Kinetics and Catalysis, Vol. 43, No. 2, 2002, pp. 189–194. Translated from Kinetika i Kataliz, Vol. 43, No. 2, 2002, pp. 209–214.

Reaction Kinetics of 2-Propanol Dehydration in Supercritical Water

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Received January 9, 2001

Abstract—A study of the kinetics and mechanism of chemical reactions in supercritical fluids is considered. An experimental procedure was proposed for examining reversible chemical reactions in supercritical water. The reaction kinetics of 2-propanol dehydration in supercritical water was studied. It was found that the uncatalyzed reactions of olefin hydrogenation by hydrogen dissolved in supercritical water occur at high rates near the critical point of water. The experimental data on the dehydration of 2-propanol in supercritical water are adequately described by first-order reaction rate equations. The rate constants and activation energies of 2-propanol dehydration near the critical point of supercritical water were found.

INTRODUCTION

On the one hand, the unique properties of supercritical fluids are responsible for an intense interest in fundamental investigations into their physicochemical properties and reactivity. On the other hand, they constitute the basis of unique technologies for the synthesis of new materials, the utilization of harmful and toxic wastes, the production of new chemicals, the conversion of heavy still bottoms, and the recovery of industrial and municipal wastes. For example, the nature of physicochemical processes occurring in the Earth's crust and atmosphere with the participation of supercritical water can be studied more thoroughly based on fundamental investigations into the properties of supercritical fluids, in particular, supercritical water.

Structural changes in supercritical fluids near the critical point, which are responsible for anomalous properties, essentially depend on the temperature, pressure, composition, external actions, hydrodynamic disturbances, and processes at the surfaces that confine the fluid. Therefore, a wide variety of mathematical, chemical, and physical techniques should be used for studying these systems both theoretically and experimentally.

The application of supercritical fluids to perform both catalyzed and uncatalyzed chemical reactions is of particular interest [1–4]. Taking into account the specific action of a supercritical solvent on the chemical transformations of both organic compounds and inorganic substances, the studies of the kinetics, mechanisms, and thermodynamics of chemical reactions are of paramount importance. As distinct from chemical reactions in gas and liquid phases, the kinetics of chemical reactions in supercritical fluids dramatically depends on pressure or, more precisely, on the density of a supercritical solvent [5].

The first stage of the study of the kinetics and equilibria of reversible reactions in supercritical fluids was devoted to the effect of the density of a solvent (supercritical water) on the dehydration reaction of 2-propanol [5]. It was found that, first, the reaction mechanism of 2-propanol dehydration in supercritical water is different from the mechanism of this reaction in the presence of a homogeneous acid catalyst [6]. Second, the rate and the equilibrium constant of this reaction essentially depend on the density of supercritical water. The main reaction mechanism was proposed for 2-propanol dehydration in supercritical water based on the experimental studies of the hydration and hydrogenation reactions of the main products of the test reaction. It was found that the density of supercritical water is a usable parameter for controlling the kinetics and selectivity of a chemical reaction.

EXPERIMENTAL

Reactors of the following two types are primarily used for performing reactions in supercritical solvents: a flow reactor and a closed autoclave reactor. To study chemical reactions in supercritical fluids, one of the above reactor types is chosen depending on the goals of the study, the type of the test reaction, the participation of a catalyst, etc. An autoclave reactor is clearly advantageous when the main goal is to study the kinetics and mechanisms of reactions in supercritical fluids close to the critical point. The properties of supercritical fluids (for example, permittivity, viscosity, and thermal conductivity), which are responsible for the effectiveness of chemical transformations, are strongly changed in the critical region with few changes in the temperature and pressure. Uniform temperatures and pressures are

