data have been previously collected for pure CO₂ at 40°C and pressures between the critical pressure of CO₂ (73.8 bar) and 216 bar. These data support the theory of local density enhancements suggested in the literature. Data taken at 50°C and pressures ranging from 70 bar to 195 bar are currently reported; they do not exhibit the molecular clustering evident closer to the critical temperature.

The data taken at 40°C are now being used to construct mathematical forms which can model these pressure-induced kinetic changes. One promising avenue of investigation involves treating the supercritical medium as a dense gas, which allows a kinetic model based on high reference pressure fugacity coefficients to be derived.

INTRODUCTION

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 SCFs 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.

BACKGROUND

A great deal of theoretical work has been done toward rate predictive models capable of correlating rate constant data versus various solvent properties and thermodynamic variables. A review of this broad field of research is beyond the scope of this work, but a thorough discussion is provided in reviews by Savage and Clifford (Clifford and Bartle, 1996; Savage, et al., 1995). For the present purpose, an overview of the most important concepts will suffice as an introduction to ways in which the data in this work could be employed in future modeling efforts.

Arrhenius Activation Energy

The most traditional method of analyzing rate data is in terms of the Arrhenius equation, which is presented as equation (1). The Arrhenius equation represents the exponential relationship between rate constant and temperature, and can be used to extract information on the activation energy, which is defined as the energy needed to bring one mole of reactants from the ground state to the transition state of the reaction (Laidler, 1987a).

$$k_c = k_o e^{\left(-\frac{E_a}{RT}\right)} \quad (1)$$

Solvent effects may be quantified using this relationship by determining the changes in activation energy that occur with changes in solvent properties (Hughes and Ingold, 1935, Tester, 1996). A solvent's effect on reaction rate is then discussed in terms

of its ability to stabilize the transition state (Laidler, 1987b). Stabilization of the transition state through changes in solvent environment produces a lower energy of activation and a faster reaction. Prediction of solvent effects on reaction rates is accomplished through a linear correlation of the log of the rate constant, which is proportional to the activation energy, versus an appropriate solvent property. Examples of solvent properties against which correlations can be made include density, dielectric constant, or a solvatochromic parameter such as α , which measures a solvent's hydrogen bond donating ability; β , which measures hydrogen bond accepting ability; or π^* , which measures polarity/polarizability (Kim and Johnston, 1987a). A drawback of this method is that a large amount of experimental rate data needs to be collected in order to apply the technique. The data must cover a wide range of solvent types and reaction conditions before solvent effects can be predicted for an uncorrelated solvent. Even if the necessary data are available, the reaction rate predicted for the new solvent may possess significant error due to unusual specific interactions between solvent and reactants.

Transition State Theory

A more rigorous approach to the prediction of solvent effects on reaction rate is provided by transition state theory. In this treatment, it is assumed that the rate of reaction is dependent on an equilibrium established between the two reactant molecules and an "activated complex".

The activated complex M is formed from the association of two reactant molecules A and B as bonds are broken and formed on the way to product. Though the activated complex is unstable along the reaction coordinate, it is considered to be a normal molecule in equilibrium with the reactants and may therefore be used in writing relationships based on thermodynamic activities (Eckert, 1967; Evans and Polanyi, 1935; Eyring, 1935).

$$K_{eq} = \frac{[M]}{[A][B]} \frac{g_M}{g_A g_B} \quad (2)$$

Equation (2) was related to chemical reaction rates by Bronsted and Bjerrum (Bjerrum, 1924; Bronsted, 1922), producing a general statement which relates the reaction rate constant to solvent effects through activity coefficients.

$$k = k_o \frac{g_A g_B}{g_M} \quad (3)$$

In equation (3), the rate constant k is a product of k_o , the rate constant in a standard state environment (where all activities are unity), and the activity coefficients of the reactants and activated complex at the actual conditions of the reaction. This relationship cannot predict absolute reaction rates, but does have the potential to predict changes in the rate constant with a change in reaction conditions. The ability of this relationship to predict reaction rates relative to the rate at a standard state is limited only

by the validity of the solution theory used to define the activity coefficients. If a solution theory possessing a small number of adjustable parameters is applicable to a given reaction, transition state theory has the potential to provide solvent effect predictions with less data than correlations based on Arrhenius activation energies.

