# Influence of Pressure on the Acid-Catalyzed Rate Constant for 1-Propanol Dehydration in Supercritical Water

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Abstract: The acid-catalyzed rate of dehydration of 1-propanol in supercritical water is first order in 1-propanol at low reactant concentrations. Studies of the reaction rate in acidic and buffered solutions lead to values of the pK, of the sulfuric acid catalyst ranging from 2.1 to 1.5 at 375 °C as pressure increases from 22.1 MPa ( $P_r = 1.002$ ) to 34.5 MPa ( $P_r = 1.563$ ). The bisulfate anion dissociates to a negligible extent in supercritical water. Because the sulfuric acid is largely dissociated under these conditions, the rate of disappearance of 1-propanol is given by  $k_{\rm H}[{\rm H}^+][{\rm C}_3{\rm H}_7{\rm OH}]$ , which is an example of specific-acid catalysis. These findings are consistent with an acid-catalyzed, concerted E2 dehydration mechanism. The measured value of  $k_{\rm H}$  is linearly dependent on the reciprocal of the dielectric constant of water. The measured decrease in  $k_{\rm H}$  between 22.1 and 34.5 MPa at 375 °C ( $T_r = 1.003$ ) is less than a factor of 3. This dependence can be used to predict accurately the rate of reaction in the close vicinity of water's critical point by the use of kinetic data obtained under supercritical conditions. From this perspective, the reaction rate exhibits no abnormal behavior in the close vicinity of water's critical point.

Increasing interest is being expressed by both chemists and chemical engineers in the use of supercritical fluids as a novel solvent medium for the practice of a wide variety of chemical reactions.<sup>1,2</sup> Much of this interest results from a recognition of the fact that dramatic changes in the fluid's macroscopic physical properties and its transport properties can be effected by modest variations in temperature and pressure near the solvent's critical point. These changes can have a dramatic influence on the rates of chemical reactions occurring within the fluid. The utility of kinetic studies at high pressure in determining properties of transition states and in influencing the course of a chemical reaction was emphasized in the early, pioneering work of Eckert.<sup>3</sup> More recently, Johnston and his co-workers reported pronounced effects of pressure on the rates of a unimolecular decomposition<sup>4</sup> and competing Diels-Alder addition reactions<sup>5</sup> in supercritical fluid solvents. In response to the need for improved methods of waste disposal, fundamental studies of noncatalytic<sup>6</sup> and catalytic oxidations<sup>7</sup> in supercritical fluids have also been reported. Similiarly, Klein and his co-workers have investigated the influence of solvent effects on the pyrolytic reactions of coal model compounds in supercritical tetralin, methanol, and water.<sup>8</sup> Reactions in supercritical fluids have also captured the attention of some physicists. In 1981, Procaccia and Gitterman<sup>9</sup> proposed that the rates of chemical reactions decrease very near the critical point. Although early Russian experimental work<sup>10</sup> supported this contention, later research revealed flaws in both the theory<sup>11</sup> of Procaccia and Gitterman and the experimental work<sup>12</sup> of Krichevskii. Thus, in spite of the burst of interest in supercritical fluids among chemists and chemical engineers, questions still

remain concerning the behavior of chemical rate constants in the close vicinity of a solvent's critical point.

Earlier work in this laboratory<sup>13</sup> revealed the acid-catalyzed dehydration of 1-propanol in near-critical and supercritical water to behave as an ideal first-order reaction with propene and 2propanol as the only products. The absence of carbon monoxide, hydrogen, propionaldehyde, and other products led us to conclude that the underlying reaction mechanism is heterolytic.<sup>13</sup> Because of the high temperatures involved (320-375 °C), inlet sulfuric acid concentrations ranging from 1 to 25 mM are sufficient to catalyze high conversions of 1-propanol in less than 1 min. The simplicity of the global rate law governing the acid-catalyzed rate of dehydration of 1-propanol in water near its critical point caused us to initiate a study of the influence of pressure in the range P>  $P_c$  on the reaction rate at temperature  $T_c$ . The objective of this study was to obtain careful measurements of the rate constant at various pressures approaching  $P_c$  along the  $T_c$  isotherm. In addition to offering insight into the influence of solvent properties on reaction rates in a supercritical fluid, these measurements also clarify the role of acid-base chemistry in supercritical water and the acid-catalyzed mechanism of alkene formation from primary alcohols in water at high temperatures.

