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Supercritical Carbon Dioxide as Reaction Medium: Examination of Its Solvent Effects in the Near-Critical Region

Yutaka Ikushima,* Norio Saito,

Government Industrial Research Institute, Tohoku, Nigatake 4-chome, Miyagino-ku, Sendai 983, Japan

and Masahiko Arai†

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan
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The consequence of the compressible properties of supercritical carbon dioxide on the Diels–Alder reaction between isoprene and methyl acrylate in the solvent is discussed on the basis of IR spectroscopic data. The transition activation volume of the reaction and the excess number of solvent molecules about the reacting species have been thermodynamically determined using the $E_T(30)$ value of supercritical carbon dioxide. They are significantly changed with density in the near-critical region, where the activation volume gets greatest negative and the excess number of solvent molecules are greatly increased. These results strongly suggest the state of aggregation of solvent molecules about the reacting species on the Diels–Alder reaction in the vicinity of the critical point. The relationship between the activated complex–solvent intermolecular forces and the isomer distribution of the Diels–Alder reaction in supercritical carbon dioxide is examined.

Introduction

Considerable attention has recently been focused on the highly compressible properties of supercritical fluids (SCFs) in the near-critical region from theoretical and experimental points of view.[1-7] Eckert and co-workers observed from density measurements as a function of solute concentration that the partial molar volumes of nonvolatile organic solutes such as naphthalene, tetrabromomethane, etc. near the critical points of carbon dioxide and ethylene get very large negative in magnitude, 100 times the solvent's bulk molar volumes.[8,9] This result suggests the state of aggregation (cluster) of solvent molecules about each solute molecule. At present, however, the strength of solute–solvent intermolecular forces concerning the aggregation has not been elucidated at the molecular level.

Spectroscopic methods have been presented as effective methods to measure directly solute–solvent intermolecular forces for dilute solutions. These methods can provide information regarding electronic transitions occurring on a molecular–microscopic level in cybotactic regions about solute molecules,[10,11] and have been recently applied to examine properties of supercritical fluids and solute–solvent intermolecular forces for dilute supercritical solutions as well.[12-15] Yonker et al. measured the Kamlet–Taft π^* solvent polarity/polarizability parameter for SCFs on the basis of solvatochromic shift of the absorption peak maximum of 2-nitroanisole.[16] The π^* solvent parameter is found to be sensitive to fluid density and increases with its density. Kim and Johnston reported that the local densities of supercritical fluids are larger than the bulk densities and suggested the formation of a cluster of solvent molecules about each solute molecule near the critical points.[17] In this way, theoretical interpretations of solvent structure about solute molecule in supercritical fluids have been proposed, but a concrete picture of the importance of solute–solvent intermolecular forces on chemical processes has been scarcely provided.[18] No detailed study has been done on how solvent-dependent processes such as reaction, extraction, separation, etc. would be affected by activities of solvent and solute molecules in SCFs media.

The solvent strength (defined here as transition energy of an indicator molecule measured by spectroscopic method) of SCFs is found to vary widely with both pressure and temperature near the critical region;[16-19] this sensitivity can be applied to the control of chemical reaction processes. A few studies have shown that the use of SCFs as reaction media leads to significant increases in the reaction rates and the variation in product distributions.[20-24] Alexander et al. measured an activation volume of as low as −500 cm^3/mol in the near-critical region for the Diels–Alder reaction between isoprene and maleic anhydride in supercritical carbon dioxide.[22] We have also recently revealed that the Diels–Alder reaction of isoprene and maleic anhydride at infinite dilution in supercritical carbon dioxide follows a two-step mechanism, showing a pressure effect on the reaction rate near the critical point with an in situ study using a high-pressure FT-IR spectroscopy.[25] Furthermore, we previously reported that the product distribution remarkably changes with density in the critical region, where the

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ortho product is formed more favorably than the para product.[25] For the reaction at atmospheric pressure, the para product with the minor steric hindrance is chiefly produced.[26] However, the consequence of the near-critical aggregation phenomena on the reaction mechanism has not been explored in microscopic level.

