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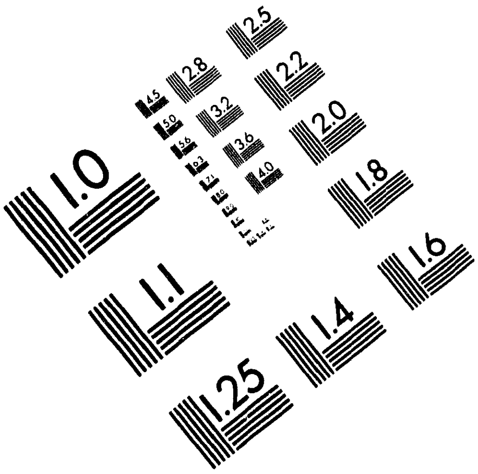

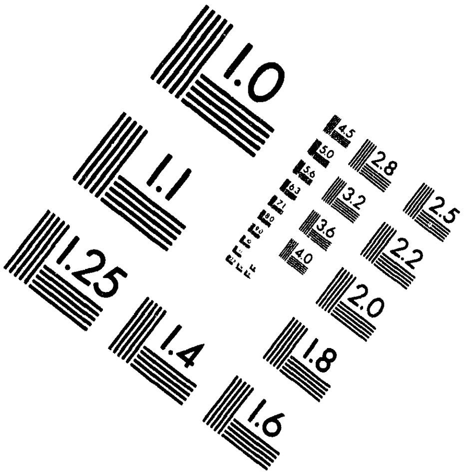

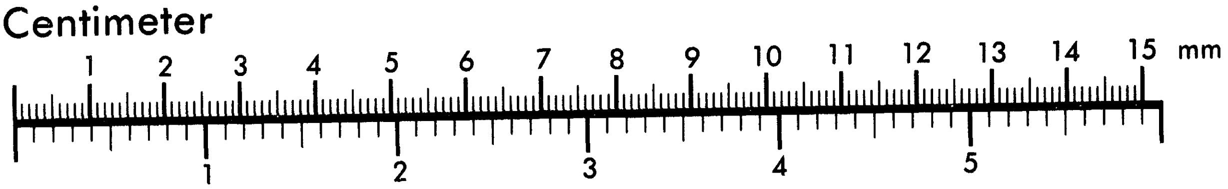

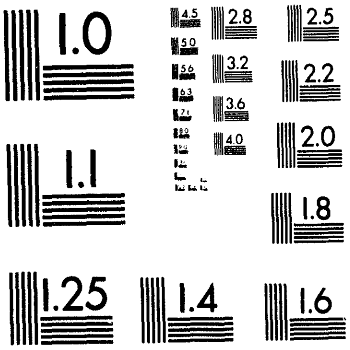

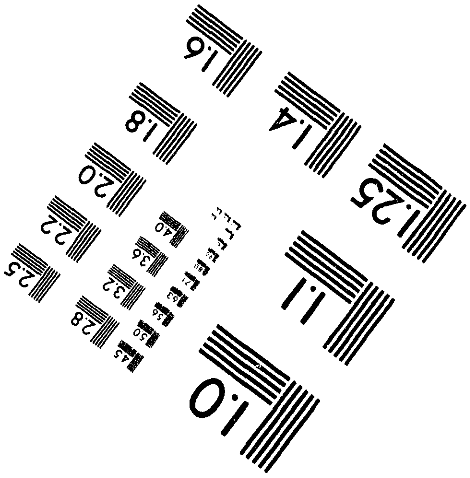

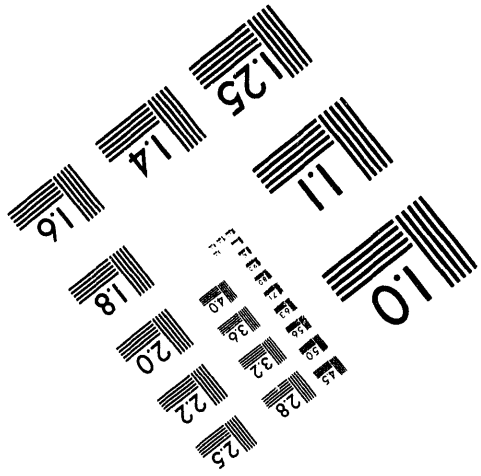

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Summary Report

on

FUNDAMENTAL KINETICS OF METHANE OXIDATION IN SUPERCRITICAL WATER

by

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with

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ABSTRACT

Fundamental understanding of the oxidation of compounds in supercritical water is essential for the design, development and operation of a supercritical water oxidation unit. Previous work in our group determined the oxidation kinetics of carbon monoxide and ethanol in supercritical water for temperatures ranging from 400 to 540°C. Oxidation studies of methane up to 700°C have recently been completed and are presented in this report. Theoretical studies of fundamental kinetics and mechanistic pathways for the oxidation of methane in supercritical water are discussed. Application of current gas phase elementary reaction models are briefly presented and their limitations discussed.