There is a substantial body of chemical information available on the formation of ethanol,<sup>14-16</sup> 2-propanol,<sup>15-18</sup> 2-butanol,<sup>19,20</sup> and various other secondary and tertiary alcohols<sup>15-18</sup> from the parent alkene by hydrolysis. Because this earlier work emphasized much lower temperatures (typically less than 200 °C), the hydrolysis of ethene and propene was determined to be irreversible and the dehydration reaction of the primary alcohol (emphasized in this work) was ignored. Excellent reviews of research concerning the hydration/dehydration chemistry before 1973 are available.<sup>2</sup> The more recent work of Whalley and Baglia<sup>15,17</sup> on the hydration of propene is particularly relevant to the findings presented in this paper. Their measurements of the reaction's activation volume, energy, and entropy led them to conclude that the transition state

(13) Antal, M. J.; Brittain, A.; DeAlmeida, C.; Ramayya, S.; Roy, J. C. In Supercritical Fluids; Squires, T. G., Paulaitis, M. E., Eds.; ACS Symposium Series 329; American Chemical Society: Washington, DC, 1987. Ra-mayya, S.; Brittain, A.; De Ameida, C.; Mok, W.; Antal, M. J. Fuel 1987, 66, 1364.

- (14) Baliga, B. T.; Whalley, E. Can. J. Chem. 1965, 43, 2453.
  (15) Whalley, E. Ber. Phys. Chem. 1966, 70, 958.
  (16) Chwang, W. K.; Nowlan, V. J.; Tidwell, T. T. J. Am. Chem. Soc.
  1977, 7233.
  - (17) Baglia, B. T.; Whalley, E. Can. J. Chem. 1964, 42, 1019.

  - (17) Bagia, B. T., Wialey, E. Can. J. Chem. 1904, 42, 1015.
    (18) Viviani, D.; Levy, J. B. Int. J. Chem. Kinet. 1979, XI, 1021.
    (19) Dietze, P. E.; Jencks, W. P. J. Am. Chem. Soc. 1987, 109, 2057.
    (20) Manassen, J.; Klein, T. S. J. Chem. Soc. 1960, 4202.
    (21) Banthorpe, D. Elimination Reactions; American Elsevier: New York,

<sup>(1)</sup> Subramanian, B.; McHugh, M. A. Ind. Eng. Chem. Process Des. Dev. 1986, 25, 1-12.

<sup>(2)</sup> Squires, T. G.; Paulaitis, M. E. In Supercritical Fluids; ACS Sym-posium Series 329; American Chemical Society: Washington, DC, 1987.
 (3) Eckert, C. A. Annu. Rev. Phys. Chem. 1972, 23, 239-264. Eckert, C. A.; Hsieh, C. K.; McCabe, J. R. AIChE J. 1974, 20, 20-35. Glugia, P. G.;

<sup>(8)</sup> Abraham, M. A.; Klein, M. T. Ind. Eng. Chem. Prod. Res. Dev. 1985, 24, 300-306. Townsend, S. H.; Abraham, M. A.; Huppert, G. L.; Klein, M. T.; Paspek, S. C. Ind. Eng. Chem. Res. 1988, 27, 143-149.
(9) Procaccia, I.; Gitterman, M. Phys. Rev. Lett. 1981, 46, 1163. Pro-

<sup>(9)</sup> Procaccia, I.; Gitterman, M. Phys. Rev. Lett. 1981, 40, 1163. Procaccia, I.; Gitterman, M. Phys. Rev. A 1982, 25, 1137. Procaccia, I.; Gitterman, M. Phys. Rev. A 1983, 27, 555.
(10) Krichevskii, I. R.; Tsekhanskaya, Y. V.; Polykova, X. A. Russ. J. Phys. Chem. 1966, 40, 715. Krichevskii, I. R.; Tsekhanskaya, Y. U.; Rozhnovskaya, L. N. Russ. J. Phys. Chem. 1966, 43, 1393.
(11) Wheeler, J. C.; Petchek, R. G. Phys. Rev. A 1983, 28. Morrison, G. Phys. A 1984, 30, 664. Milner S. T.; Martin P. C. Phys. Rev. A 1986, 43, 1296.

Phys. Rev. A 1984, 30, 664. Milner, S. T.; Martin, P. C. Phys. Rev. A 1986, 33, 1996.

<sup>(12)</sup> Greer, S. C. Phys. Rev. A 1985, 31, 3240.

<sup>1963;</sup> p 145. Knozinger, H. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Interscience: New York, 1971; Part 2, p 641. Saunders, W. H.; Cockerill, A. F. Mechanisms of Elimination Reactions; Wiley: New York, 1973; p 221.