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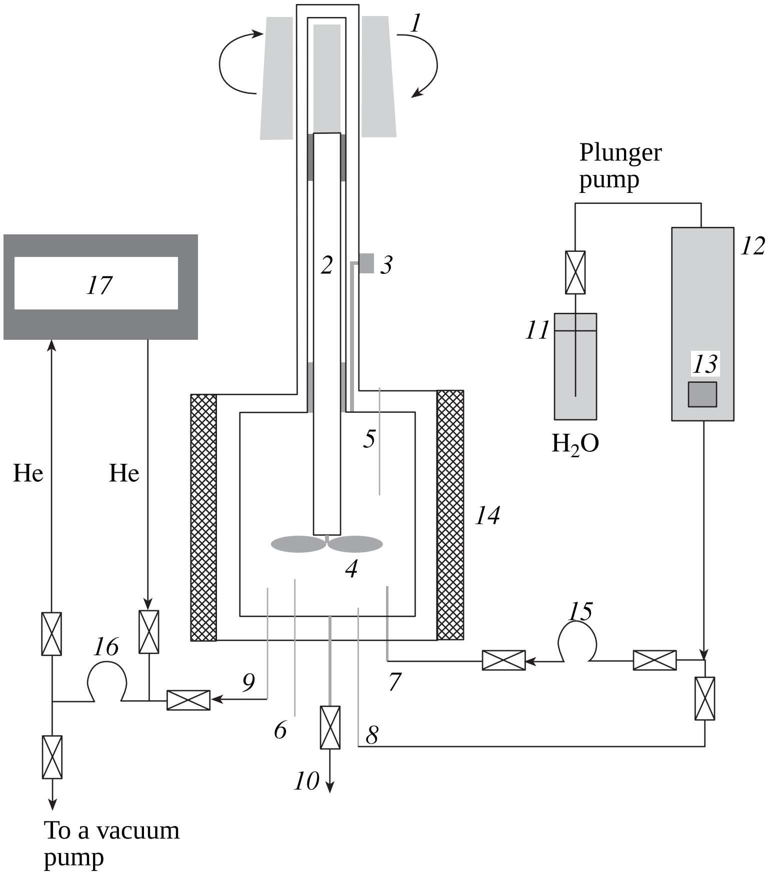

Fig. 1. Schematic diagram of the experimental setup for performing chemical reactions in supercritical fluids: (*1*) magnetic stirrer; (*2*) magnetic stirrer shaft with a propeller; (*3* and *13*) pressure gauges; (*4*) propeller; (*5* and *6*) thermocouples; (*7* and *8*) sample and water inlets of the reactor, respectively; (*9*) sample outlet for analysis; (*10*) waste; (*11*) reservoir for water; (*12*) plunger pump; (*14*) furnace; (*15*) sample loop for injecting initial samples; (*16*) inlet valve with a sample loop for reaction products; and (*17*) gas chromatograph.

much more difficult to maintain in flow reactors than in autoclave reactors. Indeed, it was experimentally found that a considerable time is taken to prepare a supercritical fluid with uniform bulk density and temperature in an autoclave reactor; in our case, several tens of minutes were required (of course, this time strongly depends on the design and volume of the reactor and on the type of the fluid). By analogy, the same residence time of the fluid in a flow reactor should be provided; however, this is very problematic.

Moreover, in the course of chemical reactions in supercritical fluids in a closed reactor, the reaction products are uniformly distributed in the bulk of the fluid. Taking into account a considerable buffer concentration of the fluid, a change in reactant concentrations or an increase in the volume of reaction products affects the properties of the supercritical fluid only slightly.

A special feature of the method proposed here for studying the kinetics of chemical reactions in supercritical fluids is that the test reactant is injected into the bulk of supercritical water, which is prepared beforehand, in a short time. As compared with chemical reactions in a flow, which are performed in flow reactors, a given density remains practically constant in a closed reactor over the entire geometrical volume of the reactor during the total residence time of reactants in the reactor.

The chemical reactions of organic compounds in supercritical water were performed in a modernized reactor consisting of a 126-cm^3 autoclave equipped with a magnetic stirrer (Fig. 1). Initially, a test reactant was placed in sample loop *15* with a known volume. The sample was introduced into the reaction volume of supercritical water with water supplied to this loop at a given flow rate with the use of a plunger pump. In the majority of cases, a 0.04-ml sample was forced with 0.5 ml of water for 6 s; thus, the test sample was injected into the reaction volume in 0.48 s. The introduced sample was completely mixed in the bulk of supercritical water within a 20-s time period at a stirrer speed of 2200–2500 rpm.

The reaction products were initially sampled for analysis into loop *16* with a volume of 6×10^{-3} ml at regular intervals. Next, the samples were injected into gas chromatograph *17* (Hewlett-Packard 5890) with a flame-ionization detector; the chromatograph was equipped with a capillary column and a packed column.

Before experiments, nitrogen was blown through water for 1.5 h to remove dissolved oxygen. The reactor was evacuated before the introduction of water. After introducing the required amount of water into the reactor, the temperature was slowly increased up to a specified value simultaneously with intense stirring. Supercritical water in the reactor was considered to attain a steady state if the measured temperature and pressure values remained unchanged for 0.5 h. The pressure of supercritical water in the reactor was measured with two high-precision gauges from Entran, and the temperatures of the fluid at two different points of the volume were measured with two microthermocouples.