In the present work, the Diels–Alder reaction between isoprene and methyl acrylate at infinite dilution in supercritical carbon dioxide has been further studied with particular attention to the near-critical region, where significant aggregation would occur and the isomer distribution greatly changes. The transition activation volume of the reaction is thermodynamically determined using the $E_T(30)$ value of supercritical carbon dioxide measured by IR spectroscopic shifts. The excess number of solvent molecules in the cybotactic region about the reacting species is statistically calculated using the difference in the $E_T(30)$ values between the cybotactic and bulk regions. In addition, the relationship between the activated complex–solvent intermolecular forces and the isomer distribution is discussed.

Experimental Section

Details concerning the experimental apparatus of on-line FT-IR system using a stainless steel reactor of volume 16 μL and the procedures used have been described elsewhere.[25,27] Liquid carbon dioxide was charged into a high-pressure syringe pump and compressed to the desired pressures. Pressure control was achieved by a back-pressure regulator and the fluctuations were less than ±0.01 MPa below 20.60 MPa. Then, 0.05 μL of isoprene and 0.05 μL of methyl acrylate were simultaneously injected from injection valves. The reactants reached the cell immediately after the injection and were held in it by stopping the flow. The reaction was conducted at 323 ± 0.1 K and 4.9–20.60 MPa and FT-IR measurements were made at certain intervals during the reaction. The initial concentrations of the reactants in the solvent were below 1%. After the reaction, the cell effluent was sampled and analyzed using gas chromatography.

The uncatalyzed Diels–Alder reaction is a second-order reaction,[28] and the rate constants of the reaction were determined from a least-squares fit of the linear form of integrated expression.[26] The rate constant is expressed in pressure-independent concentration unit such as mole fraction. When pressure-dependent units such as moles/liter are used, the method must be corrected by a term including the compressibility of the solution.[29]

Results and Discussion

1. Characterization of Cybotactic Region about Solute with the $E_T(30)$ Parameter. Solvatochromic methods can provide solute–solvent intermolecular forces in the cybotactic regions about solute molecules based on electronic transitions occurring on a molecular–microscopic level[10,11] and have been recently applied to dilute supercritical solutions. Kim and Johnston presented the density of ethylene in the solute-organized cybotactic region (local region) about phenol blue using solvatochromic scale, E_T, which is defined as the transition energy of phenol blue in a solvent.[17] However, characterization of the cybotactic region about solutes in supercritical carbon dioxide has been scarcely performed in microscopic level.

The transition energy of pyridinium N-phenoxide betaine dye, $E_T(30)$, is one of the solvatochromic parameters used most widely and possesses great advantages.[30-32] The $E_T(30)$ scale is known to correspond to the magnitude of solute–solvent interaction forces.

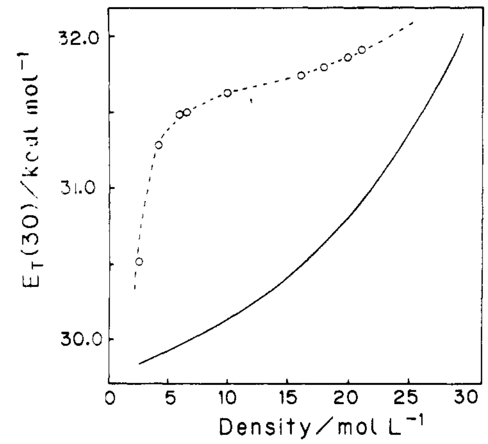

Figure 1. The $E_T(30)$ values in the dye-organized cybotactic (---) and bulk (—) regions of supercritical carbon dioxide as a function of density at 323 K.

