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Solvent Effects on a Diels−Alder Reaction in Supercritical Water: RISM-SCF Study

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Abstract: A Diels−Alder reaction in supercritical water is studied by means of combined electronic structure and liquid state theories. The target system is the cycloaddition of cyclopentadiene with methyl vinyl ketone. The rate and the yield of the reaction in supercritical water are calculated and compared with those in ambient water. The activation free energies of the two isomers, cis and trans, are compared. The results are in agreement with the experimentally observed increase of the rate and the yield. The solvation effect for the rate constant is decreased in supercritical water, but the rate is increased because of the thermal excitation rather than the solvation effect. The trans-conformer has shown less activation energy in ambient water and supercritical water compared to the cis-conformer. The estimated yield in supercritical water is more than 600 times higher than in ambient water. The high yield in supercritical water is due to the high solubility of the reactants to supercritical water.

Introduction

The Diels−Alder reaction is a synthetic method which has been most widely employed for the production of polycyclic ring systems. In the early 1980s, Breslow et al. showed that using water as solvent accelerates the Diels−Alder reaction dramatically.[1] The observation has reversed the traditional notion that pericyclic reactions are insensitive to solvent effects. However, the low solubility of nonpolar solute in aqueous solvents restricts the choice of reagents or requires special additives. In this regard, supercritical water (SCW)[2,3] deserves attention due to its unique properties: it can dissolve a variety of solutes, both polar and nonpolar, depending on temperature and pressure. Recently, the Diels−Alder reactions in SCW, with several different diene/dienophile combinations, have been experimentally examined,[4] and it has been reported that SCW gives rise to higher yields compared to ambient water (AW), while extremely increasing the reaction rate. When it is compared with the usual organic solvent, SCW not only gives us higher yield and rate of the reaction but also provides further benefit concerned with the environmental protection: it is free from discharging harmful organic solvent into the environment. Thus, it is important to elucidate the mechanism of the reaction at the molecular level, and to answer the questions: why is the reaction rate accelerated when the media is changed from organic solvent to AW and SCW, and why is the yield drastically enhanced in SCW compared to AW?

Theoretical studies of organic reactions in solution require descriptions of the electronic structure of molecules involved in the reaction and for solvent properties, which are closely coupled with each other. In the earlier work on an S_N2 reaction in SCW,[5−8] the continuum solvent model and the corresponding theory were applied. The method provides a reasonable account for the solvation free energy in terms of the agreement with experiments with respect to “number”. The electronic structure and optimized geometry in SCW were also obtained. The approach has attracted people in the field, because it requires much less computational effort. The method, however, is not capable of providing any structural information for solvation, and thereby does not match with the electronic structure theory in terms of the level of description. Moreover, the quantitative agreement with experiments itself should not be regarded as a great achievement, because the theory usually relies on a substantial number of adjustable parameters. Another method applied for the same reaction system is molecular simulations.[9−11] The approaches have been very successful to account for the free energy change of solvation and its structure. However, their computational demands prevent one from evaluating the electronic structure of species involved in the reaction, which is subject to the field of solvent. Since change in the electronic structure is the primary cause of chemical reactions, the method has to overcome the high barrier to be applied to such problems. As an alternative to those mentioned above, we have proposed a new approach called “RISM-SCF/MCSCF” for calculating the electronic structure of a molecule in solution, which combines the integral equation theory of molecular liquids (RISM) and the ab initio molecular orbital theory (SCF/MCSCF).[12−14] The method determines self-consistently the

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electronic structure of a solute and the solvent distribution around it. One of the advantages of our method is that it enables us to change easily thermodynamic conditions of the system, such as temperature and density. Thus, it is suitable for investigating the chemical reaction in solvent, including SCW, which requires numerical analyses in wide range of temperature and pressure.[15]

