ether, 142-96-1; isopropyl ether, 108-20-3; tetrahydrofuran, 109-99-9; p-dioxane, 123-91-1; acetone, 67-64-1; 2-butanone, 78-93-3; cyclohexanone, 108-94-1; ethyl acetate, 141-78-6; acetonitrile, 75-05-8; N,Ndimethylformamide, 68-12-2; N,N-dimethylacetamide, 127-19-5; hexamethylphosphoramide, 680-31-9;  $\gamma$ -butyrolactone, 96-48-0; nitromethane, 75-52-5; dimethyl sulfoxide, 67-68-5; benzene, 71-43-2; toluene, 108-88-3;

# Pressure Tuning of Chemical Reaction Equilibria in Supercritical Fluids

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Supercritical fluid solvent effects were studied for the tautomeric equilibria of 2-hydroxypyridine and 2-pyridone at infinite dilution, both experimentally and theoretically. The fluids were propane at 393 K and 1,1-difluoroethane at 403 K, and pressures ranged from 21 to 206 bar. The equilibrium constant,  $K_{e}$ , which was measured by in situ UV spectroscopy, increased 4-fold for a pressure increase of 40 bar in 1,1-difluoroethane, with a partial molar volume change on reaction reaching -1400 cm<sup>3</sup>/mol. A thermodynamic model was developed to increase the range of pressures studied and to explore temperature effects. The tuning of chemical reaction equilibria is a powerful technique for characterizing a key advantage of supercritical fluid solvents, which is their enormous adjustability.

# Introduction

An extremely pronounced pressure effect was discovered for the rate constant of the unimolecular decomposition of  $\alpha$ -chlorobenzyl methyl ether in supercritical 1,1-difluoroethane.<sup>1</sup> A change in pressure of only 15 bar increased the rate constant by an order of magnitude, which corresponds to activation volumes reaching -6000 cm<sup>3</sup>/mol. This suggests rate constants and equilibrium constants of certain reactions could be adjusted over a wide range by modest changes in temperature or pressure of the solvent in the critical region. Our present objective is to examine the characteristics of pressure effects on a reversible reaction in supercritical 1,1-difluoroethane and propane, both experimentally and theoretically. This study complements a recent investigation of the reversible redox reaction of the  $I_2/I^-$  couple in supercritical water.<sup>2</sup> Together these studies explore reactants that are nonpolar, polar, and ionic and supercritical solvents that are nonpolar (propane), and polar (1,1-difluoroethane and water) to achieve a molecular understanding of pronounced pressure effects in terms of the relevant physical and chemical properties.

A small change in the pressure near the critical point of the solvent causes a large change in density-dependent properties such as the solubility parameter, refractive index, dielectric constant, and solvatochromic polarity parameter.<sup>3,4</sup> This suggests that pressure may be used to manipulate reactions in supercritical fluids, on the basis of a thermodynamic solvent effect. There are two major ways to utilize these large pressure effects in supercritical solvents: (1) The equilibrium position in a reversible reaction may be adjusted and controlled over a continuum by varying pressure, without the need for a harsh chemical change, for example, in pH. (2) The nature of transition states and reaction mechanisms may be explored in a fundamental manner by perturbing the strength of a single solvent by using variations in pressure. These methods present unique opportunities to investigate solvent effects in a single fluid, without the complications that arise from studying a reaction in a variety of solvents differing in chemical structure.

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The classic tautomeric equilibria (see Figure 1) between 2hydroxypyridine and 2-pyridone<sup>5-8</sup> was chosen for study for several reasons. Since the stoichiometric coefficients are the same for the reactant and product, pressure does not appear explicitly in the expression for the equilibrium constant. As a result, changes in the equilibrium position with pressure are due exclusively to nonidealities, that is, molecular interactions in the fluid. The pressure effect on the position of equilibria is due overwhelmingly to polarity differences between the tautomers, since the sizes are very similar. This greatly simplifies the interpretation as it provides a means to focus on the solvent polarity effect. Other reasons for studying this reaction are that the solvent effect is wellcharacterized in liquid solvents, side reactions may be eliminated, and equilibration is rapid and can be monitored in situ spectroscopically.<sup>8,9</sup> The equilibrium constant,  $K_c = c_3/c_2$ , is sensitive with respect to the solvent environment, as it varies from 0.4 in the gas phase<sup>9</sup> to about 900 in aqueous solution.<sup>10,11</sup> As the solvent polarity increases, the equilibrium shifts toward 2-pyridone (2a) because of the highly polar mesomeric form (2b, see Figure 1). Since this reaction is a classic model for structure-stability relationships,<sup>7</sup> the results should be useful for predicting the effects of supercritical fluids on a wide variety of reactions.

The solvent effect or pressure effect in a supercritical fluid is influenced by the clustering of the solvent molecules about the solute molecules. Recently, solvatochromic probes have been used to investigate clustering of pure<sup>3,4,12,13</sup> and mixed<sup>14</sup> fluids in the local environment about a solute. A theoretical model has been developed by using Kirkwood-Buff solution theory to describe the clustering phenomena<sup>3,4,15,16</sup> as well as solubility phenomena.<sup>17</sup>

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Figure 1. Tautomerization of 2-hydroxypyridine (1) and 2-pyridone (2a, 2b).

The pressure and temperature effects on the equilibrium constant will be used to determine partial molar volume and enthalpy changes on reaction, which indicate the difference of solvent clustering about the reactant and product. Partial molar volumes<sup>18</sup> and partial molar enthalpies are extremely difficult to measure in supercritical fluids, whereas in situ spectroscopic measurements of equilibrium constants are relatively simple. This measurement technique is a convenient and rapid method to probe the nature of clustering in supercritical fluids.

Significant solvent effects have also been observed in Diels-Alder cycloaddition of maleic anhydride and isoprene.<sup>19</sup> Pressure adjustment of rate constants have been used to alter the selectivity of several parallel reaction networks.<sup>20-23</sup> Supercritical water is an interesting solvent in that it dissolves many organic compounds, as well as gases and salts,<sup>24,25</sup> and can be used with oxygen to oxidize hazardous wastes. Supercritical carbon dioxide was used to extract acetic acid in the free acid form from a fermentation broth by manipulating the acid-base equilibria in the aqueous phase.<sup>26</sup> It was also used with acetic acid as a cosolvent to manipulate an acid-base equilibrium constant for the extraction of mevinolin, a pharmaceutical compound.<sup>27</sup> A fundamental understanding of reaction equilibria in supercritical fluids would be useful for characterizing supercritical fluid solvation at the molecular level and for developing practical applications.