RESULTS AND DISCUSSION

As mentioned above, the effects of the density of supercritical water on the reaction equilibrium and rate of 2-propanol dehydration at a constant temperature were studied previously [5]. In these experiments, it was found that propylene (C_3H_6), propane (C_3H_8), propyne (C_3H_4), acetone (C_3H_6O), and 1-propanol (C_3H_8O) are the main reaction products of 2-propanol dehydration in supercritical water. Methane and trace ethane (C_2H_6) were detected in insignificant amounts. It is likely that methane was partially formed from carbon or high-molecular-weight carbonaceous compounds deposited on the reactor walls in the course of previous operation for many tens of hours.

To reveal the mechanisms of reactions responsible for the formation of the above products, the reactions of 1-propanol dehydration, propylene and propyne hydration, and propylene and acetone hydrogenation were performed separately under analogous conditions. These studies resulted in the conclusion that the following reactions occur in the dehydration of 2-propanol in supercritical water:

$$CH_3CHOHCH_3 \longrightarrow C_3H_6 + H_2O, \qquad (I)$$

$$C_3H_6 + H_2O \longrightarrow CH_3CH_2CH_2OH, \qquad (II)$$

$$CH_3CHOHCH_3 \longrightarrow C_3H_6O + H_2, \qquad (III)$$

$$C_3H_6 + H_2 \longrightarrow C_3H_8, \qquad (IV)$$

$$C_3H_4 + H_2O \longrightarrow C_3H_6O, \qquad (V)$$

$$C_3H_6 \longrightarrow C_3H_4 + H_2. \qquad (VI)$$

Here, the parent 2-propanol is consumed in two parallel reactions (I) and (III). The resulting propylene can participate in two other reactions (II) and (IV). Based on the available experimental data, it is difficult to separate the contributions of reactions (III) and (V) to the formation of acetone. There is no doubt that acetone is formed by reaction (V). Indeed, C_3H_4 is present in the products of 2-propanol dehydration in supercritical water, whereas we experimentally found that the reaction of propyne hydration in supercritical water only results in the formation of acetone. The rate of this reaction is much higher than the rate of reaction (I). Therefore, propyne is not accumulated in the reaction mixture, and its concentration passes through a maximum. However, there is only indirect evidence that propyne can be formed by reaction (VI).

Another conceivable reaction that results in the formation of acetone is noteworthy: reaction (III) of 2-propanol dehydrogenation in supercritical water to form acetone and hydrogen. To reveal the contribution of this reaction, we calculated the equilibrium state of the reaction mixture (with consideration for its imperfection) at temperatures and pressures analogous to experimental values. The equilibrium compositions were determined by minimizing the Gibbs free-energy function

$$G = \sum_i \mu_i n_i \longrightarrow \min$$

at constant T and P taking into account the material balance. Here, μ_i and n_i are the chemical potentials and the numbers of moles of mixture components, respectively.

The chemical potential of the ith component of the mixture was calculated by the expression

$$\mu_i = \mu^0 + RT\ln f_i(y, T, P),$$

where μ_i^0 is the chemical potential under standard conditions, and y is the mole fraction vector of components. The fugacities (f_i) of mixture components were calculated by the Redlich–Kwong–Soave equation of state [7].

The calculations demonstrated (Tables 1 and 2) that, if acetone is entered in the list of products, 2-propanol is primarily converted by reaction (III); however, this was not observed in real experiments. If reaction (III) is removed from the set of reactions (I)–(V), the calculated composition of an equilibrium reaction mixture is close to the experimental composition under supercritical conditions. Taking into account that, as a rule, the equilibrium composition of reaction products calculated by thermodynamic models approaches the experimental composition with reasonable accuracy, we can conclude that reaction (III) in supercritical water is a slow step in comparison with the other one.

In addition to the equilibrium compositions of the reaction products of 2-propanol dehydration, Tables 1 and 2 summarize the fugacity coefficients of particular reaction mixture components; these coefficients characterize the departure from an ideal state.

Mathematical Treatment of Experimental Data

The mathematical treatment of experimental data was performed according to previously developed procedures [8–10]. The equations of the mathematical model were solved with the use of the KINET II program package, which balances original experimental data, identifies kinetic models, and calculates reaction rate and equilibrium constants and activation energies.