Scatchard and Hildebrand's regular solution theory estimates activity coefficients for an ideal system in which only dispersion forces need be considered, so it can be used to provide a simple example of how (3) can be modified for practical application (Hildebrand and Scott, 1962; Hildebrand, 1964 #105). In the Scatchard and Hildebrand model, a solubility parameter, δ , is defined for the solvent and for each reactant, based on the "cohesive energy density" of the material - an experimentally measurable value that represents the strength of dispersion forces as the energy needed to isothermally vaporize a given molar volume of liquid to the ideal gas state. When δ is related to the activity of a component, the following simple relationship results.

$$RT \ln g_j = v_j (d_j - \bar{d})^2 \quad (4)$$

$$\bar{d} \equiv \sum_i^m \Phi_i d_i \quad (5)$$

Substitution into (3) leads to the following useful result. Note that for work done with dilute reactants, $\bar{d}$ is approximately equal to the solubility parameter of the solvent δ_s .

$$\ln\left(\frac{k}{k_o}\right) = \frac{v_A(d_A - d_S)^2 + v_B(d_B - d_S)^2 - v_M(d_M - d_S)^2}{RT} \quad (6)$$

Local Density Enhancement

The rate predictive model based on regular solution theory would probably not work in the near critical region of a solvent, due to the tendency of a near critical solvent to exhibit densities in the vicinity of the reactants that are higher than the density of the bulk fluid. This local density enhancement represents a significant change in solvent properties unrelated to dispersion forces, and the regular solution theory based model would fail to account for its effects.

Local density enhancement is brought about by short-range solute-solvent interactions at solvent densities between 0.4 and 0.8 times the critical density (Brennecke, et al., 1990; Eckert and Knutson, 1993; Kim and Johnston, 1987b; Paulaitis and Alexander, 1987). Local density enhancement has the effect of creating local or “true” reactant concentrations which differ from the concentrations found in the bulk fluid.

Local density enhancements have been investigated using a solvatochromic method which correlates shifts in the transition energy of spectroscopic absorption maxima to changes in density in the immediate vicinity of a probe molecule. This provides a means of measuring density enhancements in a supercritical solvent, and subsequently correcting measured rate constants for these enhancement effects (Kim and Johnston, 1987a). Application of this method to an esterification reaction in supercritical CO₂, for example, suggests that, in at least some cases, changes in the rate constant near the critical pressure

may be explained largely by the effect of density enhancement on local concentration, rather than by physical or thermodynamic effects (Brennecke, et al., 1994).

In conclusion, solvent characteristics peculiar to supercritical fluids, such as local density enhancement and high solvent compressibility near the critical point, present challenges to those who wish to develop predictive models of chemical reaction rates in supercritical solvents. A number of general theories capable of predicting solvent effects on reaction rates already exist. The challenge is to incorporate expressions which account for supercritical fluid solvent properties into these theories.

PROCEDURES

Fluorescence apparatus

Reaction kinetics were followed spectroscopically by fluorescence. The equipment used to make these measurements was configured in the manner illustrated in Figure 1. Light from a Spectral Energy SX1000-2 Xenon UV lamp was passed through a Kratos Analytical Model GM252 monochromator, producing an excitation light beam at a single wavelength. The excitation beam was split into two beams using a half-silvered mirror, producing an excitation beam and a reference beam.

The reference beam was directed into a Kratos D 500 Side-On Photomultiplier Tube (PMT), which produced an amperage output measured using a Keithley Instruments 414A Picoammeter. The excitation beam was directed into the optical cell containing the experimental sample of anthracene. The fluorescence of anthracene produced an emission beam of light, which was directed into a second GM252 monochromator where it was filtered to a single wavelength of light. The filtered emission wavelength was directed into a second D 500 PMT, which produced an amperage output that was measured using a Keithley 485 Autoranging Picoammeter.

Each picoammeter produced an analog output voltage in proportion to beam intensity, designated as Signal A for the emission beam intensity and as Signal B for the reference beam intensity. The ratio of these two signals - A/B - varied with changes in

Figure 1. An overview of the high pressure fluorescence apparatus used for kinetic measurements.

fluorescent emission intensity, but it did not vary with fluctuations in lamp intensity. The emission intensity of the sample was recorded as the numerical value of the ratio A/B.