Figure 1. Dependence of the dielectric constant of water on pressure at 375 °C.22

includes the alkene, one molecule of water, and a proton. Recently, a careful kinetic analysis of their own results, as well as the earlier data of Manassen and Klein,<sup>20</sup> caused Dietze and Jencks<sup>19</sup> to conclude that acid-catalyzed oxygen exchange into 2-butanol and hydration of 1-butene do not proceed through a common carbocation intermediate. In accord with earlier workers, Dietze and Jencks note that their experimental data are consistent with parallel, concerted reaction mechanisms for oxygen exchange and hvdration.

Variations of a chemical reaction rate with variations in pressure near the solvent's critical point can be interpreted to result from changes in the solvent's dielectric constant or changes in the concentration of the activated complex formed during the reaction. As illustrated in Figure 1, the dielectric constant, D, of water<sup>22</sup> increases rapidly as pressure is increased above  $P_c$  (22.06 MPa) at temperature 375 °C ( $T_c = 373.98$  °C). The influence of variations in the dielectric constant on the rate of a chemical reaction involving a charged species with a dipole depends upon the charge of the ion, the dipole moment of the dipole and activated complex, and the radii of the reactants and the activated complex, as well as the ionic strength of the solvent. The work of Laidler and Eyring<sup>23,24</sup> predicts a linear dependence of  $\ln k$  on 1/D for reactions involving a charged species with a molecule possessing a significant dipole moment. Variations in hydrostatic pressure may also exert a direct influence on the reaction rate by affecting the concentration of the activated complex. Thermodynamic arguments concerning the influence of pressure on the concentration of the activated complex<sup>25</sup> lead to the relationship

$$(\partial \ln k_{\rm c}/\partial P)_{\rm T} = -\Delta V^*/RT + (1-n)k_{\rm T} \tag{1}$$

where  $k_c$  is the reaction rate constant in concentration units,  $\Delta V^*$ is the activation volume change for the reaction, n is the sum of the stoichiometric coefficients of the reactants (where the coefficient is unity for the transition state), and  $k_{\rm T}$  is the isothermal compressibility of the fluid.

### **Experimental Section**

Methods. The two tubular flow reactors employed in this work have been described in earlier publications.<sup>13,26</sup> The characterization of these reactors with nondimensional numbers is detailed elsewhere.27 An

Table I. First-Order Behavior of 1-Propanol at 375 °C and 34.5 MPa with 5 mM Sulfuric Acid Catalyst

inlet propanol concn/M	residence time/s	conversn <sup>a</sup> /%
0.05	16.5	75 ± 1
0.1	17.1	75 ± 1
0.2	17.1	$75.5 \pm 0.5$
0.5	17.1	$72 \pm 1$
2	17.1	$49 \pm 1$

 $a \pm$  represents the sample standard deviation.

analysis of characteristic times associated with these nondimensional numbers reveals that each reactor performs as an ideal plug flow reactor.27

All reactant solutions were prepared with degassed, distilled water. Fisher certified-grade 1-propanol and Fisher HPLC-grade 2-propanol were used as the reactants. No impurities were detected in these reagents by HPLC or GC analyses. The sulfuric acid used was a Fisher certified-grade 10 N solution.

Analysis. At each operating condition, triplicate samples of the reactor effluent were collected at room temperature for analysis. Ouantification of liquid products was accomplished by triplicate analyses of each of these samples with a Waters high-performance liquid chromatograph (Model 6000A solvent delivery system, Perkin-Elmer LC 600 autosampler, and a differential refractometer) and a Hewlett-Packard Model 3388A integrator. An Alltech C<sub>18</sub> column was employed with degassed, distilled water as the solvent at a flow rate of 2 mL/min.

Gaseous products were analyzed with a Hewlett-Packard Model 5840 gas chromatograph equipped with a flame ionization detector. A Poropak Q column with 8.5% hydrogen in helium as the carrier at a temperature of 200 °C was used to separate the gaseous products. 1-Propanol, 2-propanol, propene (99% pure Matheson CP grade), and air standards were used for calibration.

Accuracy of Measurement. The pressure variation due to the backpressure regulator was maximum ( $\pm 0.3$  MPa) at the higher flow rates (>4 mL/min). At low flow rates (<1 mL/min), the reactor pressure varied within  $\pm 0.1$  MPa. Typical variations in the reaction temperature along the length of the reactor were less than 2 °C. Variations in the reaction temperature between experiments were less than 2 °C. Measured radial temperature gradients were almost always within 3 °C. The estimated flow rate did not vary by more than 0.05 g/min during the course of an experiment. The maximum error in the effective reactor length, estimated by the distance over which warming and cool down of the reactant take place, was less than 10% of the reactor length.