In the present paper, we will study the Diels−Alder reactions in SCW as well as in AW by means of the RISM-SCF/MCSCF method, and try to answer the questions raised earlier in the section: why is the reaction rate accelerated when the media is changed from organic solvent to AW and SCW, and why is the yield drastically enhanced in SCW compared to AW? As a target system, we chose the cycloaddition of cyclopentadiene (CP) with methyl vinyl ketone (MVK), which has been well-studied by experimental and theoretical approaches.[1,16−19] The dienophile can take two different conformations, *s*-cis or *s*-trans, which may bind with the diene to make a transition structure in two possible conformations, exo or endo. Therefore, four possible combinations, endo−cis, endo−trans, exo−cis and endo−trans, are conceivable for the structure of transition state (TS). Previous ab initio calculations[20] showned that the endo−cis transition structure is of the lowest energy in several Diels−Alder reactions, but Assfeld et al. showed in a recent calculation[23] that the endo−trans transition structure becomes more stable in the reaction of CP and methyl acrylate in aqueous solution. Thus, we performed calculations on both the endo−cis and endo−trans reactions, and also examined which is the more stable transition structure for this reaction system in AW and SCW. The exo TS are not considered since their energies are substantially greater than those of the endo TS in aqueous solution.[24]

Methods

The detailed explanations of the RISM-SCF/MCSCF method are omitted. We refer readers who are interested in the methodology to previous articles.[12−14] The geometry of the reactants, the TSs, and the products were fully optimized in gas phase at the restricted Hartree−Fock level by using a double-ζ valence (DZV) basis set.[25] Those geometries determined in gas phase were maintained for all the RISM-SCF calculations. Vibrational frequencies were calculated at the same level, and TSs were confirmed to have only one imaginary frequency. In the calculation for ideal terms of Gibbs free energy ($\Delta F^{\mathrm{ideal}}$) of the solute molecules, the zero-point vibrational energy is taken into account. The imaginary frequency for transition states was ignored in calculations for the vibrational energy. Here, we assume that a solute molecule feels a mean field potential, and consequently its kinetic energy does not depend on its position, and the $\Delta F^{\mathrm{ideal}}$ for solute molecules was not changed in gas or solvent. The solvation free energies ($\Delta\mu$) were calculated with the equation consistent with the HNC closure.[27]

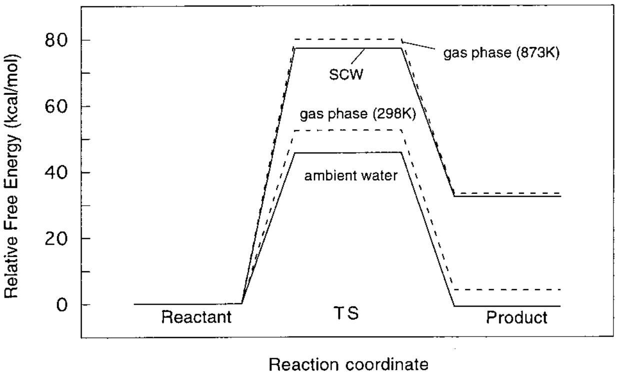

Figure 1. The total free energies of TS and the products relative to those of the reactants for the end-trans reaction.

$$\Delta\mu = \frac{\rho}{2\beta}\sum_{\alpha\in u}\sum_{\gamma\in v}\int_0^{\infty} 4\pi r^2\, \mathrm{d}r\left(h_{\alpha\gamma}(r)^2 - 2c_{\alpha\gamma}(r) - h_{\alpha\gamma}(r)c_{\alpha\gamma}(r)\right) \quad (1)$$

where ρ is the number density of solvent and $\beta = 1/k_{\mathrm{B}}T$ (k_{B} is the Boltzmann constant). The indices u and v respectively denote solute and solvent. $h(r)$ and $c(r)$ stand for the site−site intermolecular pair correlation functions and the direct correlation functions, respectively. The total energy of the solute molecule in solvent and in gas phase was respectively defined by

$$F_{\mathrm{total,gas}}(\mathrm{solute}) = E_{\mathrm{elec,gas}}(\mathrm{solute}) + \Delta F^{\mathrm{ideal}}(\mathrm{solute}) \quad (2)$$

$$F_{\mathrm{total,solv}}(\mathrm{solute}) = E_{\mathrm{elec,solv}}(\mathrm{solute}) + \Delta F^{\mathrm{ideal}}(\mathrm{solute}) + \Delta\mu(\mathrm{solute}) \quad (3)$$

where $E_{\mathrm{elec,gas}}$ and $E_{\mathrm{elec,solv}}$ represent the electronic energy of the solute in gas phase and water, respectively. In solution, the electronic structure of the solute changes from that in gas phase due to the solute−solvent interaction. The energy change of the electronic structure associated with solvation (ΔE_{re}) is defined as follows:

$$\Delta E_{\mathrm{re}}(\mathrm{solute}) = E_{\mathrm{elec,solv}}(\mathrm{solute}) - E_{\mathrm{elec,gas}}(\mathrm{solute}) \quad (4)$$