It is convenient to represent the reaction sequence of 2-propanol dehydration, which was taken for processing the kinetic data and finding the rate constants of particular steps, as follows:

$$\begin{tikzcd} A \arrow[r, shift left, "k_1"] \arrow[d, "k_3"'] & B \arrow[l, shift left, "k_2"] \arrow[r, "k_5"] \arrow[d, "k_4"] & C, \\ D & G \end{tikzcd} \tag{VII}$$

where A is 2-propanol, B is propylene, C is 1-propanol, D is acetone, and G is propane.

Note that we assumed $k_5 = 0$ because in this series of experiments low concentrations of 1-propanol were detected in the reaction products, as compared with the concentrations of other reactants. Then, in accordance with scheme (VII), we can write a system of four differential equations for finding reaction rate constants on the assumption that the reaction follows first-order kinetics. Table 3 compares the calculated and experimental data.

Temperature Effect on the Reaction Rate of 2-Propanol Dehydration

The effect of temperature on the rate of 2-propanol dehydration in supercritical water was studied at three densities of water fluids equal to 0.24, 0.34, and 0.42 g/ml. The reaction kinetics will be primarily considered for a supercritical water density of 0.34 g/ml. This is because the density of water at the critical point is 0.32 g/ml; therefore, the state of water at a density of 0.24 g/ml and at a temperature higher than 378°C cannot be referred to as supercritical. This state of the fluid is to the right of a saturation curve in the phase diagram *P–T*, and it corresponds to superheated vapor in a near-critical state. Nevertheless, a comparison of data on reaction rates and equilibria in near-critical and supercritical regions is also of considerable interest to us.

The consideration given below is of importance for refining the procedure of kinetic experiments under supercritical conditions near the critical point of a solvent, taking into account that the reaction rate of 2-propanol dehydration is highly sensitive to changes in the density of supercritical water [5]. As noted above the present goal is to study the reaction rate under changes in the reaction temperature at a constant density of the supercritical fluid. This density is calculated as the ratio of the amount of water fed into a reactor to the reactor volume. In an ideal case, with a constant amount of water in the reactor, a change in the temperature results in a corresponding change in the pressure within the reactor so that the fluid density remains constant. However, because the fluid is highly compressible and nonideal, its density can be weakly changed with temperature and, correspondingly, pressure. Another reason for

Table 1. Equilibrium composition of the reaction products of 2-propanol dehydration (T = 393°C, P = 280 atm; $[CH_3CHOHCH_3]_0$ = 1 and $[H_2O]_0$ = 1000 mole fractions)

Component	Equilibrium composition, mole fractions	Fugacity coefficient
H_2	0.2170	5.2538
C_3H_4	0	2.0164
C_3H_6	0.0083	2.0170
C_3H_8	0.3870	2.0570
$CH_2OHCH_2CH_3$	0.0001	0.9018
$CH_3CHOHCH_3$	0.0005	1.2113
C_3H_6O	0.6050	0.9224
H_2O	1000.3943	0.6149

Table 2. Equilibrium composition of the reaction products of 2-propanol dehydration (T = 393°C, P = 280 atm; $[CH_3CHOHCH_3]_0$ = 1 and $[H_2O]_0$ = 1000 mole fractions)

Component	Equilibrium composition, mole fractions	Fugacity coefficient
H_2	0.0000	5.2532
C_3H_4	0.0091	2.0162
C_3H_6	0.9004	2.0169
C_3H_8	0.0101	2.0568
$CH_2OHCH_2CH_3$	0.0223	0.9017
$CH_3CHOHCH_3$	0.0581	1.2112
H_2O	1000.9169	0.6149

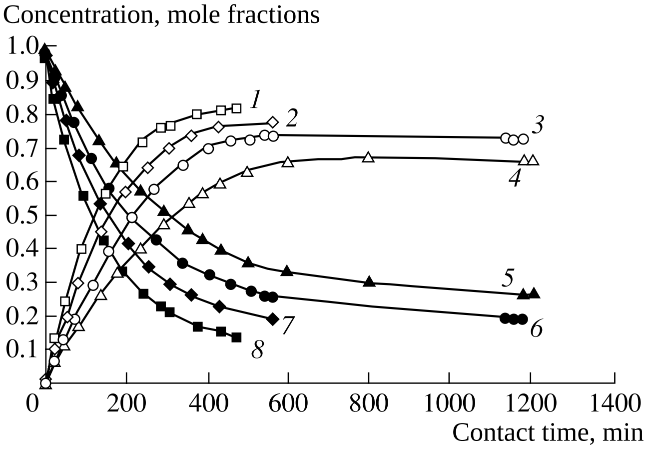

Fig. 2. Mole fractions of (*1*–*4*) 2-propanol and (*5*–*8*) propylene in the reaction mixture of 2-propanol dehydration in supercritical water (supercritical water density of 0.34 g/ml) as functions of contact time at (*4*, *5*) 381, (*3*, *6*) 393, (*2*, *7*) 403, and (*1*, *8*) 413°C.