It is important to note that kinetic measurements in a fluid near its critical point are very difficult to accomplish because the fluid properties are very sensitive to small variations in temperature and pressure near the critical point. A 2 °C error in temperature can cause a 50% change in the fluid's specific volume, hence, a 50% deviation in the calculated residence time and a large error in the estimated apparent rate constant. Furthermore, properties of water are tabulated at discrete intervals of 5 °C or more <sup>28</sup> This problem was alleviated by two-dimensional interpolation of the NBS/NRC data (with use of the routine CSAKM of the International Mathematical and Statistical Library) to obtain values of the specific volume at intermediate temperatures and pressures. Because the solute concentrations studied in this work were low (typically 0.1-1% by mole), we assume that the properties of the reactant-product mixtures are adequately represented by those of pure water.

#### **Results and Discussion**

It is not obvious that thermodynamics will favor the dehydration of 1-propanol to propene in water at 34.5 MPa and 375 °C. However, a simple thermodynamic calculation using generalized fugacity coefficients predicts conversions of 1-propanol to propene in excess of 90% at these conditions. Hence, we anticipated the nearly complete conversion of 1-propanol to propene, even in supercritical water.

Experiments with 1-propanol as the reactant and sulfuric acid as the catalyst resulted in the formation of 2-propanol, propene, and water. However, experiments that used 2-propanol as a reactant with sulfuric acid catalyst resulted in the formation of propene and water as the sole products: no 1-propanol was detected. Consequently, in the following discussion we treat the conversion of 1-propanol to propene as an irreversible reaction.

<sup>(22)</sup> Quist, A. S.; Marshall, W. L. J. Phys. Chem. 1965, 69, 3165.
(23) Laidler, J. K.; Eyring, H. Ann. N.Y. Acad. Sci. 1940, 34, 303. See also: Amis, E. S.; Hinton, J. F. Solvent Effects on Chemical Phenomena; Academic Press: New York, 1973; pp 240-242.
(24) Laidler, J. K. Chemical Kinetics, 3rd ed.; Harper and Row: New York.

York, 1987

<sup>(25)</sup> Van't Hoff, J. H. Vorlesungen uber thorelische und physikalische chemie; Braunschweig, 1898. Hamann, S. D.; Bradley, R. S. High Pressure Physics and Chemistry; Academic Press: New York, 1963; Vol. 2, p 163.

<sup>(26)</sup> Narayan, R.; Antal, M. J. In Supercritical Fluid Science and Tech-

 <sup>(20)</sup> Narayan, K.; Antai, M. J. III Supercritical Full Science and Technology; Johnston, K. P., Penninger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989.
 (27) Ramayya, S. M.S. Thesis, University of Hawaii at Manoa, 1986.
 DeAlmeida, C. P. M.S. Thesis, University of Hawaii at Manoa, 1987. Cutler, Almeida, C. P. M.S. Thesis, University of Hawaii at Manoa, 1987. Cutler, A. H.; Antal, M. J.; Jones, M. Ind. Eng. Chem. Res. 1988, 27, 691.

<sup>(28)</sup> Haar, L.; Gallagher, J. S.; Kell, G. S. NBS/NRC Steam Tables; NBS: Washington, DC, 1984.

Table II.First-Order Behavior of 1-Propanol at 375 °C and 22.1MPa with 5 mM Sulfuric Acid Catalyst

inlet propanol concn/M	residence time/s	conversn <sup>a</sup> /%	$k_{app}^{b}/s^{-1}$
0.01	6.0	$51 \pm 1$	$0.121 \pm 0.011$
0.02	5.8	$53 \pm 2$	$0.132 \pm 0.027$
0.05	9.1	$64 \pm 1$	$0.111 \pm 0.009$
0.1	6.1	$35 \pm 3$	$0.071 \pm 0.084$
0.2	7.8	$31 \pm 4$	$0.048 \pm 0.090$
1	6.3	9 ± 1	$0.016 \pm 0.020$

″± 1	epresents	the	sample	standard	deviation.	<sup>b</sup> ± gives	the	95%
confide	nce interv	al or	the bas	sis of the	Student's t	-distribution	n.	



Figure 2. First-order behavior  $(k_{app} = 0.03 \pm 0.01 \text{ s}^{-1})$  of 0.05 M 1propanol with 2 mM sulfuric acid at 375 °C and 27.5 MPa.

Experiments with NaHSO<sub>4</sub> alone evidenced no catalytic effect on the dehydration reaction. This result indicates the negligible role of the  $HSO_4^-$  ion as an acid catalyst for the dehydration reaction.