Motivation and Scope

Oxidation in supercritical water is currently being used to dispose of a wide variety of hazardous chemical wastes[3,4]. The Los Alamos National Laboratory is currently involved in research sponsored by the HAZWRAP program of the USDOE to investigate fundamental chemical kinetics and other important process elements associated with oxidation in supercritical water. In addition, NASA is interested in developing methods for treating human metabolic products for space station applications. Oxidation in supercritical water is one of the technologies being evaluated as a method of treatment.

In supercritical water oxidation, organics, air (or oxygen) and water are brought together in a mixture at pressures of approximately 250 atm and temperatures above 400°C. At these conditions, organic oxidation is initiated spontaneously and the heat of combustion is released within the fluid, typically resulting in temperature increases to 550-650°C. Organics are destroyed rapidly with conversions in excess of 99.99% at reactor residence times of less than 1 minute. Heteroatoms are oxidized to acids which can be precipitated out as salts by adding a base to the feed[5]. The oxidation of a variety of organics in supercritical water has been demonstrated by several authors. Price[6] eliminated 88-93% of the liquid TOC (total organic carbon) and Modell et al.[3] oxidized several toxic chlorinated hydrocarbons in supercritical water, destroying at least 99.99% of the organic chlorides and 99.97% of the TOC.

Water is considered supercritical if its temperature and pressure exceed 374.3°C and 217.6 atm. At and above these conditions, the fluid density is a strong function of both temperature and pressure and leads to large changes in the physical properties of water, particularly its solvation behavior[7]. Under supercritical conditions, water behaves like a dense gas with a high solubility of organics[8], complete miscibility in all proportions with oxygen and air[9], light organic gases[10] and carbon dioxide[11]. In addition, supercritical water exhibits high diffusivities[12], low viscosity[13] and low solubility and dissociation of inorganics, particularly salts[14,15]. These solvation properties together with the high temperature and pressure make supercritical water an ideal medium for oxidation of organic wastes, since organics and oxygen can be intimately mixed in a single homogeneous phase, and inorganic salts can be readily removed from solution by precipitation.

Although the technical feasibility of the supercritical water oxidation (SCWO) process has been demonstrated, little information is available on the reaction kinetics and mechanisms responsible for the observed oxidation rates. Such information is useful for design and development of a SCWO process, and for the evaluation of alternative process configurations. Although many wastes will contain complex compounds, the rate determining step in the oxidation of these compounds is frequently the oxidation of carbon monoxide and ammonia to carbon dioxide and nitrogen respectively. The oxidation kinetics of carbon monoxide, ammonia, and other simple compounds are therefore necessary for the design of a SCWO unit. Previous work by Helling and Tester[16] determined the oxidation kinetics of carbon monoxide in supercritical water for temperatures ranging from 400 to 540°C and for a range of carbon monoxide and oxygen concentrations. The oxidation kinetics of ammonia and ethanol were also investigated[17] although apparatus constraints limited ammonia conversions to 5% at which reliable kinetic data could not be obtained. The oxidation kinetics of methane in supercritical water up to 700°C has recently been measured. Experiments are currently being conducted to determine reaction kinetic parameters for oxidation of other simple molecules in supercritical water, such as methanol, higher hydrocarbons, ammonia and mixtures of ammonia and co-oxidants.

Experimental Kinetics Studies

The apparatus used to conduct oxidation studies of methane was that of Helling and Tester[16]. The constant temperature sand bath which previously limited operation to 550°C was replaced with a higher temperature bath which permitted stable operation to 700°C. The reactor consisted of a 4.27 m of 0.635 cm o.d X 0.211 cm i.d. Inconel 625 tubing, and was immersed in the sand bath for temperature control. Fluid compositions were determined using gas chromatography. Further experimental details are discussed in Helling and Tester[16].