Regarding the potential functions for solute molecules, CH, CH_2, and CH_3 groups are treated as united atoms, and the potential functions consist of the Lennard-Jones (L−J) and Coulomb interaction. The L−J parameters for the united atoms are taken from the OPLS.[21,22] However, all the L−J diameters used here are increased by 0.4 Å, since RISM-SCF calculations for TSs did not converge. For transition states, these parameter were fixed at the same values as those of corresponding sites in the reactants. As a model for solvent water molecules, we employed a SPC-like model,[26] which has been successfully used in liquid state simulations. The temperature and density of the surrounding water we examined in this study were 298 K, 1.0 g/cm^3 for ambient water and 873 K, 0.6 g/cm^3 for supercritical water. The reason we have chosen the relatively high density of SCW is that the RISM method becomes less reliable when density is further decreased.

Results and Discussion

Stabilization of the Transition State in Ambient Water. The key results are shown in Figure 1 which exhibits the energy diagram for the reaction through the endo−cis transition structure in gas phase, in AW (298 K, 1.0 g/cm^3), and in SCW (873 K, 0.6 g/cm^3). All the energy levels are determined by regarding the reactants at corresponding temperature as a

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Table 1. Changes in the Activation Free Energy from Gas Phase to AW ($\Delta\Delta F^{\ddagger} = \Delta F^{\ddagger}_{\mathrm{AW}} - \Delta F^{\ddagger}_{\mathrm{gas}}$) and to SCW ($\Delta\Delta F^{\ddagger} = \Delta F^{\ddagger}_{\mathrm{SCW}} - \Delta F^{\ddagger}_{\mathrm{gas}}$)

	$\Delta\Delta F^{\ddagger}$ (kcal/mol)	$\Delta\mu^{\ddagger}$ (kcal/mol)	$\Delta E^{\ddagger}_{\mathrm{re}}$ (kcal/mol)
		AW	
trans	−7.54	−9.02	1.48
cis	−6.90	−10.98	4.09
		SCW	
trans	−3.40	−3.82	0.42
cis	−2.71	−3.43	0.72

standard. The activation free energy [$\Delta F^{\ddagger}_{\mathrm{gas}} = F_{\mathrm{total,gas}}(\mathrm{TS}) - F_{\mathrm{total,gas}}(\mathrm{reactants})$] computed in gas phase at 278 K is 52.48 kcal/mol. The $\Delta F^{\ddagger}_{\mathrm{AW}}$ is calculated to be 45.58 kcal/mol: it is reduced by 6.90 kcal/mol from gas phase to AW (Table 1). This change originates essentially from the differences of the electrostatic reorganization energy [$\Delta E^{\ddagger}_{\mathrm{re}} = \Delta E_{\mathrm{re}}(\mathrm{TS}) - \Delta E_{\mathrm{re}}(\mathrm{reactants})$] and the solvation free energy [$\Delta\mu^{\ddagger} = \Delta\mu(\mathrm{TS}) - \Delta\mu(\mathrm{reactants})$] between the reactant and TS. In Table 1, the change between these two energy contributions is compiled. As seen in the table, the stabilization of TS comes from a decrease in the solvation free energy associated with the reaction process from the reactant to TS, which includes geometrical change, giving rise to "desolvation" of water molecules at contact. The solvation free energy can be roughly decoupled into two contribution: the electrostatic and hydrophobic effects. To estimate the contribution of the hydrophobic effect, the geometry of the reactants was altered to that of TS, while the charges on the sites were fixed. Consequently, the change in the solvation free energy comes from the loss of the water molecules contacting to the nonpolar groups of the reactants and can be attributed to the hydrophobic effect. Then, the hydrophobic component is estimated to be −5.03 kcal/mol, which accounts for one-half of $\Delta\mu^{\ddagger}$. However, this model possibly overestimates the hydrophobic component because the significant geometrical change may perturb the electronic structure of the solute and may remove the hydrogen bonding to the carbonyl oxygen of reactant, MVK. These effects can give rise to some positive contribution to the hydrophobic component. On the basis of the analysis, the other half of $\Delta\mu$ should come from the electrostatic effect, including the hydrogen bonding around the carbonyl oxygen. Therefore, both the hydrophobic effect and the electrostatic effect contribute equally to the decrease in the solvation free energy. Figure 2a shows the radial distribution functions (rdfs) of water oxygen and hydrogen around the carbonyl oxygen of MVK, TS, and product in AW. The height of the first peak of hydrogen's rdfs directly signifies the degree of hydrogen bonding. As shown in Figure 2a, rdfs for the endo–cis reaction indicate that there is no significant change in height of the first peak when the reaction proceeds from the reactant to TS. At first glance, it appears that the hydrogen bonding is not enhanced. However, considering that a water molecule cannot access the carbonyl oxygen of TS geometrically more than that of the reactant, MVK, the hydrogen bonding for TS must be stronger than that for the reactant, though the height of the first peak in rdfs does not change. The (electronic) reorganization energy, ΔE_{re}, is increased by 4.09 kcal/mol in the reaction from the reactants to TS in case of the endo–cis reaction (Table 1). The more susceptive the solute molecule is to electrostatic effects, the more increased the reorganization energy is. In our case, electrostatic effects are attributed to hydration. Thus, hydration to the carbonyl group induces an increase in the reorganization energy. As the reactants reach TS, the reorganization energy is increased. This also supports the statement mentioned previously that hydrogen bonding is enhanced in TS compared to the reactant, MVK. Concerning the solvation free energy, both the hydrophobic effect and the electrostatic effect equally contribute to the stabilization of TS. At the same time, however, the enhanced hydrogen bonding for TS brings about an increase in the reorganization energy. The contribution of the hydrogen bonding to $\Delta\Delta F^{\ddagger}$ is calculated to be −1.87 kcal/mol as a whole. The contribution of the reorganization energy to the activation energy, $\Delta E_{\mathrm{re}}{}^{\ddagger}$, seems to compensate for the decrease of the solvation free energy due to the hydrogen-bonding effect. Thus, the main contribution to the stabilization for the endo–cis TS can be attributed to the hydrophobic effect.