To calculate a reaction rate constant with plug flow reactor data, it is first necessary to establish the reaction order. A rigorous test of first-order dependence involves demonstrating the null influence of initial reactant concentration on conversion at constant catalyst concentration, residence time, temperature, and pressure. Data in Table I show that at 375 °C and 34.5 MPa, for sufficiently low reactant concentrations, the conversion of 1-propanol remains constant for 1 order of magnitude variation in inlet propanol concentration. Experiments at 22.1 MPa and 375 °C also verified first-order behavior over a smaller range of 1-propanol concentration (0.01-0.05 M). Since it was not possible to compare the conversions directly at 22.1 MPa, due to differing residence times, the apparent first-order rate constants were evaluated according to the formula

$$k_{\text{add}} = -(\ln (1-c))/\theta \tag{2}$$

where c is the reactant conversion and  $\theta$  is the plug flow residence time. Table II displays values of  $k_{app}$ , which are constant over a range of 0.01–0.05 M inlet 1-propanol concentration. Hence, we conclude that, with an inlet 1-propanol concentration of 0.05 M (or less), eq 2 can be used to evaluate the apparent first-order rate constant over the range of operating pressures (22.1–34.5 MPa) employed in this study.

To further verify the first-order nature of the reaction, a study of the influence of residence time on 1-propanol conversion was undertaken with both reactors. Data displayed in Figure 2 are consistent with an irreversible, first-order reaction. It is noteworthy that data from the two reactors lie on a straight line that intercepts the origin. This result corroborates our belief that negligible reaction occurs during the heatup period in either reactor. The two data points with residence times of 8.6 and 21.8 s are at the extreme limits of operation of the two reactors used in this research. Consequently, some departures from ideal, isothermal plug flow are expected. We believe that the small deviations of these two points from the otherwise linear behavior of the data are a result of these departures from ideality.



Figure 3. Dependence of  $k_{app}$  on initial sulfuric acid concentration (with and without salt) for 1-propanol (<0.1 M) disappearance at 375 °C: (a) 34.5 MPa, resulting in the value  $k_{\rm H} = 31 \pm 6 \, ({\rm mol}/L)^{-1} \, {\rm s}^{-1}$ ; (b) at various pressures and initial reactant concentrations, resulting in values for  $k_{\rm H}/({\rm mol}/L)^{-1} \, {\rm s}^{-1}$  of 35 ± 5 at 28.8 MPa, 38 ± 10 at 22.8 MPa, and 80 ± 17 at 22.1 MPa with 0.05 M 1-propanol reactant.



Figure 4. Dependence of the acid-catalyzed rate constant  $k_{\rm H}$  on the dielectric constant at 375 °C (with 95% confidence intervals on the basis of Student's *t*-distribution). The inset displays the dependence of  $k_{\rm H}$  on pressure at 375 °C.

Parts a and b of Figure 3 display values of  $k_{app}$  at the critical point and three supercritical pressures, as a function of the inlet acid concentration,  $[H_2SO_4]_0$ , at reaction temperature and pressure (RTP). Evidently, the apparent rate constant is linearly dependent on the inlet  $H_2SO_4$  concentration. If the acid dissociation constant  $K_a$  for  $H_2SO_4$  at RTP were large, then  $[H^+] \cong [H_2SO_4]_0$  and the reaction would be an example of specific-acid catalysis with  $k_{app} \cong k_H[H^+]$ . On the other hand, if  $K_a$  were small, then  $[H_2SO_4]_0$  and the reaction would be an example of general-acid catalysis with  $k_{app} \cong (H_2SO_4)_0$  and the reaction would be an example of general-acid catalysis with  $k_{app} \cong k_A[H_2SO_4]$ . More generally, since no conversion is observed in the absence of  $H_2SO_4$ , we have  $k_{app} = k_H[H^+] + k_A[H_2SO_4]$ . Data from the work of Quist, Marshall,

<b>Table III.</b> I-Propanol Conversions at 3/5 °C in a Sulfuric Acid/HSO <sub>4</sub> Bu
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pressure/MPa	residence time/s	inlet propanol concn/M	sulfuric acid/mM	sodium bisulfate/mM	conversn <sup>2</sup> /%	$k_{app}^{b}/s^{-1}$
34.5	2.8	0.1	20	100	61 ± 1	0.337 ± 0.027
34.5	2.7	0.1	100	500	<b>49 ±</b> 1	0.251 • 0.019
22.1	7.2	0.02	20	100	70	0.168°

 $a \pm represents the sample standard deviation. <math>b \pm gives the 95\%$  confidence interval on the basis of the Student's *t*-distribution. <sup>c</sup> Indicates only one measurement.