Methane Oxidation in Supercritical Water

The oxidation kinetics of methane (CH_4) in supercritical water in the temperature range 640 - 700°C and at a pressure of 242 atm (24.5 MPa) was measured. Reactor residence times ranged from 5.6 to 11.1 seconds. Table 1 shows the experimental conditions and results for fifteen oxidation runs. In most cases, the feed concentrations were kept at stoichiometric amounts of oxygen for complete conversion of CH_4 to H_2O and CO. The calculated rate constant in column 6 is for an assumed first order rate with respect to methane concentration. Column seven shows the ratio of carbon dioxide to carbon monoxide detected in the product from the reactor.

An Arrhenius plot for an assumed first order rate constant for methane oxidation is shown in Figure 1 together with the errors (98% confidence limits) associated with each measurement. Also shown is the weighted least-squares regression line to the data, where the weights were taken as proportional to k_i^2/σ_i^2.[18] The variances, σ_i^2, for each data point were generated using a Monte Carlo error analysis correlated to estimates of errors in the measured data. From the regression line, the activation energy was estimated to be $E_a = 156.9 \pm 34.7$ kJ/mole, where the stated error is at the 98% confidence limit. The overall first order rate expression for the oxidation of methane is;

$$-\frac{d[CH_4]}{dt} = 10^{7.1 \pm 1.9}\exp(-156.9 \pm 34.7/RT)[CH_4] \qquad (1)$$

Figure 1 clearly reveals those data points whose deviation from the regressed line cannot be attributed to experimental error alone. For these measurements, it is likely that some variable not appearing in the regressed equation yet still affecting the reaction rate is responsible for the deviation. Since the plot assumes that rate depends only on methane concentration to the first power, it is possible that the changing concentration of oxygen from run to run (due mainly to changes in fluid density with temperature) is responsible for the observed variation. In addition, the true order with respect to methane concentration may be different from one, leading to a dependence of the assumed first order rate constant on methane concentration as well as oxygen concentration. A regression of the data to the form;

$$- \frac{d[CH_4]}{dt} = A \exp(-E_a/RT)[CH_4]^a[O_2]^b \qquad (2)$$

was attempted to separate the effect of concentration of methane and oxygen on the reaction rate. Least-squares regression of the data to the above expression gave (where all errors are at the 98% confidence limit);

$$- \frac{d[CH_4]}{dt} = 10^{3.5 \pm 0.8} \exp(-153.1 \pm 33.1/RT)[CH_4]^{0.29 \pm 0.39}[O_2]^{0.13 \pm 0.33} \qquad (3)$$

The activation energy is not significantly different from the value obtained assuming first order kinetics with respect to methane. In addition, the error associated with the activation energy is only slightly smaller than that obtained assuming first order kinetics, indicating that no significant improvement is obtained by assuming the more complicated expression (2). The reaction orders with respect to both methane and oxygen have large errors associated with them. Variations in the feed concentration were restricted to the pressure range attainable in the feed saturators and the methane feed concentration was at its upper limit in order to produce measureable concentrations of carbon dioxide in the product gas. Consequently, the methane and oxygen concentration remained virtually constant from run to run, varying only with changes in fluid density. Therefore, the regressed reaction orders are probably only artifacts of the manner in which the experiments were carried out. We plan to correct these limitations in future tests.

Discussion

The oxidation of methane to carbon dioxide in supercritical water can be viewed as proceeding through two global steps. The first step is oxidation to carbon monoxide;

$$CH_4 + \frac{3}{2} O_2 \longrightarrow CO + 2H_2O \qquad (4)$$

followed by direct oxidation of carbon monoxide to carbon dioxide (reaction(5)) or oxidation via the water gas shift reaction (6);

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2 \qquad (5)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (6)$$

The rate limiting step for the oxidation of methane to carbon dioxide was found to be reaction (4). This is supported by the very small amounts of carbon monoxide detected in the product gas. From Table 1, the ratio of carbon dioxide to carbon monoxide detected in the product gas ranges from a factor of approximately 2 at low temperatures (640°C) to 30 at high temperatures (700°C). This is in keeping with our previous work[16] which indicated high conversions of carbon monoxide to carbon dioxide (exceeding 95%) at similar residence times in the temperature range 640-700°C.