#### **Experimental Section**

The compound 2-hydroxypyridine (Aldrich, >97%) was purified by vacuum sublimation<sup>28</sup> to produce white crystals. The purity of the tautomeric mixture was greater than 99% as determined by gas chromatography. The gases 1,1-difluoroethane (Linde, >98%) and propane (Big Three Industries, >99.5%) were used as received. The absorbance of impurities in these fluids was less than 0.15 absorbance units at 250 nm at 200 bar and even smaller at longer wavelengths.

UV absorbance spectra were measured in a Cary (Varian) 2290 spectrophotometer to determine the equilibrium constant, by using a 6.35-cm o.d. by 1.75-cm i.d. stainless steel high-pressure cylindrical cell with 2.5-cm diameter by 1-cm thick sapphire windows. The path length of the cell was 1 cm. The details of the experimental apparatus are described elsewhere.<sup>4,15</sup> The temperature was controlled to within  $\pm 0.1$  °C by using an Omega 6000 series

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Figure 2. Equilibrium constant for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical propane (measured at 393 K, O; predicted by using eq 11 and Table IV, -).

temperature controller and a platinum resistance thermometer. The pressure was controlled by using a 60-cm<sup>3</sup> syringe pump and was measured to within  $\pm 0.1\%$  with a Heise 710A digital pressure gauge. The pressure varied less than 0.15 bar (2 psi) during a spectral scan.

Self-association of 2-pyridone, which is prevalent particularly in a nonpolar solvent, can modify substantially the position of the tautomeric equilibria. Self-association of 2-pyridone is negligible at low concentrations on the order of  $10^{-7}$  M at ambient temperature and at  $10^{-5}$  M at 100 °C.<sup>29</sup> In the present study, the temperature was at least 120 °C with concentrations on the order of  $10^{-4}$  M at the higher pressures to  $10^{-5}$  M at lower pressures where the solubility was limited, so self-association is negligible.

A solution containing  $10^{-5}$  g of a 2-hydroxypyridine/2-pyridone mixture in *n*-hexane was loaded into the cell, and the solvent was evaporated. The UV absorption spectra were recorded at the desired pressure two to three times to obtain average absorbance values. The absorbance values were corrected with previously measured spectra for the pure solvent at each pressure. The uncertainty in the corrected absorbances was about 5% due to the low values of concentration. The experiments were performed in order of increasing pressure to keep all of the solute inside the cell, as the diffusion in the 508- $\mu$ m-i.d. tubing was negligible. Further details are given elsewhere.<sup>30</sup>

With use of the Beer-Lambert law, the ratio of the absorbance of 2-hydroxypyridine to that of 2-pyridone may be written by a simplified expression:

$$\frac{A(\lambda_2)}{A(\lambda_3)} = \frac{\epsilon_2(\lambda_2)}{\epsilon_3(\lambda_3)} \frac{c_2}{c_3} + \frac{\epsilon_3(\lambda_2)}{\epsilon_3(\lambda_3)}$$
(1)

where  $\epsilon_2$  and  $c_2$  are the extinction coefficient and concentration of pure 2-hydroxypyridine, and  $\epsilon_3$  and  $c_3$  those of pure 2-pyridone; the subscript 1 will be used later for the solvent. The equation is simplified because  $\epsilon_2(\lambda_3)$  is essentially zero.<sup>30</sup> The maximum absorbance wavelengths of 2-hydroxypyridine,  $\lambda_2$ , are at 270 nm in both solvents, while those of 2-pyridone,  $\lambda_3$ , are at 302 and 297 nm in 1,1-difluoroethane and propane, respectively.

The ratio  $\epsilon_2(\lambda_2)/\epsilon_3(\lambda_3)$  was determined by using the methylated derivatives 2-methoxypyridine and 1-methyl-2-pyridone as chromophores, since they do not tautomerize.<sup>9,31</sup> This ratio  $\epsilon_2(\lambda_2)/\epsilon_3(\lambda_3)$  was 0.78 in ethanol, which is in close agreement with the value of 0.80 reported previously.<sup>9</sup> The wavelengths  $\lambda_2$  and  $\lambda_3$  were 270 and 302 nm, respectively. The value of  $\epsilon_3(\lambda_3)$  varied insignificantly from 297 to 302 nm. However, the value of  $\epsilon_3(\lambda_2)$  varied strongly as a function of the solvent, due to solvatochromic shifts. To determine  $\epsilon_3(\lambda_2)/\epsilon_3(\lambda_3)$  accurately, a model liquid solvent was chosen in which the maximum wavelength,  $\lambda_3$ , matched that of the supercritical fluid. The values of  $\lambda_3$  were 298 nm for hexane and 302 nm for ethanol, which match those of

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Figure 3. Equilibrium constant for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical 1,1-difluoroethane (measured at 403 K, O; predicted by using eq 11 and Table IV, —).