Figure 5. Concerted, E2 mechanism of 1-propanol dehydration.

and Jolley<sup>29</sup> enable us to estimate (by extrapolation) the  $pK_a$  of sulfuric acid at 375 °C and 34.5 MPa to be 2.3. This value predicts 70% or more dissociation of sulfuric acid (with concentrations between 1 and 2.8 mM) at 34.5 MPa and 375 °C. The above observations suggest that the acid exists mainly as  $H_3O^+$  and the reaction is primarily specific-acid-catalyzed.

Several experiments were executed with the salt NaHSO<sub>4</sub> added to the usual 1-propanol/sulfuric acid mixture. As displayed in Figure 3a, the addition of this salt had absolutely no observable effect on the rate of dehydration of 1-propanol. Recalling that the bisulfate anion HSO<sub>4</sub><sup>-</sup> alone is not an acid catalyst for the reaction at RTP, this result further reveals the absence of any primary or secondary salt effects on the reaction chemistry in this concentration range at RTP. At higher concentrations of 1propanol (0.5 M), the addition of the salt lowered the reaction rate, presumably due to a secondary salt effect.

Two sets of the data in Figure 3b correspond to different initial concentrations of 1-propanol. It is important to note that although the data for 0.5 M 1-propanol at 22.1 MPa lie outside the range of first-order dependence (Table II), the first-order rate constant is nevertheless linearly dependent on the initial acid concentration. This behavior highlights the need to clearly establish first-order behavior by studying the dependence of conversion on reactant concentration (as in Tables I and II) prior to detailing the effect of catalyst concentration.

To further test the roles of specific- versus general-acid catalysis in the dehydration reaction, we attempted to execute dehydration experiments using a buffer of sulfuric acid and NaHSO<sub>4</sub>. The influence of buffer strength on rate constant is a classical test of specific- vs general-acid catalysis.<sup>24</sup> Because H<sub>2</sub>SO<sub>4</sub> is a moderately strong acid at RTP, relatively high concentrations of acid and salt are required to establish a buffer.<sup>30</sup> Table III displays the experimental data in the putative supercritical buffer with a 1:5 molar ratio of H<sub>2</sub>SO<sub>4</sub> to NaHSO<sub>4</sub>. Unfortunately, at 34.5 MPa, higher concentrations of acid and salt (than those displayed in Table III) caused the 10-port sampling valve to leak, while at 22.1 MPa the reactor plugged (presumably due to the decreased solubility of the salt in water near its critical point). Consequently, we were unable to unequivocally establish the influence of buffer strength on the rate constant.

If we assume that the data in Table III reflect specific-acid catalysis in a true buffer with  $[H^+] = K_a C_a/C_s$  where  $C_a$  and  $C_s$  are the total acid and salt concentrations,<sup>30</sup> then using the relationship  $k_{app} = k_H[H^+]$ , we can employ the unbuffered relationship

$$[H^+] = (-K_a + (K_a^2 + 4K_aC_a)^{1/2})/2$$
(3)

to obtain

$$K_{a}C_{a}/C_{s} = (-K_{a} + (K_{a}^{2} + 4K_{a}C_{a}^{*})^{1/2})/2$$
 (4)

where  $C_a^*$  is the unbuffered initial acid concentration that results

in the same value of  $k_{app}$  as was obtained with the buffer. Referring to Table III and Figure 3, we find  $C_a^* = 8 \text{ mM}$  at 34.5 MPa and  $C_a^* = 2 \text{ mM}$  at 22.1 MPa. Rearranging eq 4, we have

$$K_{\rm a} = C_{\rm a}^{*} / ((C_{\rm a}/C_{\rm s}) + (C_{\rm a}/C_{\rm s})^2)$$
(5)

Thus, our measurements of  $k_{app}$  in acid and buffer permit us to estimate the  $pK_a$  of  $H_2SO_4$  at 375 °C and 34.5 MPa to be about 1.5 and at 22.1 MPa to be about 2.1. These values corroborate our belief that low concentrations of  $H_2SO_4$  are highly dissociated in supercritical water near its critical point.

Figure 4 summarizes our results as graphs of  $\ln k_{\rm H}$  versus P and 1/D. The data displayed in Figure 4 together with eq 1 permit us to estimate the activation volume  $\Delta V^4$  for the reaction, which ranges from 70 cm<sup>3</sup>/mol for  $P \gg P_{\rm c}$  to 1200 cm<sup>3</sup>/mol for  $P \cong P_{\rm c}$  at  $T \cong T_{\rm c}$ . These values enjoy good agreement with those of Johnston and his co-workers<sup>4,5</sup> for completely different reactions; however, they are much larger than the value -9.6 cm<sup>3</sup>/mol reported by Baglia and Whalley<sup>17</sup> for the reverse reaction (propene hydration) at 100 °C.