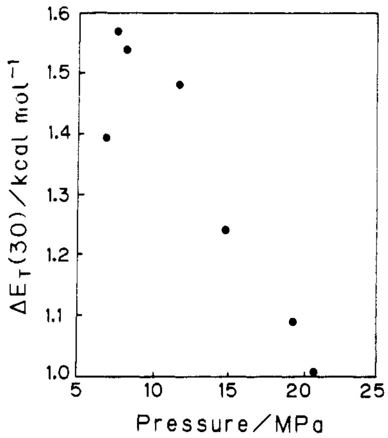

Figure 2. Difference in $E_T(30)$ value between the cybotactic and bulk regions vs pressure at 323 K for carbon dioxide.

Little has been known about the $E_T(30)$ value in the dye-organized cybotactic region in supercritical carbon dioxide, and we have recently estimated the density dependence of the $E_T(30)$ value using the Kamlet–Taft π^* value determined with IR spectroscopic method as well as the Kirkwood function and the Onsager reaction field function.[19] Furthermore, Bekárek et al. reported that the $E_T(30)$ value for the bulk region can be correlated well with solvent dielectric constant, e, and solvent refractive index, n, for 40 non-hydrogen-bonding donor (HBD) aliphatic solvents with a correlation coefficient (r) of 0.96 by[33]

$$E_T(30) = 72.02[f(e)]^2 - 29.16f(e,n^2) + 29.87 \qquad (1)$$

where $f(e)$ is the Kirkwood function $[f(e) = (e-1)/(2e+1)]$ and $f(e,n^2)$ represents the $f(e)\cdot f(n^2)$. Supercritical carbon dioxide is known to be non-HBD solvent,[19] and the $E_T(30)$ value of the bulk supercritical carbon dioxide can be calculated by eq 1. The refractive index and the dielectric constant of supercritical carbon dioxide as a function of temperature and pressure can be determined from the Lorents–Lorenz equation and a virial expansion of the Clausius–Mossotti function with respect to density, respectively, by

$$(n^2-1)/(n^2+2) = A_R d_m + B_R d_m^2 + \ldots \qquad (2)$$

$$(e-1)/(e+2) = A_E d_m + B_E d_m^2 + \ldots \qquad (3)$$

where d_m is the molar density; A_R and B_R the first and second refractivity virial coefficients, respectively; and A_E and B_E the first and second dielectric virial coefficients, respectively.[34,35]

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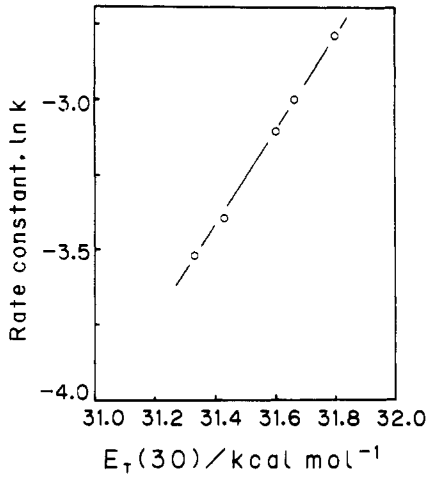

Figure 3. Relationship between the rate constant for the Diels–Alder reaction between isoprene and methyl acrylate and the $E_T(30)$ value of supercritical carbon dioxide at 323 K.

Figure 1 shows the $E_T(30)$ values for the dye-organized cybotactic region measured by the IR method[19] and for the bulk region calculated by eqs 1–3. The former $E_T(30)$ increases greatly as the density increases up to about 10 mol L^{-1} and then it increases only slightly at higher density. The $E_T(30)$ values for the cybotactic region are much higher than those for the bulk in the range of density examined, in particular at density lower than 20 mol L^{-1}. This implies that the solute–solvent interactions in the cybotactic region are even higher than expected from the bulk density. This can be regarded as follows: the local density of solvent molecules surrounding a solute molecule is even larger than the bulk density. This will be discussed in terms of cluster size concept.

Figure 2 gives the difference in the $E_T(30)$ value, $\Delta E_T(30)$, between the cybotactic and bulk regions against pressure. The difference remarkably increases as the compressibility of the solvent increases, and the solute–solvent intermolecular forces in the cybotactic region in carbon dioxide are found to be greatly enhanced near the critical point. The great increase in $\Delta E_T(30)$ would be an indirect evidence for the aggregation of the solvent molecules about solute near the critical point.