TABLE I: Equilibrium Constant for the Tautomerization of 2-Hydroxypyridine/2-Pyridone in 1,1-Difluoroethane and in Propane

	equilib const $K_c$				
pressure, bar	1,1-difluoroethane (T = 403 K (T <sub>r</sub> = 1.04))	propane ( $T = 393 \text{ K} (T_r = 1.06)$ )			
20.68	0.82				
24.13	0.90				
27.58	0.98	0.89			
31.03	1.03				
34.47	1.12	0.94			
37.92	1.22				
41.37	1.36	0.98			
44.82	1.53				
45.02		1.06			
48.26	1.69	1.15			
51.71	2.19	1.23			
55.16	2.54	1.40			
58.60	2.96				
62.05	3.44	1.61			
68.95	3.86	1.72			
82.74	4.32	1.80			
103.4	4.64	1.94			
137.9		2.01			
206.8	5.77	2.08			

supercritical propane and difluoroethane, respectively. The ratio  $\epsilon_3(\lambda_2)/\epsilon_3(\lambda_3)$  was 0.30 ± 0.02 for 1-methyl-2-pyridone in ethanol and was  $0.35 \pm 0.02$  for 2-pyridone in hexane. The overall accuracy in the equilibrium constant,  $K_c = c_3/c_2$ , was approximately  $\pm 10\%$  for  $K_c = 0.8$  and  $\pm 35\%$  for  $K_c = 6$ , whereas the precision was significantly better.30

## Results

The equilibrium constants,  $K_c = c_3/c_2$ , in 1,1-difluoroethane  $(T_c = 386.7 \text{ K}, P_c = 45 \text{ bar})$  and in propane  $(T_c = 369.8 \text{ K}, P_c$ = 42.5 bar) are given in Table I and Figures 2 and 3. The  $K_c$ increases by a factor of 7 in 1,1-difluoroethane for a pressure range 21-207 bar, while it more than doubles in propane over the same pressure range. In the highly compressible near-critical region, the slope of  $K_c$  versus pressure is extremely pronounced in both solvents. At pressures greater than 100 bar,  $K_c$  is less sensitive with respect to pressure in both solvents because the density is a weaker function of pressure, that is, the isothermal compressibility is small. This insensitivity is typical for reaction equilibria in liquid solvents, where pressure changes of more than a kilobar are needed to produce an order of magnitude change in  $K_c$ .<sup>32</sup>

At 403 K and at a low pressure of 21 bar,  $K_c$  in 1,1-difluoroethane is 0.82 compared with a value of  $0.4 \pm 0.4$  at a similar temperature in the vapor phase.9 At 41 bar, the value increases to 1.4, which is comparable to the value of 1.6 in cyclohexane at a similar temperature.<sup>7</sup> The larger equilibrium constants at higher pressures are typical of those measured in polar liquid solvents. For example, the value of  $K_c$  in chloroform is 6, although there



Figure 4. Kirkwood model for solvent polarity effect on  $K_c$  for tautomerization of 2-hydroxypyridine/2-pyridone (supercritical 1,1-difluoroethane at 403 K, O; supercritical propane at 393 K, □).

**TABLE II: Comparison of Properties of Supercritical** 1,1-Difluoroethane and Propane

	propane		1,1-difluoroethane	
	28 bar	207 bar	21 bar	207 bar
dipole moment, <sup>a</sup> D	0	0	2.3	2.3
dielectric const <sup>b</sup>	1.05	1.54	1.2	4
polarizability per vol <sup>c</sup>	0.13	0.13	0.086	0.086

"Reference 58. "Calculated from ref 34. "Data from ref 59.

is a large uncertainty since only a single wavelength was used.<sup>5,7</sup>

## Discussion

Solvent Effects from the Kirkwood Theory. Solvent effects involving dipoles are often described qualitatively by using the Kirkwood theory,<sup>33,34</sup> which for the reaction of interest gives

$$RT \ln K_c = \frac{3}{8} \left( \frac{1-\epsilon}{1+\epsilon} \right) \left( \frac{\mu_2^2}{r_2^3} - \frac{\mu_3^2}{r_3^3} \right)$$
(2)

where  $\mu$  and r are the dipole moment and molecular radius, respectively. This approach was applied previously for the keto-enol equilibria of ethyl acetoacetate and acetylacetone.35 Figure 4 shows the results for the new data in two solvents. It is apparent that  $K_c$  reaches larger values in the polar solvent, 1,1-difluoroethane, because the range in  $\epsilon$  is larger for a given range in reduced pressure. At a given value of  $\epsilon$ , it is interesting that  $K_c$  is larger for propane. This may be explained by the larger value of the polarizability per volume of propane at a given value of  $\epsilon$  (see Table II). Consequently, the induction forces, where a molecule induces a dipole in the solvent, would be stronger in propane. Since the dipole moment of the product 2-pyridone is larger than that of the reactant 2-hydroxypyridine,  $K_c$  increases as the polarizability per volume of the solvent increases. As the critical point is approached at the lower pressures, fluctuation correlation lengths increase to a point where the fluid density is not uniform,<sup>36</sup> so the Kirkwood theory is very limited.

Correlation of Equilibrium Constants with Solvatochromic Parameters. Solvatochromatic scales are used commonly to correlate the effect of the polarity and polarizability of a solvent on equilibrium constants and reaction rate constants in liquids<sup>8</sup> and recently in supercritical fluids.<sup>1,4</sup> Gordon and Katritzky<sup>37</sup> used the Kosower Z parameter as a solvatochromic indicator to correlate tautomeric equilibrium constants of pyridones in alcohol-water mixtures. We have chosen to use the transition energy,  $E_{\rm T} = hc/\lambda_{\rm max}$ , of phenol blue, since data are available in supercritical 1,1-difluoroethane.1

The logarithm of  $K_c$  of 2-hydroxypyridine/2-pyridone in 1,1difluoroethane is shown vs  $E_{T}$  of phenol blue in the same solvent

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Figure 5.  $K_c$  for tautomerization of 2-hydroxypyridine/2-pyridone versus  $E_T$  of phenol blue in supercritical 1,1-difluoroethane at 403 K.



Figure 6. Partial molar volume change on reaction for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical propane at 393 K (experimental, O; predicted by using eq 15; —).

in Figure 5. The solvent effects on electronic excitation and tautomerization are expected to be similar, so that the correlation is linear. In each process, induction and permanent dipole interactions are the key interactions that cause the solvent effect. The solvent stabilizes the more polar state, i.e., the excited electronic state of the solvatochromic dye or the more polar tautomer to a greater extent than the less polar ground state of the dye or the less polar tautomer.