Clearly the effect of pressure on the rate constant may be physically interpreted as an activation volume effect or an effect of changes in the solvent's dielectric constant. In fact, a formal expression may be derived that expresses  $\Delta V^*$  in terms of  $\partial D/\partial P^{3.4}$ Nevertheless, in this particular case the evident linear dependence of ln  $k_{\rm H}$  on 1/D causes us to prefer an interpretation based on the influence of the dielectric constant. If measurements of ln  $k_{\rm H}$  vs 1/D for D > 7.5 had been used to predict the value of  $k_{\rm H}$ at  $P = P_{\rm c}$  (D = 3.6), the value obtained would have been 65 (mol/L)<sup>-1</sup> s<sup>-1</sup>, which is in good agreement with the measured value of 80 (mol/L)<sup>-1</sup> s<sup>-1</sup>.

The foregoing results are consistent with the role of an acidcatalyzed, concerted E2 mechanism<sup>31</sup> (see Figure 5) in the dehydration chemistry. Assuming the protonated intermediate quickly reaches a steady-state concentration, the rate of disappearance of alcohol A is easily shown to be

$$\frac{d[A]}{dt} = \frac{-k_1 k_2 [A] [B^-] + k_{-1} k_{-2} [H_2 O] [O] [B^-]}{k_1 [A] + (k_{-1} + k_2) [B^-] + k_{-2} [H_2 O] [O]} [HB]_0$$
(6)

where [O] is the concentration of olefin  $C_3H_6$ ,  $[HB]_0$  is the initial concentration of acid, and  $[B^-]$  is the concentration of the conjugate base. Recognizing that the concentration of the protonated intermediate must be small in order to satisfy the steady-state approximation, we have

$$(k_{-1} + k_2)[B^-] \gg k_1[A] + k_{-2}[H_2O][O]$$

and recalling that equilibrium strongly favors the dehydration reaction (i.e.,  $k_{-1}k_{-2}[H_2O][O][B^-] \simeq 0$ ), eq 6 becomes the first-order expression

$$d[A]/dt = -\{k_1k_2/(k_{-1} + k_2)\}[A][HB]_0$$
(7)

We note that the  $E_2$  reaction mechanism can be expected to be first order only when all of the assumptions detailed above are

<sup>(29)</sup> Quist, A. S.; Marshall, W. L.; Jolley, H. R. J. Phys. Chem. 1965, 69, 2726.

<sup>(30)</sup> Hand, C. W.; Blewitt, H. L. Acid-Base Chemistry; Macmillan: Riverside, NJ, 1986.

<sup>(31)</sup> Swain, C. G. J. Am. Chem. Soc. 1950, 72, 4578.

satisfied.

If the acid HB is  $H_3O^+$ , the reaction is specific-acid-catalyzed. Although water (the conjugate base of  $H_3O^+$ ) plays an important role in the reaction mechanism,<sup>31,32</sup> it does not appear in the rate expression (7). This is consistent with our omission of the dependence of  $k_{app}$  on [H<sub>2</sub>O], even though the concentration of water varied significantly over the pressure range of interest. The bisulfate anion HSO<sub>4</sub>- could also act as a base in the second step of the mechanism;<sup>31</sup> however, its concentration is very low relative to water, and experiments revealed no influence of the anion on the reaction rate. The decrease in rate constant with increasing dielectric constant is consistent with the formation of an activated complex that is less polar than the reactants, which is the case of the concerted E2 mechanism displayed in Figure 5. Similarly, the lack of influence of the ionic strength of the medium on the rate constant is also consistent with the E2 mechanism, since the modified Brønsted-Bjerrum equation for ion-neutral molecule interactions predicts a negligible influence of ion strength on reaction rate. The large positive value of  $\Delta V^*$  may be interpreted to be an artifact of electrostriction effects: the local electric field of the activated complex is weaker than that of the dipole and ion reactants, resulting in less electrostriction of the solvent molecules and a positive activation volume. Detailed numerical simulations of the acid-catalyzed disappearance of 1-propanol and the appearance of 2-propanol (with propene) in supercritical water also indicate the role of a concerted E2 mechanism in the dehydration of 1-propanol.<sup>26</sup> These simulations exploit the departures from first-order behavior emphasized earlier to discriminate between the E2 and E1 reaction mechanisms. Although discussions of the mechanism of propene hydration/propanol dehydration usually emphasize the role of a carbocation intermediate, 14-21 recent studies have given increasing attention to the possibility of a concerted mechanism that avoids the formation of the charged carbocation intermediate. For example, Dietze and Jencks<sup>19</sup> note

(32) Lowry, T. M. J. Chem. Soc. 1927, 2554.