The optical cell was constructed from 316 stainless steel and was configured for solvent introduction and removal as in Figure 2. The windows were made from quartz, and were positioned at right angles to one another so that as little of the excitation light as possible would exit the cell with the emission light. The seals for cell windows were o-rings made of Teflon. All tubing and fittings were stainless steel and were manufactured by Swagelok or HiP. CO₂ was delivered to the cell using an ISCO Model 260D syringe pump, which fed through a Valco 6-port sample injection valve. A Teflon coated stirbar was used to provide agitation of the cell contents.

Pressure was measured using a Druck PDCR 911 transducer attached to a Druck DPI 60 digital readout. The pressure transducer and readout were calibrated using a Ruska dead weight calibration apparatus, and were found to be accurate to +/- 1 psi.

Internal temperatures were measured using a 1/16" grounded Omega Type K thermocouple in an inconel sheath. It was mounted with its tip in direct contact with the reactant solution. The thermocouple was attached to a readout with resolution to 0.1°C. The thermocouple was calibrated against a platinum resistance thermometer, and was found to be accurate to +/- 0.1°C.

Internal temperature was controlled using a second 1/8" Type K thermocouple mounted with its tip in the steel of the cellblock. The thermocouple was attached to an Omega CN9000A controller which used four cartridge heaters mounted in the steel of the cell block to maintain cell temperature. Temperature control of cell contents was within +/- 0.2°C.

Kinetic Analysis

The reaction of PTAD with anthracene is an elementary bimolecular reaction, so, if one reactant is present in excess, pseudo first order kinetics can be used to extract rate constants from concentration versus time data. UV spectroscopy was used for the analysis of the reaction rate of PTAD and anthracene in liquid solvents (Konovalov, Breus et al. 1979) by following the decay of PTAD over time. In order to apply pseudo first order kinetics, anthracene needs to be present in excess. Though an excess of anthracene is possible in liquids, PTAD solubility in supercritical CO₂ is on the order of 10⁻³ mol/L, and anthracene solubility is on the order of only 10⁻⁵ mol/L. The dilemma was solved by using fluorescence spectroscopy instead of UV. Fluorescence spectroscopy can detect concentrations of anthracene as low as 10⁻⁷ mol/L, making it possible to have PTAD present at an initial excess of 100:1 and still follow a change in anthracene concentration over two orders of magnitude.

In order to calculate the rate constant of the reaction conveniently from fluorescence emission data, it was possible to use Beer's law to relate pseudo first order rate constants directly to changes in emission signal. Solution of the differential equation (9) relating concentration changes of one reactant to the concentration of both reactants leads to (10) when PTAD is assumed to be in great excess and therefore constant throughout the reaction.

$$\frac{dc_{AN}}{dt} = k_c c_{PTAD} c_{AN} \quad (9)$$

$$\ln\left(\frac{c_{AN}}{c_{ANo}}\right) = - (k_c c_{PTADo})t \quad (10)$$

Simple experiments involving incremental additions of anthracene to a liquid solvent indicated that the fluorescence of anthracene follows Beer's Law (11) as long as the anthracene is dilute (i.e. less than 10^{-5} mol/l), and the emission wavelength monitored is well removed from wavelengths at which self-absorption may occur. The path length "l" in Beer's Law does not change during a run, so (11) may be written once for initial conditions and again for an arbitrary time t. The ratio of these equations may be substituted into (10), leading to (12). Equation (12) allows the pseudo first order rate constant to be derived directly from emission data without knowing the exact concentration of anthracene in the cell.

$$e = \epsilon l c_{AN} \quad (11)$$

$$\ln\left(\frac{e_{AN}}{e_{ANo}}\right) = -k_c c_{PTADo} t \quad (12)$$

Kinetic Measurements in Pure Supercritical CO₂

Stock solutions of PTAD and anthracene were prepared in acetone. A fresh PTAD stock solution was prepared each day. A known quantity of each stock solution was placed into the optical cell using a Gilman Pipet, with PTAD in excess by a factor of 40. The cell was dried under vacuum for 5 minutes. Care was taken to insure that the two stock solutions did not contact one another during drying. Dryness of the cell was determined by visual inspection.

Data acquisition software was started, and the cell was pressurized with pure CO₂ from the ISCO syringe pump. The time and pressure at which the cell reached the desired temperature was recorded, and the reaction was observed for about twenty minutes. Kinetic analysis was performed only on data collected while the cell was at within +/- 0.2°C of the desired temperature. The cell was cleaned thoroughly with acetone between each experiment.