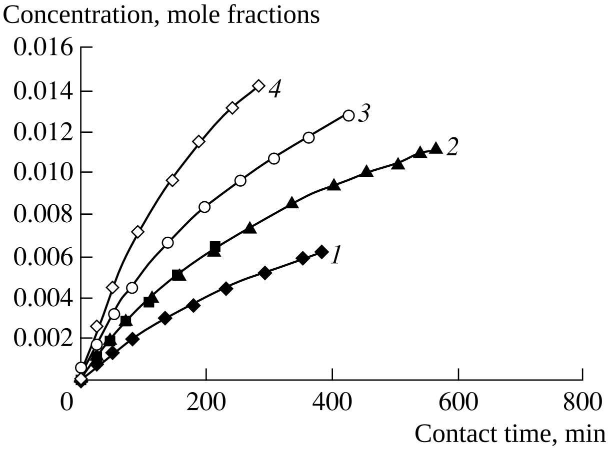

Fig. 3. Mole fractions of acetone in the reaction mixture of 2-propanol dehydration in supercritical water (supercritical water density of 0.34 g/ml) as functions of contact time at (*1*) 381, (*2*) 393, (*3*) 403, and (*4*) 413°C.

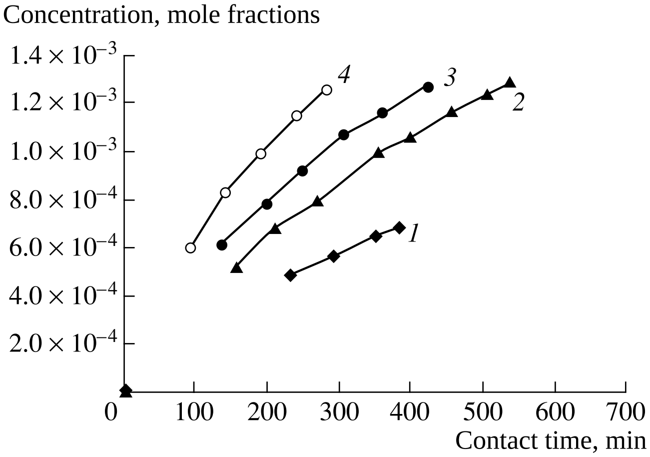

Fig. 4. Mole fractions of 1-propanol in the reaction mixture of 2-propanol dehydration in supercritical water (supercritical water density of 0.34 g/ml) as functions of contact time at (*1*) 381, (*2*) 393, (*3*) 403, and (*4*) 413°C.

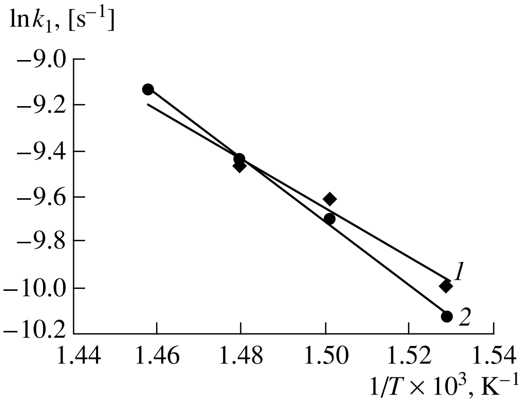

Fig. 5. Temperature dependence of the rate constant of reaction (I). Supercritical water densities are (*1*) 0.24 and (*2*) 0.34 g/ml.

the inconstancy of supercritical water density under changes of temperature can be a change in the amount of water that occupied the dead volume of the reactor because part of it goes into the bulk of the fluid. As a result, the effect of density additionally influences the temperature dependence of the reaction rate.

The above consideration can substantiate possible experimental errors in studies of the kinetics and thermodynamics of reversible chemical reactions in supercritical fluids.