"It is possible that the reaction mechanisms are concerted because simple secondary carbocations do not have a significant lifetime in the presence of water." Our findings are consistent with this viewpoint.

#### Conclusions

(1) The  $pK_a$  of sulfuric acid in supercritical water decreases from about 2.1 to 1.5 at 375 °C ( $T_r = 1.003$ ) as pressure increases from 22.1 MPa ( $P_r = 1.002$ ) to 34.5 MPa ( $P_r = 1.563$ ). The bisulfate anion does not measurably dissociate under these conditions.

(2) The acid-catalyzed rate of disappearance of 1-propanol in supercritical water under these conditions is given by  $k_{\rm H}$ .  $[H^+][C_3H_7OH]$ , which is an example of specific-acid catalysis.

(3) These findings are consistent with an acid-catalyzed, concerted E2 dehydration mechanism.

(4) As pressure increases from 22.1 to 34.5 MPa,  $k_{\rm H}$  decreases by about a factor of 3 at 375 °C. This decrease is linear in 1/D, where D is the dielectric constant of water.

(5) From the linear dependence of  $k_{\rm H}$  on 1/D, the reaction rate in the close vicinity of water's critical point can be predicted by its behavior at higher pressures.

(6) Viewed in this context, we detect no abnormal behavior of the reaction rate in the close vicinity of water's critical point.

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Registry No. H<sub>2</sub>O, 7732-18-5; CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, 71-23-8; H<sub>2</sub>SO<sub>4</sub>, 7664-93-9.

# Enhanced Silvlation Reactivity of a Model for Silica Surfaces

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Abstract: The relative silulation reactivities of structurally similar silanols (1-4a) containing one, two, and three potentially hydrogen-bonded siloxy groups have been explored for the first time. In the absence of amine bases, silvlation with TMSCI is sluggish and there is very little kinetic selectivity for silylation of either isolated silanols or intramolecularly hydrogen-bonded silanols. In the presence of Et<sub>3</sub>N or pyridine, the rates for silvlation of all types of silanols are greatly increased and there appears to be a slight kinetic preference for the silvlation of vicinally hydrogen-bonded silanols over isolated, non-hydrogen-bonded silanols. Most significantly, there is remarkable selectivity for the monosilylation of 1 in the presence  $Et_3N$ . The experimental results suggest that the most reactive sites for silvlation of hydroxylated silica surfaces may be those possessing at least three mutually hydrogen-bonded hydroxy groups.

Surface-modified silicas<sup>1</sup> are an important class of materials which have been used extensively as stationary phases in chromatography.<sup>2</sup> Modified silicas have also found a number of other useful applications, such as ion collection,<sup>3</sup> heterogeneous hydrogenation catalysts,<sup>4</sup> inorganic polymer fillers,<sup>5</sup> and drug delivery agents.<sup>6</sup> For all of these applications the surface properties of silica are specially tailored by chemically attaching organic groups

 <sup>(1) (</sup>a) Leyden, D. E., Ed. Chemically Modified Surfaces: Silanes, Surfaces, and Interfaces; Gordon Breach: New York, 1985. (b) Leyden, D. E.; Collins, W. T., Ed. Silylated Surfaces; Gordon Breach: New York, 1980.
 (2) (a) Unger, K. K.; Janzen, R.; Jilge, G.; Lork, K. D.; Anspach, B. In Weth Deformation Limit Characteristics Unsuper Version 2014.

High Performance Liquid Chromatography; Horvath, Cs., Ed.; Academic Press: New York, 1988; Vol. 5, pp 1–93 and references cited therein. (b) Unger, K. K. Porous Silica; Elsevier: New York, 1979, and references cited therein.

<sup>(3) (</sup>a) Leyden, D. E.; Luttrell, G. H.; Sloan, A. E.; De Angelis, N. J. Anal. Chim. Acta 1976, 84, 97.

<sup>(4) (</sup>a) Iwasawa, Y., Ed. Tailored Metal Catalysts; D. Reidel: Boston, (a) Indiana, I., D. Indirea Includication Catalysis, D. Rolden. Disolat. Biological Solution Complexes;
 (b) Reidel: Boston, MA, 1985, and references cited therein.
 (c) a) Plueddemann, E. P. Silane Coupling Agents; Plenum Press; New York, 1982.
 (b) Arkles, B. Chemiech 1977, 7, 713.
 (c) Unger, K.; Rupprecht, H.; Valentin, B.; Kircher, W. Drug Dev. Ind.

Pharm. 1983, 9, 69-91.