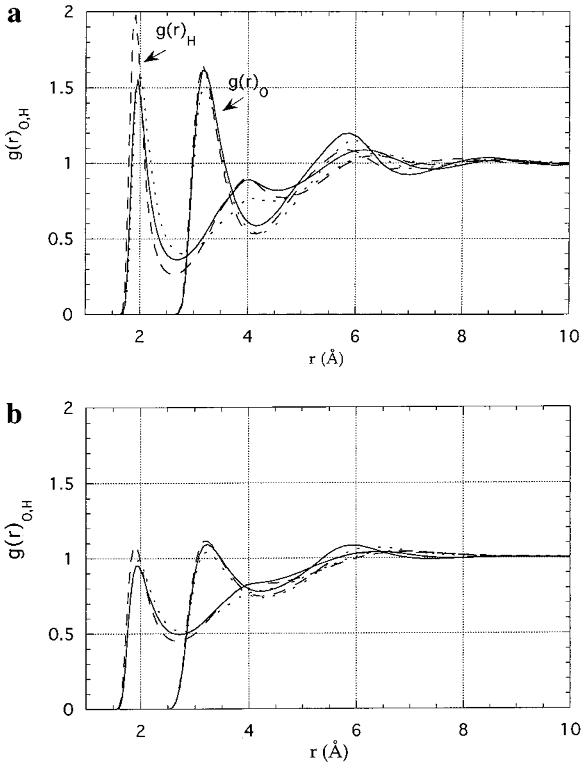

Figure 2. Radial distribution functions of water oxygen (g_{O}) and hydrogen (g_{H}) around the carbonyl oxygen of s-cis MVK (continuous line), endo–cis TS (dotted line), and endo–cis product (dashed line) in AW (a) and in SCW (b).

On the other hand, the estimated $\Delta F^{\ddagger}_{\mathrm{gas}}$ is 54.25 kcal/mol at 298 K for the endo–trans reaction. Compared with the endo–cis reaction, it is higher by 1.77 kcal/mol. However, the activation free energy is reduced by 7.54 kcal/mol from gas phase to AW (Table 1). The value indicates that the endo–trans TS in AW is more stabilized than the endo–cis TS. By the component analysis for the solvation free energy described above, the hydrophobic component is calculated to be −4.99 kcal/mol, indicating that hydrophobic effect for stabilizing the endo–trans TS is essentially equal to the case for the endo–cis TS. The rest of the decrease in the solvation free energy can be attributed to the electrostatic effect. As seen in rdfs for the endo–trans TS (Figure 3a), the hydrogen bonding is clearly enhanced compared to that for the reactant in contrast to the endo–cis case.