Correlation of the Partial Molar Volume Change on Reaction. The effect of pressure on  $K_c$  is related to the difference in the partial molar volumes of the products and reactants, that is, the partial molar volume change on reaction,  $\Delta \bar{v}_{rxn}$ , by the expression<sup>38</sup>

$$RT(\partial \ln K_c/\partial P)_T = -\Delta \bar{v}_{rxn} + \nu k_T = -(\bar{v}_3 - \bar{v}_2) + \nu k_T \quad (3)$$

where  $\bar{v}_2$  and  $\bar{v}_3$  are the partial molar volumes of 2-hydroxypyridine and 2-pyridone, respectively,  $k_T$  is the isothermal compressibility, and  $\nu$  is defined as the sum of the stoichiometric coefficients (for this reaction,  $\nu = 0$ ). The  $\Delta \bar{v}_{rxn}$  is shown over a wide pressure range in Figures 6 and 7 for propane and 1,1-difluoroethane, respectively. At the pressure where the compressibility reaches a maximum,  $\Delta \bar{v}_{rxn}$  becomes the most negative, that is, -900 cm<sup>3</sup>/mol in propane and -1400 cm<sup>3</sup>/mol in 1,1-difluoroethane. Other investigators have observed a correspondence between partial molar volumes and the compressibility of the solvent.<sup>1,18</sup> Above about 50 bar, the magnitude of  $\Delta \bar{v}_{rxn}$  decreases sharply with increasing pressure as does the compressibility. At 200 bar,  $\Delta \bar{v}_{rxn}$ is -37 cm<sup>3</sup>/mol in 1,1-difluoroethane and -16 cm<sup>3</sup>/mol in propane, which is much closer to the values that would be observed in liquid solvents.

The extremely pronounced values of partial molar volumes near the point of maximum compressibility may be understood upon examination of the thermodynamic relationship

$$\bar{v}_i = v k_T n (\partial P / \partial n_i)_{T, V, n_{j \neq i}}$$
(4)

where v is the molar volume of the solvent,  $n_i$  is the number of moles of component *i*, and *n* is the total number of moles of the



**Figure 7.** Partial molar volume change on reaction for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical 1,1-difluoroethane at 403 K (experimental, O; predicted by using eq 15, —).



Density (mole/l)

**Figure 8.**  $K_c$  for tautomerization of 2-hydroxypyridine/2-pyridone vs density (experimental, O; predicted by using eq 11, --).

mixture. At infinite dilution,  $\bar{v_i}^{\infty}$  diverges as the compressibility of the solvent diverges at the critical point.<sup>18</sup>

The  $\Delta \bar{v}_{rxn}$  data will be correlated by using only one adjustable constant, the difference between the solute-solvent van der Waals attraction constants for the tautomers,  $\Delta a$ . Once this parameter is regressed, it will be used to predict  $\Delta v_{rxn}$  and  $K_c$  at other temperatures and the partial molar enthalpy change on reaction,  $\Delta \bar{h}_{rxn}$ , in both propane and 1,1-difluoroethane.

Figures 2 and 3 show that  $K_c$  is a highly nonlinear function of pressure, but Figure 8 shows that log  $K_c$  is a relatively linear function of density. The complex effect of pressure on density, that is,  $k_T$ , has been removed and may be explained thermodynamically. We begin with the relationship

$$\left(\frac{\partial \ln K_c}{\partial \rho}\right)_T = \frac{1}{\rho k_T} \left(\frac{\partial \ln K_c}{\partial P}\right)_T \tag{5}$$

where  $\rho = n/V$  is the mixture density. Combining eq 3-5 yields

$$RT\left(\frac{\partial \ln K_c}{\partial \rho}\right)_T = -\rho^{-2}n\left[\left(\frac{\partial P}{\partial n_3}\right)_{T,V,n_1,n_2} - \left(\frac{\partial P}{\partial n_2}\right)_{T,V,n_1,n_3}\right]$$
(6)

where component 1 is the solvent and  $\rho$  is the density of the mixture. The density derivative may be described in a fundamental manner by using statistical mechanics. On the basis of the Kirkwood-Buff solution theory, O'Connell showed that<sup>39</sup>

$$\bar{v}_i = k T k_T \left\{ 1 - \rho \sum_j y_j \int c_{ij}(\mathbf{r}) \, \mathrm{d}\mathbf{r} \right\}$$
(7)

where k is Boltzmann's constant,  $c_{ij}(\mathbf{r})$  is the direct correlation function, and  $y_i$  is the mole fraction of component *i*. At infinite dilution, eqs 4, 6, and 7 can be combined to give

$$\left(\frac{\partial \ln K_c}{\partial \rho}\right)_T = \int \{c_{13}(\mathbf{r}) - c_{12}(\mathbf{r})\} \, \mathrm{d}\mathbf{r}$$
(8)

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molecule	surface area, $Å^2/molecule$	vol, Å <sup>3</sup> /molecule	mean radius, <sup>c</sup> Å/molecule
propane	63.6 <sup>b</sup>	47.6 <sup>b</sup>	2.25
1,1-difluoroethane	79.5ª	52.1ª	2.51
2-hydroxypyridine	110ª	86.5ª	2.96
2-pyridone	114ª	85.9ª	3.00

<sup>a</sup> Based on ref 60. <sup>b</sup> Based on ref 61. <sup>c</sup> Based on surface area (see Appendix).

Equation 6 and likewise eq 8 are highly useful in that they provide a means to compare directly solute-solvent molecular interactions for the two reacting species without the complexities that arise from  $k_T$ .

According to the van der Waals theory of fluids, the pressure may be separated into a repulsive and an attractive contribution so that the partial molar volume change on reaction may be written as

$$\Delta \bar{v}_{rxn} = v k_T n [(\partial P/\partial n_3)^{rep} - (\partial P/\partial n_2)^{rep} + (\partial P/\partial n_3)^{att} - (\partial P/\partial n_2)^{att}]_{T,V,n_i}$$
(9)

where  $n_i$  refers to the other two components for each derivative. The difference between the repulsive terms is negligible since the sizes of the tautomers are essentially the same (see Table III). Consequently,  $\Delta \bar{v}_{rxn}$  will be dominated by the term due to the solute-solvent attractive forces. The term  $(\partial P/\partial n_3)^{att}$  is more negative than  $(\partial P/\partial n_2)^{att}$  since 2-pyridone has a higher dipole moment and thus interacts more strongly with the solvent. This causes  $\Delta \bar{v}_{rxn}$  to be negative, causing K<sub>c</sub> to increase with pressure.