Figures 2–4 demonstrate the mole fractions of 2-propanol, propene, and other main reaction products of 2-propanol dehydration as functions of contact time at a supercritical water density of 0.34 g/ml over a temperature ranging from 381 to 413°C. Let us consider the behaviors of these functions. The mole fractions of 2-propanol and propylene as functions of contact time (Fig. 2) at a density of 0.34 g/ml are very similar to analogous functions at the other two densities tested. Figure 2 indicates the mole fractions at contact times longer than 1200 min.

Table 3 summarizes the experimental and calculated mole fractions of 2-propanol, propylene, acetone, and propane at 413°C and various contact times. In all cases, the data calculated with the use of the model are consistent with the experimental results. Table 4 summarizes the reaction rates and confidence intervals cal-

Table 3. Comparison between the experimental and calculated data on the composition of reaction mixtures (supercritical water density of 0.34 g/ml; $T = 413°C$)

Contact time, min	Composition of the reaction mixture, mole fractions							
	$CH_3CH_2OHCH_3$	C_3H_6	C_3H_6O	C_3H_8	C_3H_8O	C_3H_6	C_3H_6O	C_3H_8
	experiment				calculation			
0	1	0	0	0	1	0	0	0
1.5	0.974	0.010	0.0006	0.0001	0.990	0.010	0.0002	0
24.17	0.846	0.131	0.0025	0.0011	0.854	0.143	0.0023	0.0004
49	0.722	0.243	0.0044	0.0020	0.730	0.265	0.0043	0.0012
92	0.559	0.403	0.007	0.0040	0.562	0.428	0.0071	0.0029
142	0.430	0.560	0.0094	0.0063	0.424	0.561	0.0095	0.0053
191	0.334	0.649	0.0110	0.0082	0.330	0.651	0.0114	0.0079
242	0.270	0.716	0.0124	0.0108	0.263	0.713	0.0129	0.0107
283	0.229	0.754	0.0135	0.0130	0.225	0.748	0.0139	0.0131
306	0.209	0.766	0.014	0.0147	0.208	0.764	0.0144	0.0144
375.5	0.172	0.796	0.0155	0.0188	0.171	0.795	0.0157	0.0186
432.5	0.152	0.809	0.0166	0.0222	0.152	0.809	0.0167	0.0220
473.5	0.140	0.813	0.0171	0.0255	0.142	0.816	0.0173	0.0245

Table 4. Reaction-rate constants of 2-propanol dehydration in supercritical water at various temperatures (supercritical water density of 0.34 g/ml)

T, °C	k_1, s^{-1}	k_2, s^{-1}	k_3, s^{-1}	k_4, s^{-1}
381	$4.03 \times 10^{-5} \pm 4.6 \times 10^{-7}$	$6.65 \times 10^{-6} \pm 1 \times 10^{-6}$	$3.73 \times 10^{-7} \pm 1.59 \times 10^{-7}$	$5.6 \times 10^{-7} \pm 2.08 \times 10^{-7}$
393	$6 \times 10^{-5} \pm 1.13 \times 10^{-6}$	$1.3 \times 10^{-5} \pm 1.3 \times 10^{-6}$	$6.3 \times 10^{-7} \pm 2.5 \times 10^{-7}$	$7 \times 10^{-7} \pm 3.3 \times 10^{-7}$
403	$8 \times 10^{-5} \pm 7.8 \times 10^{-7}$	$1.45 \times 10^{-5} \pm 7.7 \times 10^{-7}$	$9.8 \times 10^{-7} \pm 1.67 \times 10^{-7}$	$6.8 \times 10^{-7} \pm 2.3 \times 10^{-7}$
413	$1.08 \times 10^{-4} \pm 1.03 \times 10^{-6}$	$1.5 \times 10^{-5} \pm 8 \times 10^{-7}$	$1.69 \times 10^{-6} \pm 4 \times 10^{-7}$	$1.12 \times 10^{-6} \pm 2.45 \times 10^{-7}$

culated by the kinetic model that corresponds to scheme (VII) in a temperature range of 381 to 413°C.

Figure 5 shows the Arrhenius plots of the rate constant k_1 of reaction (I) at supercritical water densities of 0.24 and 0.34 g/ml. The activation energies of the reaction are approximately equal to 20 and 26 kJ/mol for fluid densities of 0.24 and 0.34 g/ml, respectively. The activation energies at the above two fluid densities are insignificantly different from each other, and this difference can be ascribed to the error of data processing.

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