The electronic reorganization energy for the endo–trans TS is increased by 1.48 kcal/mol compared to that for the trans MVK. This value is much less than that for the endo–cis reaction. The total contribution of hydrogen-bonding effect including $\Delta E^{\ddagger}_{\mathrm{re}}$ and $\Delta\mu^{\ddagger}$ is estimated as −2.55 kcal/mol. The result indicates that the hydrogen-bonding effect preferentially stabilizes the endo−trans TS more than the endo−cis TS. Therefore, the enhanced hydrogen-bonding effect, coupled with the electronic structure, is certainly an important factor to explain the degree of stabilization of TS, in contrast to the hydrophobic effect, which is almost constant.

The actual TSs would be determined by competition of two energy contributions: the electronic energy of an isolated molecule and the solvation free energy. The endo−trans TS has a greater dipole moment than the endo−cis TS in the gas phase, and the difference in the dipole moment is enlarged in aqueous solution. Due to coupling of the dipole moment with solvent, the endo−trans TS gains greater energy of stabilization by 0.64 kcal/mol compared to the endo−cis TS. As long as the present reaction is concerned, the contribution from the electronic energy seems dominative over that from the solvation free energy. Consequently, the endo−cis TS is more stable than the endo−trans TS, thus the endo−cis reaction preferentially occurs. Those results, however, imply the existence of the Diels−Alder reactions, which may take place preferentially through the endo−trans TS in aqueous solution.

Mechanism of Rate Acceleration in SCW. The activation free energy, $\Delta F^{\ddagger}_{\mathrm{SCW}}$, for the endo−cis reaction in SCW at 873.15 K is found to decrease by 2.71 kcal/mol compared with that in gas phase, $\Delta F^{\ddagger}_{\mathrm{gas}}$. The degree of stabilization in SCW, which is due to a decrease in the solvation free energy, is smaller than that in AW (Table 1). On the basis of the same analysis carried out in the previous section, contribution from the hydrohobic effect is 2.66 kcal/mol, which accounts for an 80% decrease in the solvation free energy in SCW, 3.43 kcal/mol. The remaining 20% of $\Delta\mu^{\ddagger}$ comes from the hydrogen-bonding effect. As seen in Table 1, the increase in the electronic energy due to solvation, or the reorganization energy, in SCW is less than that in AW. In SCW, the electrostatic effects due to hydration become relatively small in comparison with the hydrophobic effect. Comparing the energy contribution of the hydrophobic effect with that of the hydrogen-bonding effect, both contributions reduce with the decreasing density of solvent water: the former reduces almost linearly and the latter drastically. The radial distribution functions in SCW shown in Figure 2b indicate that the hydrogen bonding is reduced drastically compared to that in AW. The result also supports that the hydrogen-bonding effect is largely decreased in SCW. Furthermore, we found that the general trend seen in AW applies to SCW as well; the activation free energy is decreased more in the endo−trans reaction. In SCW, the decrease in the free energy of the endo−trans TS is greater than that of the endo−cis TS by 0.69 kcal/mol (Table 1).

Concerning the electronic-structure change in TS, two different characters are conceivable: the "charge transferred (localized)" and "concerted (delocalized)" characters. In case of the endo−cis reaction, the charge in TS transferred from the diene to the dienophile in the gas phase is $0.1266|e|$, while that in AW is $0.2098|e|$. The results strongly suggest that the contribution of the charge transfer mechanism is largely enhanced by the solvent effect in AW. The increase of the charge transfer in AW is thought to be due to hydrogen bonding around the carbonyl oxygen. The partial charge is found to be localized around the carbonyl group in TS. The charge transfer in SCW is less by $0.0408|e|$ than that in AW. By comparing the reaction in SCW to that in AW, it is found that the solvation effect in SCW becomes weaker than that in AW, although the substantial effect of solvent on the chemical reactions largely remains in SCW. These results seem quite reasonable if one considers that the density of water molecules in SCW is low and that the solvation effect in SCW is less than in AW. Thus, the mechanism of acceleration for the Diels−Alder reaction in SCW is considered to be different from that in AW.