Figure 2. An overview of the optical cell and the apparatus used for the injection of cosolvents.

RESULTS AND DISCUSSION

Modeling of Kinetic Data in Pure Supercritical CO₂

Rate constants were previously obtained for the reaction in pure CO₂ at 40°C and at pressures ranging from the critical pressure of CO₂ (73.8 bar) to 216 bar. Rate constant values are plotted in Figures 3 and 4. Two views are provided for the purpose of making the cluster of points at 95 bar more readable. Near the critical temperature, the reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are as much as 26 times greater than those above 110 bar. The average estimated error in rate constant values was 20% at higher pressures, increasing to as much as 70% near the critical pressure.

The drop in rate constant with increasing pressure is similar to the result obtained for the esterification of phthalic anhydride with methanol in supercritical CO₂ [Brennecke, et al, 1994]. The bimolecular rate constant for the phthalic anhydride reaction also decreased at pressures above the critical pressure and produced rate constant enhancements near the critical pressure similar in magnitude to those observed for the PTAD reaction. Brennecke estimated the local concentration of methanol around a phthalic anhydride molecule using an analogy with solvatochromic work using phenol-blue [Johnston, 1987 #58]. She determined that, in the region near the critical pressure, local concentration was higher than bulk concentrations by a factor of 5. When this increase in local concentration was accounted for, and rate constants were calculated using local concentration values, the reaction showed only a slight sensitivity to pressure in the region near the critical pressure.

Figure 3. Rate constants for the reaction of PTAD with anthracene in pure CO₂ at 40°C.

Figure 4. Rate constants having values less than 5 l/mol s for the reaction of PTAD with anthracene in pure CO₂ at 40°C.

In order for a local concentration increase to occur in the reaction of PTAD with anthracene, it is necessary for solute-solute clustering to be present along with solute-solvent clustering. Evidence for solute-solute clustering in dilute solutions is found in work by Kurnik [Kurnik, 1982 #98], so clustering effects on local concentrations are one possible explanation of the rate constant trends found in this work.

The construction of mathematical models capable of predicting these kinetic changes is now underway. The simplest promising avenue of investigation involves the assumption that the clustering effects are minimal, and that the kinetics may be successfully modeled as a function of changes in bulk fluid properties. The supercritical CO₂ can then be treated as a dense gas, which allows the following kinetic model based on high reference pressure fugacity coefficients to be derived (Eckert, 1974).

$$\frac{k}{k_o} = \frac{f_A f_B z}{f_M} \quad (7)$$

Here, f 's are fugacity coefficients, and z is the usual compressibility factor of the gaseous mixture. Currently, a computer program for evaluating these fugacity coefficients at arbitrary pressures is being written. Evaluation of the fugacity coefficient model against experimental data using this program will continue into the next quarter.

Kinetic Data in Pure Supercritical CO₂ at 50°C

Rate constants were obtained for the reaction of PTAD with anthracene in pure CO₂ at 50°C and at pressures ranging from the critical pressure of CO₂ (73.8 bar) to 195

bar. Rate constant values at both 40°C and 50°C are plotted in Figure 5. At 40°C, the reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are 25 times greater than those above 110 bar. At 50°C, the reaction rate constant shows only a slight change with pressure around the critical pressure. This slight increase in rate as pressure decreases is predicted by transition state theory (Evans and Polanyi, 1935; Brennecke, et al, 1994). The modest rate constants near the critical pressure indicate that molecular clustering is minimal at this temperature.

Figure 5. Rate constants for the reaction of PTAD with anthracene in pure CO_2 at 50°C.

CONCLUSION

Kinetic data have been previously collected for pure CO₂ at 40°C and pressures between the critical pressure of CO₂ (73.8 bar) and 216 bar. These data support the theory of local density enhancements suggested in the literature. Data taken at 50°C and pressures ranging from 70 bar to 195 bar are currently reported; they do not exhibit the molecular clustering evident closer to the critical temperature.

The data taken at 40°C are now being used to construct mathematical forms which can model these pressure-induced kinetic changes. One promising avenue of investigation involves treating the supercritical medium as a dense gas, which allows a kinetic model based on high reference pressure fugacity coefficients to be derived.