An Arrhenius plot for both methane and carbon monoxide oxidation in supercritical water is shown in Figure 2. In the temperature range 640-700°C, the first order rate constant for carbon monoxide oxidation is two orders of magnitude greater than methane oxidation, indicating that the oxidation of methane to carbon monoxide is slow followed by rapid oxidation to carbon dioxide. It is interesting to note that methane oxidation is the more highly activated reaction, indicating that at some temperature the oxidation of carbon monoxide to carbon dioxide becomes rate limiting. By extrapolation, the Arrhenius lines would intersect at approximately 3400°C, far exceeding practical operating temperatures of a SCWO unit. Thus, for current operating ranges of a SCWO unit, the oxidation of methane to carbon monoxide is the rate limiting step.

The parallel water-gas shift reaction (6), which accounted for a large percentage of the carbon monoxide oxidized in previous experiments[16], was found to be negligible in the oxidation of methane. No hydrogen was detected in the product gas for all fifteen runs. From measurements made on the water-gas shift reaction[16] an extrapolation to 700°C indicates that the rate constant for the water gas shift reaction is an order of magnitude lower than direct oxidation and therefore any hydrogen produced would be in such low concentration as to be undetectable on our gas chromatograph.

Several measurements of methane oxidation in the gas phase have been made, most involving flame studies[19,20,21] and may be useful in interpreting kinetic data for oxidation in supercritical water. Unfortunately, these measurements are frequently characterized by poor reproducibility due, in part, to the effect of the reactor surface on the combustion rate. In addition, chain-branching is known to occur in methane combustion[20], leading to formation of C_2 hydrocarbons which combust to finally give carbon dioxide. Measurement of methane oxidation kinetics by Kozlov[22] gave the expression;

$$-\frac{d[CH_4]}{dt} = \frac{7x10^8 \exp(-251/RT)}{T} [CH_4]^n [O_2]^m \qquad (7)$$

where the activation energy is in kJ/mole and the orders of the reaction,n,m were found to be temperature dependent. Over the temperature range 600-930°C, the order with respect to methane was found to vary linearly from 1.15 to -0.5. The order with respect to oxygen was found to vary from 2.0 to 1.5 over the range 740 to 1030°C. Using m=2 and n=0.65, at 700°C in equation (7) with average concentrations of methane and oxygen as occurred in our supercritical oxidation run, gives an estimate for the rate of methane oxidation. The predicted rate of 3.81×10^{-21} gmole/cm^{3}sec is thirteen orders of magnitude lower than the observed rate of 8.88×10^{-8} gmole/cm^{3}sec. This huge difference illustrates the inapplicabiliy of gas phase combustion data to oxidation in supercritical water. Enikolopyan[19] measured the oxidation of methane in the presence of some water (<1%) at low pressures (235 mmHg) and obtained 179.9 ± 4 kJ/mole for the activation energy. This is relatively close to the value of 156.9 ± 34.7 kcal/mole obtained for oxidation in supercritical water, although any agreement must be regarded as fortuitous at this stage. These measurements were carried out in the temperature range 423-513°C. His estimated reaction order with respect to methane was 1.62 and for oxygen was 0.96. Unfortunately, pre-exponential factors are not reported and reaction rates are reported in terms of total pressure change, making comparison with our supercritical oxidation work difficult.

Elementary Reaction Modeling

The failure of global gas phase models to predict methane oxidation in supercritical water has prompted the use of elementary reaction modeling. This approach was adopted by Helling and Tester[16] in the modeling of carbon monoxide oxidation in supercritical water. Although the elementary reaction model was found to be better than the best empirical global models, conversions were still significantly underpredicted. More importantly, the elementary reaction model was unable to predict the formation of hydrogen from the water-gas shift reaction, although hydrogen was included in the network of equations[16].