The attractive contribution may be calculated by using the van der Waals equation of state along with the van der Waals 1 quadratic mixing rule:40

$$n\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}}^{\text{att}} = -2a_{1i}\rho^2 \tag{10}$$

where  $a_{1i}$  is the van der Waals unlike pair attraction parameter between the solvent and solute i. Equations 6 and 10 can be combined to show

$$\ln K_{c} = \frac{2\Delta a\rho}{RT} + \frac{1}{RT} \int_{0}^{\rho} \rho^{-2} n \left[ \left( \frac{\partial P}{\partial n_{3}} \right)_{T,V,n_{2},n_{1}}^{\text{rep}} - \left( \frac{\partial P}{\partial n_{2}} \right)_{T,V,n_{1},n_{3}}^{\text{rep}} \right] d\rho + \ln K_{a}(T)$$
(11)

where  $\Delta a = a_{13} - a_{12}$ . It is clear that  $\ln K_a(T)$  is the temperature-dependent constant of integration, since the first two terms become zero in the ideal-gas low-density limit. It is instructive to explore eq 11 by using the relationship

$$\ln K_a = \ln K_v + \ln K_\phi + \ln K_P \tag{12}$$

where  $K_a = a_3/a_2$ ,  $K_{\phi} = \phi_3/\phi_2$ ,  $K_y = y_3/y_2$ , a is the activity, and  $\phi_i$  is the fugacity coefficient of component *i*. For the tautomeric equilibria of interest,  $K_P = 1$  and  $K_c = K_y$ . Since  $K_a$  is independent of pressure, eq 12 shows that the changes in  $K_c$  are due exclusively to the ability of the supercritical solvent to adjust the tautomers' fugacity coefficients with small changes of pressure or temperature. Since<sup>40</sup>

$$\ln \phi_i = \frac{1}{RT} \int_V^{\infty} \left[ \left( \frac{\partial P}{\partial n_3} \right)_{T,V,n_2,n_1} - \frac{RT}{V} \right] dV - \ln \left( \frac{PV}{RT} \right)$$
(13)

 $\ln K_{\phi}$  is equal to the negative of the first two terms in eq 11. A comparison of eqs 11 and 12 further confirms that  $\ln K_a(T)$  is the constant of integration.

TABLE IV: Regressed Parameters from the ln K<sub>c</sub> vs Density Data for Tautomerization of 2-Hydroxypyridine/2-Pyridone in Supercritical Propane and 1,1-Difluoroethane

solvent	$\Delta a,$ (L/mol) <sup>2</sup> bar	Ka	
1,1-difluoroethane at 403 K	3.963	0.6	
propane at 393 K	1.927	0.8	

Since the integral in eq 11 involving the repulsive forces is essentially zero for the reaction of interest, eq 11 predicts that  $\ln K_c$  is linear in density. The small deviation from linearity for the data shown in Figure 8 may be caused by two effects. The van der Waals equation is not accurate near the critical point due to the mean field approximation because fluctuation correlations are not modeled properly as the critical point is approached.<sup>36,41</sup> A secondary effect is due to the influence of the repulsive forces caused by the small difference in the sizes and shapes of the tautomers (see Table III). This small effect was modeled by using the hard convex body theory of Naumann and Leland<sup>42</sup> as discussed in the Appendix.

The parameters  $\Delta a$  and  $\ln K_a(T)$  were regressed by using eq 11 to minimize the sum of the square of the errors, and the results are shown in Figure 8 and Table IV. The contribution of the repulsion forces is relatively small yet included as described in the Appendix. The sign of  $\Delta a$  is positive because of the larger dipole moment for the product 2-pyridone. As explained previously, the accuracy of the van der Waals attractive term decreases significantly near the critical point; therefore, the regression was limited to  $\rho/\rho_c = \rho_r > 1.3$  as suggested previously<sup>18,43</sup> and to  $\rho_r < 1/1.3$  on the basis of critical exponents.<sup>41</sup> The densities for propane and 1,1-difluoroethane were calculated by using an extremely accurate equation of state44 and the Peng-Robinson equation of state, respectively. The average absolute deviations

$$AAD = \frac{1}{N_{i=1}^{N}} \left| \frac{K_{ci}^{\text{calcd}} - K_{ci}^{\text{exptl}}}{K_{ci}^{\text{exptl}}} \right|$$
(14)

are 4% and 13% for tautomerization in propane and 1,1-difluoroethane, respectively. The regression for propane is more accurate than that for 1,1-difluoroethane because a more accurate equation of state was used to calculate the density.

The results in Table IV show that  $K_a$  is 0.8 in propane at 393 K and 0.6 in 1,1-difluoroethane at 403 K. Since the uncertainty in the densities for 1,1-difluoroethane decreases the reliability of the regression, the value of 0.8 in propane will be used later in this paper to predict  $K_c$  at other temperatures. This value is consistent with  $K_a = K_c = 0.4 \pm 0.4$  measured in the gas phase at 403 K.9

Now that the  $\Delta a$  has been estimated, it can be used along with eq 9 and 10 to calculate  $\Delta \bar{v}_{rxn}$ , that is

$$\Delta \bar{v}_{rxn} =$$

$$-2k_T \Delta a\rho + v k_T n[(\partial P/\partial n_3)_{T,V,n_2,n_1}^{\text{rep}} - (\partial P/\partial n_2)_{T,V,n_1,n_3}^{\text{rep}}]$$
(15)

The results from this calculation are shown in Figures 6 and 7. The slight variation in the curve in Figure 7 is most likely due to the error introduced by estimating the density of 1,1-difluoroethane with the Peng-Robinson equation of state.

Partial Molar Volume Change on Reaction at Other Temperatures and Its Relationship to Clustering. The  $\Delta \bar{v}_{rxn}$ 's at various temperatures are predicted by using eq 15, and the results for 1,1-difluoroethane are shown in Figure 9. The shapes of these curves follow those of the isothermal compressibility,<sup>18</sup> that is, the magnitude decreases and the peak width increases as temperature is increased above the critical temperature. At a reduced

<sup>(40)</sup> Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. Molecular Thermodynamics of Fluid-Phase Equilibria; Prentice-Hall: Englewood Cliffs, NJ, 1986; pp 40-41, 57.