The relative rate constant in AW and in SCW in the corresponding temperature could be roughly estimated from the activation energy on the basis of the simple transition state theory. The following analysis is performed conerning the reaction through the endo−cis TS. Suppose the rate of this reaction simply follows the Arrhenius equation, the relative rate constant is expressed as

$$k(T_1)/k(T_2) = \exp\{-(\Delta F^{\ddagger}(T_1)/RT_1 - \Delta F^{\ddagger}(T_2)/RT_2)\} \quad (5)$$

It should be noted that eq 5 depends on an assumption that the prefactor in the rate expression, $k = \kappa \exp(-\Delta E^{\ddagger}/RT)$, is independent of temperature. The rate constants in AW and in SCW are, respectively, 1.14×10^6 and 4.76 times greater than those in gas phase at the corresponding temperature due to stabilization of the transition state by solvent. The accelerations are caused by the solvent effect, as we mentioned in previous paragraph. The estimated rate of the reaction in gas phase at 873 K is 3.03×10^{19} times greater than that at 298 K. From these values, the relative rate constant in SCW compared to that in AW is estimated to be 1.27×10^{13}; the rate constant in SCW is extremely increased. Although the solvation effect for the rate constant is appearently decreased in SCW, the rate is dramatically increased because of the thermal activation rather than the solvation effect.

Physical Origin of the High Yield in Supercritical Water. To compare the yield of the reaction in SCW to that in AW, the following analysis is performed for the endo−cis reaction. The yields of a reaction in an experimental system are determined not only by the equilibrium constant but also by the solubility of the reactants in solvent, because undissolved molecules cannot participate in the reaction. Therefore, we define an effective yield constant (K_{eff}) by a product of the Henry's law constant of the reactants (K_{H}) and the equilibrium constant of the reaction (K) as

$$K_{\mathrm{eff}} = K_{\mathrm{H}}K \quad (6)$$

The Henry's law constant is obtained from the solvation free energy of the solute molecule dissolved into the solvent from the gas phase (ref).

$$K_{\mathrm{H}} = \exp(-\Delta\mu/RT) \quad (7)$$

The equilibrium constant K is related to the free energy difference between the reactant and the product [$\Delta F^{\phi} = F_{\mathrm{total}}(\mathrm{product}) - F_{\mathrm{total}}(\mathrm{reactants})$] in the solvent,

$$K = \exp(-\Delta F^{\phi}/\mathrm{RT}) \quad (8)$$

As is listed in Table 2, the product in AW is stabilized more than the reactant in terms of the both energy components; [$\Delta\mu^{\phi} = \Delta\mu(\mathrm{product}) - \Delta\mu(\mathrm{reactants})$] and the reorganization energy [$\Delta E^{\phi}_{\mathrm{re}} = \Delta E_{\mathrm{re}}(\mathrm{product}) - \Delta E_{\mathrm{re}}(\mathrm{reactants})$]. In case of the endo−cis product, the decrease in $\Delta\mu^{\phi}$ and $\Delta E^{\phi}_{\mathrm{re}}$ is −5.91 and 0.85 kcal/mol, respectively. From the same analysis carried out in TS, the hydrophobic component of the stabilization for the product is −4.23 kcal/mol, which accounts for 70% of the solvation free energy. Compared to the case of TS (Table 1), changes in the reorganization energy in AW are relatively small, indicating that electrons in the product molecule are delocalized more than those in TS. As seen in Figure 2a, the hydrogen

Table 2. Changes in the Free Energy of the Reaction from Gas Phase to AW ($\Delta\Delta F^{\phi} = \Delta F^{\phi}_{\mathrm{AW}} - \Delta F^{\phi}_{\mathrm{gas}}$) and to SCW ($\Delta\Delta F^{\phi} = \Delta F^{\phi}_{\mathrm{SCW}} - \Delta F^{\phi}_{\mathrm{gas}}$)

	$\Delta\Delta F^{\phi}$ (kcal/mol)	$\Delta\mu^{\phi}$ (kcal/mol)	$\Delta E^{\phi}_{\mathrm{re}}$ (kcal/mol)
		AW	
trans	−3.63	−4.10	0.47
cis	−5.06	−5.91	0.85
		SCW	
trans	−0.87	−0.95	0.08
cis	−1.02	−1.13	0.11