REFERENCES

- Bjerrum, N., *Z. Physik. Chem.*, **108**, 82 (1924).
- Brennecke, J. F., J. B. Ellington, and K. M. Park, "Effect of Local Composition Enhancement on the Esterification of Phthalic Anhydride with Methanol in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **33**, 965 (1994).
- Brennecke, J. F., D. L. Tomasko, J. Peshkin, and C. A. Eckert, "Fluorescence Spectroscopy Studies of Dilute Supercritical Solutions," *Ind. Eng. Chem. Res.*, **29**, 1682 (1990).
- Bronsted, J. M., *Z. Physik. Chem.*, **102**, 169 (1922).
- Clifford, T., and K. Bartle, "Chemical reactions in supercritical fluids," (1996).
- Eckert, C. A., "Molecular Thermodynamics of Chemical Reactions," *I&EC*, **59**, 20 (1967).
- Eckert, C. A., and B. L. Knutson, "Molecular Charisma in Supercritical Fluids," *Fluid Phase Equilib.*, **83**, 93 (1993).
- Ely, J. F., W. M. Haynes, and B. C. Bain, "Isochoric (p, Vm, T) measurements on CO₂ and on (0.982CO₂ + 0.018 N₂) from 250 to 330 K at pressures to 35 MPa," *J. Chem. Thermodynamics*, **21**, 879 (1989).
- Evans, M. G., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).
- Eyring, H., *J. Chem. Phys.*, **3**, 107 (1935).

Hildebrand, J. H., and R. L. Scott *Regular Solutions*; Prentice-Hall: Englewood Cliffs, N. J., 1962.

Hughes, E. D., and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

Ikushima, Y., S. Ito, T. Asano, T. Yokoyama, N. Saito, K. Hatakedo, and T. Goto, "A Diels-Alder Reaction in Supercritical Carbon Dioxide Medium," *Journal of Chemical Engineering of Japan*, **23**, 96 (1990).

Isaacs, N. S., and N. Keating, "The Rates of a Diels-Alder Reaction in Liquid and Supercritical Carbon Dioxide," *J. Chem. Soc., Chem. Commun.*, 876 (1992).

Johnston, "Adjustment of the Selectivity of a Diels-Alder Reaction Network Using Supercritical Fluids," *Chem. Eng. Comm.*, **63**, 49 (1988).

Johnston, K. P., D. H. Ziger, and C. A. Eckert, "Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented Van der Waals Treatment," *Ind. Eng. Chem. Fundam.*, **21**, 191 (1982).

Kim, S., and K. P. Johnston, "Clustering in Supercritical Fluid Mixtures," *AIChE J.*, **33**, 1603 (1987a).

Kim, S., and K. P. Johnston, "Molecular Interactions in Dilute Supercritical Fluid Solutions," *Ind. Eng. Chem. Res.*, **1987**, 1206 (1987b).

Konovalov, A. I., I. P. Breus, I. A. Sharagin, and V. D. Kiselev, "Solvation Effects in the Diels-Alder Reactions of 4-Phenyl-1,2,4-Triazoline-3,5-Dione with Anthracene and Trans, Trans-1,4-Diphenyl-1,3-Butadiene," *Zhurnal Organicheskoi Khimii*, **15**, 361 (1979).

Laidler, K. *Chemical Kinetics*; Third ed.; HarperCollins Publishers, Inc.: New York, 1987a.

Laidler, K. J. *Chemical Kinetics*; Third ed.; HarperCollins Publishers: New York, 1987b.

Paulaitis, M. E., and G. C. Alexander, "Reactions in supercritical fluids. A case-study of the thermodynamic solvent effects on a Diels-Alder reaction in supercritical carbon dioxide.," *Pure and Appl. Chem.*, **59**, 61 (1987).

Sauer, J., "Diels-Alder Reactions II: The Reaction Mechanism," *Angew. Chem. Internat. Edit.*, **6**, 16 (1967).

Savage, P. E., S. Gopalan, T. I. Mizan, C. J. Martino, and E. E. Brock, "Reactions at supercritical conditions: applications and fundamentals," *AIChE Journal*, **41**, 1723 (1995).

Weinstein, R. D., A. R. Renslo, R. L. Danheiser, J. G. Harris, and J. W. Tester, "Kinetic Correlation of Diels-Alder Reactions in Supercritical Carbon Dioxide," *J. Phys. Chem.*, **100**, 12337 (1996).