<sup>(41)</sup> Reichl, L. E. A Modern Course in Statistical Physics; University of Texas: Austin, TX, 1980; p 130.

<sup>(42)</sup> Naumann, K.-H.; Leland, T. W. Fluid Phase Equilib. 1984, 18, 1.
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(44) Hang, T.; Leland, T. W.; Ely, J. Paper presented at the 1984 Winter National Meeting of the American Institute of Chemical Engineers, Atlanta, Computer National Meeting of the American Institute of Chemical Engineers, Atlanta, GA, 1984.



Figure 9. Partial molar volume change on reaction for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical 1,1-difluoroethane.

temperature of 1.003, the minimum  $\Delta \bar{v}_{rxn}$  in 1,1-difluoroethane and propane are -20400 and -15200 cm<sup>3</sup>/mol, respectively. The larger magnitude for  $\Delta \bar{v}_{rxn}$  in the more polar solvent, 1,1-difluoroethane, is due to a larger value of  $\Delta a$  and a slightly larger  $k_T$ . The  $\Delta a$  is greater for the more polar solvent 1,1-difluoroethane, which forms stronger dipole-induced dipole and dipoledipole interactions with each of the tautomers.

To explore the condensation or clustering of a solvent about a solute, it is useful to define a cluster size,  $n_2^{e}$ , as follows:

$$n_2^{e} = (\rho_{12}^{1} - \rho) V_{12} \tag{16}$$

where  $\rho$  is the bulk solvent density,  $\rho_{12}^{-1}$  is the average local density of solvent, 1, surrounding solute, 2, within the cluster, and  $V_{12}$ is volume of the cluster. It has been shown that  $\bar{v}_i^{\infty}$  is related directly to the relative amount of solvent clustering about the solute molecule, by the equation<sup>3,4,15,16,45</sup>

$$n_2^{\mathbf{e}} = \rho(kTk_T - \bar{v}_2^{\infty}) \tag{17}$$

For the tautomeric reaction

$$n_3^{\rm e} - n_2^{\rm e} = -\rho \Delta \bar{v}_{\rm rxn} \tag{18}$$

where  $n_3^{e}$  and  $n_2^{e}$  are the average numbers of solvent molecules clustered about a 2-pyridone molecule and a 2-hydroxypyridine molecule, respectively, in excess of the bulk values. The values of  $\Delta \bar{v}_{rxn}$  of -20 400 and -15 200 cm<sup>3</sup>/mol correspond to differences in average solvent cluster sizes between the tautomers of 94 and 76 molecules, respectively. This provides a quantitative description of the change in cluster size which results from an increase in the solute-solvent attraction force.

The results are significant because the difference in clustering has been measured without making simplifying assumptions that are required when using other techniques. In nonreacting systems, the quantities that indicate the degree of clustering,  $\bar{v}_i$  and  $\bar{h}_i$ , are either difficult to measure directly in supercritical fluids<sup>18</sup> or must otherwise be estimated by assuming the solutes obey Henry's law.<sup>46,47</sup> The fundamental relationship is<sup>47</sup>

$$\left(\frac{\partial \ln x_i}{\partial P}\right)_{T,eq} = \frac{v^s - \bar{v}_i}{(\partial \mu_i^s / \partial \ln x_i)}$$
(19)

where  $v^s$  is the molar volume of the solid solute *i* and  $\mu_i^g$  is the chemical potential of the solute in the gas phase. To calculate the  $\bar{v}_i$  from solubility data, Henry's law

$$\left(\frac{\partial \mu_i^{\mathfrak{g}}}{\partial \ln x_i}\right)_{T,P} = RT \tag{20}$$

must be applied to give the result

$$\left(\frac{\partial \ln x_i}{\partial P}\right)_{T, eq} = \frac{v^s - \bar{v}_i}{RT}$$
(21)

(45)  $n_j^{e}$  is designated as  $\xi_j$  in ref 16.

(47) Gitterman, M.; Procaccia, I. J. Chem. Phys. 1983, 78, 2648.



Figure 10. Van't Hoff plot for tautomerization of 2-hydroxypyridine/ 2-pyridone in supercritical 1,1-difluoroethane at constant values of reduced pressure.

But in the present study, the slope of the log  $K_c$  vs pressure curve yields  $\Delta \bar{v}_{rxn}$  without assuming any functional form for the chemical potential (see eq 3).

Prediction of  $K_c$  at Other Temperatures. Given  $K_a$  is 0.8 at 393 K, it can be calculated at any temperature by using the Van't Hoff relationship

$$\ln\left(\frac{K_a}{K_{a1}}\right) = -\frac{\Delta H^{\circ}}{R} \left(\frac{1}{T} - \frac{1}{T_1}\right)$$
(22)

where  $\Delta H^{\circ} = -2.6 \pm 1.2 \text{ kJ/mol}$ , which was measured by using photoelectron spectroscopy over the temperature range 323-703 K.<sup>48</sup> With a known  $K_a(T)$ ,  $K_c$  can be calculated at any temperature and pressure by using eq 11. The results for the solvents propane and 1,1-difluoroethane are shown in Figures 2 and 3. These graphs illustrate the effect of temperature approaching the critical point. The slope of  $K_c$  vs pressure at 370 K ( $T_r = 1.0005$ ) approaches infinity for the reaction in propane, and the same behavior is observed in 1,1-difluoroethane at the same  $T_r$ . Near the critical point ( $T_r = 1.0005$ ,  $P_r = 1$ ), a pressure increase of only 0.2 bar will increase  $K_c$  by about 20%; however, this sensitivity falls off rapidly.