Several models exist for modeling gas phase combustion of methane such as the Warnatz model[20]. Elementary reaction modeling of methane oxidation in supercritical water has recently been attempted by Rofer,Streit et al.[23] Using a model developed at the Los Alamos National Laboratory for the low temperature gas phase combustion of methane at pressures below 100 atm, four model simulations were run. The first three simulations were done at 550,600 and 650°C. In all three cases, close to zero conversions were predicted, well under the observed conversion of approximately 10%.. For the fourth simulation (at 650°C), four reactions describing the high-pressure unimolecular dissociation of hydrogen, methane, formaldehyde and water were added. With these changes, a slight amount of methane oxidation was predicted (0.5%) but still well under the observed amount. Perhaps more significantly, the model predicted carbon monoxide as the major product rather than carbon dioxide. This is not surprising since the model used an elementary reaction network for carbon monoxide oxidation that was shown to underpredict conversions to carbon monoxide.[16]

The inability of the elementary reaction model to predict conversion of carbon monoxide to carbon dioxide prompted Rofer et al[23] to re-examine the carbon monoxide mechanism used by Helling and Tester[16]. Using more recent reaction rate constants and adjusting some of the unimolecular rates to their high pressure values resulted in only slight improvement in predicting hydrogen production, while the predicted conversion of carbon monoxide was still significantly lower than that observed. Currently, no model, either elementary or global, can quantitativley describe oxidation in supercritical water.

The failure of gas phase models to describe oxidation in supercritical water leads to speculation on the possible effect of the solvent on reaction rates. Helling and Tester[16] suggested the possibility of "cages" of water molecules around reactants, as previously speculated by Abraham and Klein[24]. The effect of such a "cage" would be to promote solute-solvent encounters and decrease solute-solute encounters. This is qualitatively consistent with the carbon monoxide oxidation results in which direct oxidation was less than that in a comparable gas phase oxidation while the water-gas shift reaction was greater than that predicted. Such a "cage" could be either the result of limited hydrogen bonding still possible at supercritical conditions, as suggested by infra-red spectra,[25] or a consequence of the dense nature of supercritical water in comparison to gas-phase oxidation conditions. In the latter case, the "solvent cage" would be typical of reactions in condensed phases in which reactions may be diffusion controlled. This is not likely in supercritical water due to high diffusion coefficients and low viscosity. A "hydrogen-bonded cage" while possible at low temperatures (around 400°C) is highly unlikely at higher temperatures and if this was a major effect, we would expect to see predictions improve as temperature is increased. This is not observed.

The possibility of ionic reactions in supercritical water was suggested by Antal et al[26] provided the $\log_{10}$ of the dissociation constant of water is greater than -14. For oxidation in supercritical water, dissociation constants[27] range from 10^{-22} to 10^{-24}. In addition, the dielectric constant of water at these conditions[28] is less than 2, indicating that supercritical water is unlikely to support ionic reactions. The reaction pathway is likely to involve a free radical network as in gas phase combustion of organics.

Before gas phase elementary reaction models become directly applicable to oxidation in supercritical water, it is likely that modifications to the rate constants will need to be made. These modifications include adjustment of pressure dependent rate constants to their values appropriate to oxidation at 250 atm, correction of existing high pressures rate constants to reflect the efficiency of the water molecule as a third body and inclusion of elementary reactions peculiar to reaction in supercritical water.

Conclusions and Current Research Directions

Kinetic data is now available for oxidation of carbon monoxide, methane and ethanol in supercritical water. Work is currently underway to determine oxidation kinetics of ammonia and methanol up to 700°C. Oxidation of ammonia is frequently the rate limiting step in oxidation of nitrogen containing organics and will occur in the combustion of human waste as an intermediate. Methanol is a common industrial solvent and is likely to occur in chemical wastes. Although understanding of the kinetics of oxidation in supercritical water has improved, current reaction mechanisms are unable to predict oxidation rates. Elementary reaction models remain the best hope for simulating oxidation in supercritical water. Several modifications to existing mechanisms need to be made however to account for the role of water in the reaction mechanism. The water-gas shift reaction appears to be a good starting point for modeling since it is directly responsible for hydrogen production in supercritical water. The failure of current elementary models to predict hydrogen production via the global water-gas shift reaction has been identified as a major deficiency in these models. Theoretical work is in progress both at MIT and at the Los Alamos National Laboratory to obtain a better fundamental understanding of reaction mechanistic pathways in supercritical water oxidation and to produce an improved elementary reaction model.