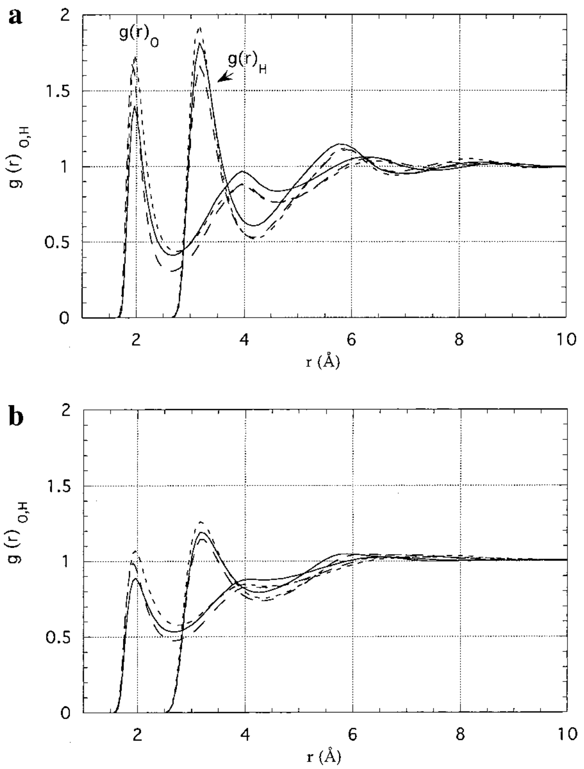

Figure 3. Radial distribution functions of water oxygen (g_{O}) and hydrogen (g_{H}) around the carbonyl oxygen of s-trans MVK (continuous line), endo−trans TS (dotted line), and endo−trans product (dashed line) in AW (a) and in SCW (b).

bonding around the carbonyl oxygen is certainly enhanced in the product. However, the hydrogen-bonding effect gives rise to −0.83 kcal/mol, and it barely contributes to stabilize the product molecule: the hydrogen-bonding effect contributes to the stabilization of the product much less than the hydrophobic effect. The total decrease in the free energy of the reaction in SCW is −1.02 kcal/mol. Solvation effects are weaker in SCW than those in AW: both the decrease in the solvation free energy and the increase in the reorganization energy are less. The hydrophobic component changes from −4.23 to −1.04 kcal/mol, although it accounts for most of $\Delta\mu^{\phi}$ in SCW, −1.13 kcal/mol. The hydrogen-bonding effect is 0.02 kcal/mol and never contributes to the stabilization of the product molecule. As seen in Figure 1, the energies of TS and the product in SCW are greatly increased compared to those in AW. The Diels−Alder reaction is the one in which two molecules are combined into one by creating two C−C bonds. When the reaction proceeds, the entropy of the system becomes smaller as a matter of course. Thus, the Gibbs free energy difference between the isolated reactant and product molecules is enlarged under the high-temperature condition. When the reaction goes through the endo−cis TS only, the equilibrium constant in AW and in SCW is calculated to be 6.27×10^{7} and 0.20, respectively. Therefore, if the yield is determined thoroughly by the equilibrium constant of the reaction, the yield in SCW can never be higher than that in the AW. That is not the case in the experimental results. The solvation free energy of the reactants, CP and MVK, in AW were respectively calculated to be 19.68 and 11.04 kcal/mol, and those in SCW were 25.48 and 20.05 kcal/mol, respectively. Then, K_{H} in SCW is estimated to be 2.08×10^{11} times greater than that in AW, taking corresponding temperatures into account. On the basis of our definition of the effective yield constant, the yield in SCW is approximately 667 times higher than in AW. Our calculation shows that the energetics of the reaction in SCW gives a disadvantage regarding the yield, but the increased solubility of the reactants in solvent provides an advantage that is enough to overwhelm the energetical disadvantage.

Conclusion

In the present paper, we have reported a theoretical study for a Diels−Alder reaction in gas phase, in ambient water, (AW) and in supercritical water (SCW) based on the RISM-SCF/MCSCF method, a combined ab initio electronic structure theory and the statistical mechanics of molecular liquids. We draw the following conclusions from the study. The reaction rate in AW is increased largely in comparison with that in gas phase through reduced activation barrier due to the hydrophobic interaction. The reaction in SCW is accelerated due to increased thermal activation, not by the same cause in AW. The reaction yield is increased dramatically in SCW due to enhanced solubility compared to that in water. Regarding Diels−Alder reactions, stereochemistry is another important issue studied by many authors. It has been observed experimentally that the endo/exo stereoselectivity of products of the reaction becomes much higher in AW than that in organic solvents, and the selectivity disappears in SCW. It will be of great interest to see microscopically why water enhances the stereoselectivity and why it disappears in SCW. Study along this line is in progress in our laboratory.

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