Partial Molar Enthalpy Change on Reaction at Different Temperatures. Just as increasing pressure near the critical point of a solvent can cause large increases in  $K_c$ , a decrease in temperature can have the same effect for this exothermic reaction due to large changes in density. Figure 10 is a Van't Hoff plot (log  $K_c$  vs 1/T at constant pressure) for  $K_c$  in 1,1-difluoroethane; similar behavior is observed in propane. Far from the critical point at a reduced pressure of 2.35 (P = 105.9 bar), the temperature effects on  $K_{\phi}$  are small; therefore, the plot of ln  $K_c$  vs 1/T is linear, on the basis of eq 22. As the critical point is approached, the temperature effect on  $K_{\phi}$  becomes pronounced. At  $P_r = 1.06$ , the Van't Hoff plot is highly nonlinear, and at  $P_r \rightarrow 1$ , the slope of the equilibrium constant should diverge at the critical temperature at constant pressure.<sup>49,50</sup>

The magnitude of these temperature effects is represented thermodynamically by the partial molar enthalpy change on reaction,  $\Delta \bar{h}_{rxn} = \bar{h}_3 - \bar{h}_2$ , that is

$$\frac{\Delta \bar{h}_{\rm rxn}}{RT^2} = \left(\frac{\partial \ln K_c}{\partial T}\right)_{P,n}$$
(23)

The standard state for the equilibrium constant has been chosen at a pressure at ideal gas conditions. The calculated values of  $\Delta \bar{h}_{rxn}$  for tautomerization in propane and 1,1-difluoroethane are shown in Figures 11 and 12, respectively. These values were calculated by numerically differentiating the  $K_c$  values, for ex-

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 <sup>(49)</sup> Krichevskii, I. R.; Tsekhanskaya, Y. V.; Rozhnovskaya, L. N. Russ.
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<sup>(50)</sup> Wheeler, J. C.; Petschek, R. G. Phys. Rev. A 1983, 28, 2442.



Figure 11. Partial molar enthalpy change on reaction for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical propane for isobars with reduced pressures 2.35, 1.41, 1.18, and 1.059.



Figure 12. Partial molar enthalpy change on reaction for tautomerization of 2-hydroxypyridine/2-pyridone in supercritical 1,1-difluoroethane for isobars with reduced pressures 2.35, 1.41, 1.18, and 1.059.

ample, those shown in Figure 10, by using the two-point central difference technique.<sup>51</sup> Near the critical point at infinite dilution,  $\bar{h}_i^{\infty}$  is proportional to  $\bar{v}_i^{\infty}$ ,<sup>52</sup> and the shape of  $\bar{v}_i^{\infty}$  follows  $k_T$ . Therefore  $\bar{h}_i^{\infty}$  follows  $k_T$ . The minima  $\Delta \bar{h}_{rxn}$  at  $P_r = 1.06$  in propane and 1,1-difluoroethane were -170 and -270 kJ/mol, respectively. The  $\Delta \bar{h}_{rxn}$  in 1,1-difluoroethane will be shown to be consistent with the difference in the degree of solvent molecules condensing about each tautomer.<sup>53</sup> The  $\Delta \bar{\nu}_{rxn}$  at the same reduced temperature and pressure is -7435 cm<sup>3</sup>/mol, corresponding to a difference in cluster sizes of 32 (see eq 18). For a  $\Delta \bar{h}_{rxn}$  of -270 kJ/mol, this value of 32 indicates that the average solute-solvent pair energy is about 8 kJ/mol, which is physically meaningful when compared to a typical pair energy of 5 kJ/mol for dispersion forces.40

Another method for evaluating the temperature effects would be to measure log  $K_c$  vs 1/T at constant density;<sup>50,54</sup> the predicted behavior for tautomerization in propane is shown in Figure 13. The fundamental equation describing this behavior is<sup>50</sup>

$$\left(\frac{\partial \ln K_c}{\partial (1/T)}\right)_{\rho} = \left(\frac{\partial \ln K_c}{\partial (1/T)}\right)_{P} - \left(\frac{\partial \ln K_c}{\partial \rho}\right)_{T} \left(\frac{\partial \rho}{\partial (1/T)}\right)_{P} \quad (24)$$

The two terms on the right-hand side of eq 24 diverge strongly at the critical point (see Figure 10), but cancellation between them must occur because  $(\partial \ln K_c/\partial (1/T))_{\rho}$  is well defined even at the critical point, as shown in Figure 13.55 The result of this can-



Figure 13. Simple representation of temperature effects at constant density for tautomerization of 2-hydroxypyridine/2-pyridone in propane  $(\rho_r = 1.0, ---; \rho_r = 1.2, ---).$ 

cellation is a simple function that is not affected by the large density effects near the critical point. Just as plotting  $\log K_c$  vs density at constant temperature removes the large compressibility effect near the critical point, plotting log  $K_c$  vs 1/T at constant density produces a simple function, as compared to log  $K_c$  vs 1/Tat constant pressure.

#### Conclusions

Supercritical fluid 1,1-difluoroethane can be used to adjust  $K_c$ for the tautomerization of 2-hydroxypyridine and 2-pyridone over a continuum from gas-phase values to those encountered in polar liquid solvents, isothermally over a relatively small pressure range. This adjustability is consistent with results obtained for the unimolecular decomposition of  $\alpha$ -chlorobenzyl methyl ether,<sup>1</sup> the  $\Delta \bar{v}_{rxn}$  for the electrode reduction of I<sub>2</sub> to I<sup>-</sup>,<sup>2</sup> the Diels-Alder reaction of maleic anhydride with isoprene,<sup>19</sup> and the parallel Diels-Alder additions of methyl acrylate and cyclopentadiene.<sup>20</sup> By use of pressure perturbations in the critical region, solvent effects may be explored in a fundamental manner, without the gross changes that take place when a reaction is studied in a series of chemical solvents of varying molecular functionality.

The spectroscopic measurement of  $\Delta \bar{\nu}_{rxn}$  and  $\Delta \bar{h}_{rxn}$  is an extremely convenient method to explore the fundamental nature of supercritical solvents, that is, large pressure and temperature effects. This technique is much faster than a previous technique based on pressure-volume-temperature-composition measurements of  $\bar{v}_i$ .<sup>18</sup> The other route to  $\bar{v}_i$ , differentiation of solubility data, is not as accurate as it depends upon the assumption of Henry's law.