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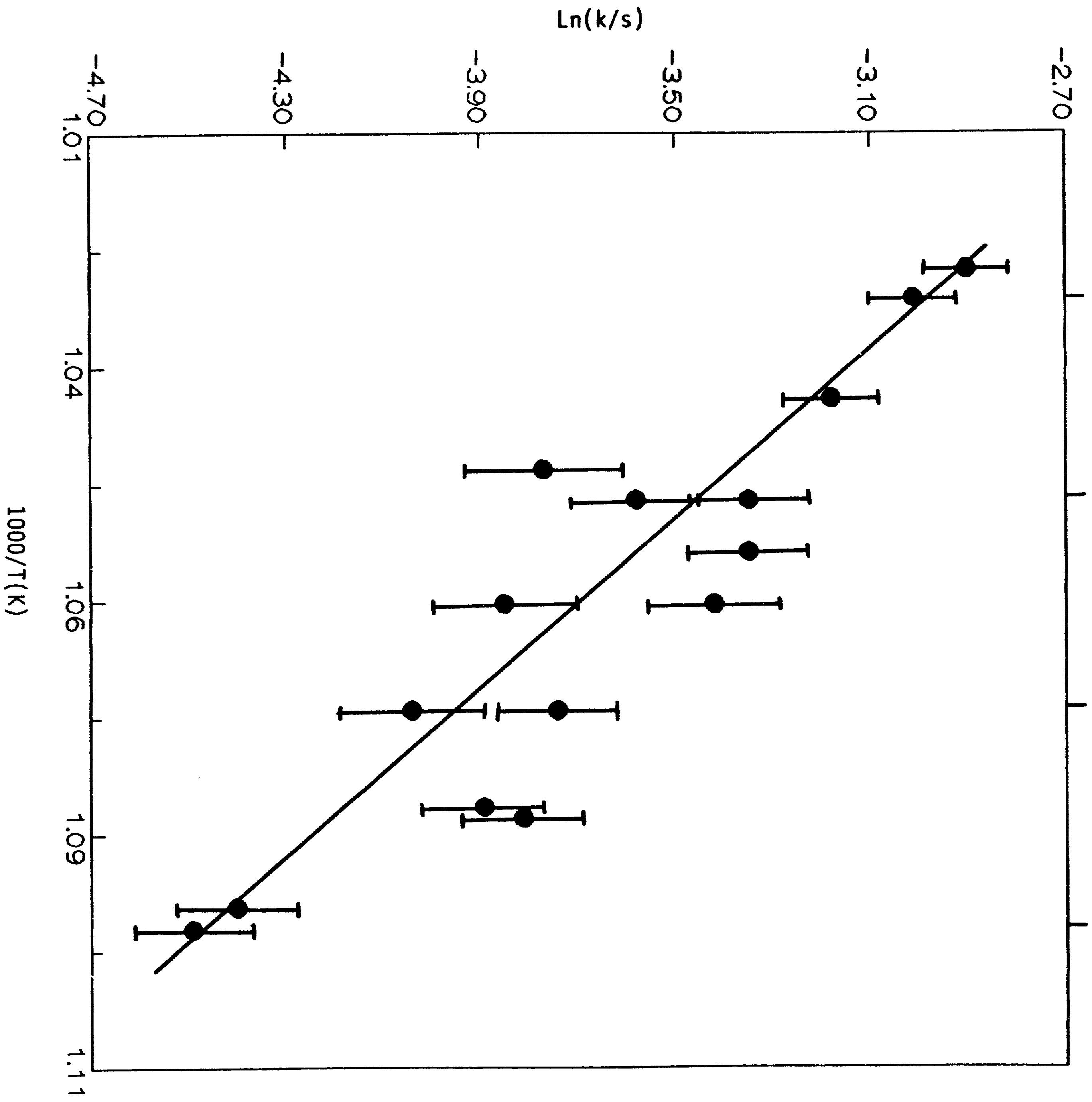
Figures and Tables

Temperature °C	CH_4/O_2 feed	Residence time seconds	Conversion %	Reaction rate 10^6gmole/cm^{3}min	ln(k) 1/s	$[CO_2]/[CO]$
640	1:2.0	6.1	6.6	1.21	-4.49	2.3
642	1:2.0	11.1	12.7	1.26	-4.40	3.6
650	1:1.0	5.6	11.6	1.35	-3.81	5.6
651	1:2.0	6.0	11.5	2.12	-3.89	12.8
660	1:2.0	5.9	13.0	2.44	-3.74	14.8
660	1:1.2	9.6	15.5	1.89	-4.04	3.3
670	1:2.1	5.8	11.6	2.15	-3.85	12.6
670	1:1.8	9.3	26.2	3.23	-3.42	11.8
675	1:2.2	6.3	19.8	3.91	-3.35	2.9
680	1:2.8	6.0	19.1	2.93	-3.35	2.5
680	1:1.2	9.0	22.1	2.67	-3.58	5.4
683	1:2.0	5.7	12.3	2.29	-3.77	14.2
690	1:2.0	8.9	30.7	3.64	-3.18	12.5
700	1:2.1	6.1	25.9	5.33	-3.01	24.1
703	1:2.1	5.6	26.5	4.82	-2.90	34.8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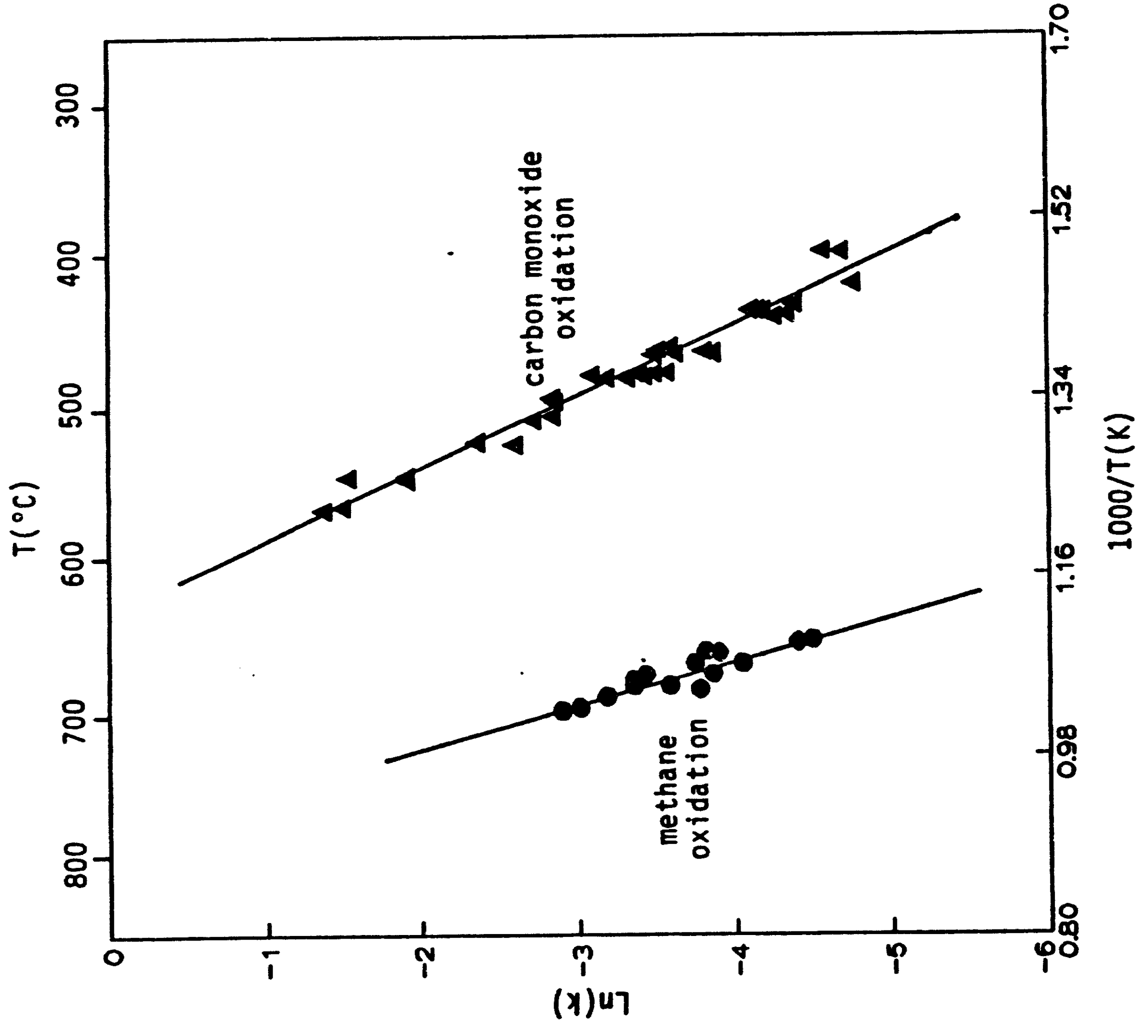

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carbon monoxide oxidation
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