Supercritical fluids accentuate pressure effects on equilibrium constants caused by differences between the polarities and sizes of reactants and products. The large isothermal compressibility promotes huge values of  $\Delta \bar{v}_{rxn}$ , for example, -20 400 cm<sup>3</sup>/mol for the tautomerization of 2-hydroxypyridine in 1,1-difluoroethane at a reduced temperature of 1.003 and a reduced pressure of 1. This corresponds to a difference in solvent condensation about the tautomers of about 100 molecules, which is a manifestation of the larger dipole moment for the product, 2-pyridone ( $\Delta a =$  $+3.96 (L/mol)^2$  bar). These differences in solvent condensation are consistent with the calculated values of  $\Delta h_{\rm rxn}$ . This fundamental description of the change in clustering as a function of the change in the solute-solvent attraction forces will aid significantly the understanding of activation volumes for reactions in supercritical media.

It is difficult to compare  $\Delta \bar{v}_{rxn}$  for a series of reactions or solvents due to the large influence of the compressibility. To make such comparisons, it is necessary to normalize  $\Delta \bar{v}_{rxn}$  by factoring out the compressibility. This normalized value describes the influence of solute-solvent molecular interactions. For the tautomeric reaction, the normalized value of  $\Delta \bar{\nu}_{\rm rxn}$  , represented by the slope of  $\ln K_c$  vs  $\rho$ , was directly related to the difference between the solvent's structure around each tautomer. This normalization procedure will be useful for future measurements of supercritical solvent effects on reversible reactions, to determine the differences

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<sup>(55)</sup> Even though mean-field theories do have inadequacies at the critical point, behavior similar to that shown in Figure 13 has been observed in a nonreacting system,<sup>56</sup> and it was modeled satisfactorily by using a similar equation of state.

<sup>(56)</sup> Diepen, G. A.; Scheffer, F. E. J. Phys. Chem. 1953, 57, 575.

in sizes and polarities of the reactants and products.

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## Appendix

The repulsive contributions to  $(\partial P/\partial n)$  are modeled by using a hard convex body equation of state:<sup>42,57</sup>

$$P_{v}/RT = \{(1 + (3\alpha - 2)y + [1.5\beta(1/\tau + 1) - 3\alpha + 1]y^{2} - 0.5\beta(5 - 3/\tau)y^{3} + 7\beta(1/\tau - 1)y^{4}\}(1 - y)^{-3}$$
(A1)

where

$$y = \rho \bar{V} \quad \alpha = (\bar{R}\bar{S})/(3\bar{V}) \qquad \beta = (\bar{S}^2 \bar{R}^2)/(9\bar{V}^2)$$
  
$$\tau = (4\pi \bar{R}^2)/\bar{S} \qquad \bar{V} = \sum_i x_i V_i \qquad \bar{S} = \sum_i x_i S_i$$

(57) De Azevedo, E. G.; Prausnitz, J. M. Fluid Phase Equilib. 1988, 41, 109.

 $\bar{R} = \sum_{i} x_i R_i \qquad \bar{R}^2 = \sum_{i} x_i R_i^2$ 

and V, R, and S are the molecular volume, radius, and surface area, respectively; and  $x_i$  is the mole fraction of component *i*. The expression for ln  $\phi_i$  is available.<sup>42</sup>

The molecular dimensions used in eq A2 are shown in Table III. The molecular volumes for propane are based on a pressure-volume-temperature correlation.<sup>61</sup> The surface area and volume for the other molecules were calculated by Prof. R. S. Pearlman. The mean radius is estimated based on the surface area,  $A_{i}$ :

$$\bar{r}_i = (A_i/4\pi)^{1/2}$$
 (A2)

**Registry No. 1**, 72762-00-6; **2a**, 142-08-5; propane, 74-98-6; 1,1-di-fluoroethane, 75-37-6.

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# Some Simple Calculations of the Density Profile of Inhomogeneous Hard Spheres Using the Lovett-Mou-Buff-Wertheim Equation with the Bulk Direct Correlation Function

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The Lovett-Mou-Buff-Wertheim (LMBW) equation relating pair direct correlation functions with singlet density profiles is considered. If the direct correlation function is approximated by its bulk value, the LMBW equation becomes the hypernetted chain (HNC) approximation or, if linearized, the Percus-Yevick (PY) approximation. For a system of particles near a hard wall, substitution of the contact value theorem into the LMBW equation leads to a modified HNC equation or, with linearization, a modified PY equation. Numerical results for hard spheres indicate that the modified HNC equation is an improvement but that the modified PY equation is not.

# Introduction

The density profile of an inhomogeneous fluid can be calculated from the Lovett-Mou-Buff-Wertheim (LMBW) equation<sup>1</sup>

$$\frac{\partial \ln g(x)}{\partial x} = -\beta \frac{\partial V(x)}{\partial x} + \int_{-\infty}^{\infty} dy \frac{\partial n(y)}{\partial y} K(x,y)$$
(1)

where  $n(x) = n(\infty) g(x)$  is the singlet density profile,  $n(\infty) = n$ , the bulk density

$$K(x,y) = 2\pi \int_0^\infty d\mathbf{r} \ rc(x,y,r) \tag{2}$$

is the kernel, V(x) is the external potential,  $\beta = 1/k_BT$ , T is the temperature, and c(x,y,r) is the direct correlation function of a pair of particles in the inhomogeneous or interfacial region. For simplicity, we have written eq 1 for a one-component fluid and

have assumed cylindrical symmetry. Thus, x and y are the normal positions of the two particles in the inhomogeneous region and r is the projection of their separation in the plane of the inhomogeneity. Extension of eq 1 to more general situations is straightforward.

For some situations, a linearized version of eq 1 is valuable.

$$\frac{\partial}{\partial x} \{g(x) \exp[\beta V(x)]\} = \int_{-\infty}^{\infty} dy \ \frac{\partial n(y)}{\partial y} K(x,y)$$
(3)

Equation 1 is based on force balance considerations and is exact. Equation 3 is, of course, not exact. In order to calculate density profiles, c(x,y,r) must be approximated. The LMBW equation is attractive for calculations of n(x) because generally direct correlation functions can be approximated more readily than pair correlation functions. As pointed out by Blum, Hernando, and Lebowitz,<sup>2</sup> for electrolytes, the LMBW equation has the added

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