2. Estimation of the Transition Activation Volume for the Diels–Alder Reaction in Supercritical Carbon Dioxide. The solvatochromic parameters such as the $E_T(30)$ value have been proved to be satisfactorily applicable to correlate solvent-dependent chemical properties such as equilibria, reaction rates, and spectral absorptions. The $E_T(30)$ value has a good relationship with solvent-dependent process parameters according to eq 4,[36,37] where

$$y = mE_T(30) + n \tag{4}$$

y represents physicochemical properties such as reaction rates and m and n are coefficients. For the Menshutkin reaction between triethylamine and iodoethane,[38] for example, reaction rates in aprotic and dipolar solvents relative to that in hexane are well correlated by $\ln (k/k_0) = 0.248E_T(30) - 6.54$ ($r = 0.920$), where k and k_0 are the rate constants for the solvent considered and the hexane, respectively. The reaction rate increases by a factor of 50 with 15 kcal mol^{-1} increase in $E_T(30)$ value. This result suggests that the transition state of this reaction is more polar than the reactants and is stabilized to a great extent in more polar solvents.[39]

For the Diels–Alder reaction between isoprene and maleic anhydride in supercritical carbon dioxide, it was indirectly proved that the intermediate at the transition state is more polar than the reactants and the reaction rate is increased with an increase in pressure.[25] The Kamlet–Taft π^* value for supercritical carbon dioxide was found to be enhanced with an increase in pressure,[16,19] and the transition state for the Diels–Alder reaction between isoprene and methyl acrylate could be stabilized in the more polar state of supercritical carbon dioxide as well. The $E_T(30)$ value determined using solvatochromic methods can characterize the polarity of solvent in the cybotactic regions about solute molecules as mentioned above, and the $E_T(30)$ value is expected to correlate rate constants for the Diels–Alder reaction between isoprene and methyl acrylate and be applicable to the clarification of intermolecular forces between the activated complex and the solvent.

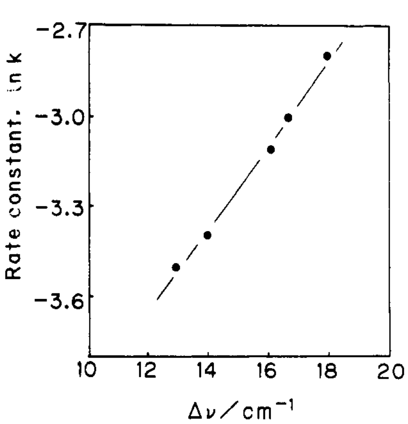

Figure 4. Relationship between $\Delta\nu$ and the rate constant for the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide as a function of pressure at 323 K.

As shown in Figure 3, a good correlation was found to exist for the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide at pressures of 6.9–19.1 MPa and 323 K. The $E_T(30)$ value is linearly related to the logarithm of the overall rate constant, k, of the reaction with $r = 0.9993$.

$$\ln k = 1.364E_T(30) - 46.160 \tag{5}$$

The $E_T(30)$ values of supercritical carbon dioxide at those pressures and temperature were previously estimated.[19] This linear relationship could reflect the great participation of activated complex–solvent intermolecular forces on the reaction rate. In order to investigate the influence in further detail, we examine the relationship between the rate constants of the Diels–Alder reaction and IR spectroscopic shifts of C=O stretching frequency of the reacting species using in situ FT-IR measurements. The degree of the C=O solvatochromic shift directly corresponds to the magnitude of the activated complex–solvent interaction forces in the complex-organized cybotactic region at the transition state. As shown in Figure 4, the rate constant is proportional to the degree of the blue shift, and the transition state is favorably stabilized with increasing polarity of supercritical carbon dioxide.

According to the transition-state theory, a chemical reaction proceeds via a transition state $X^\ddagger$. Consider a simple reaction:

$$A + B \rightleftarrows X^\ddagger \rightarrow \text{product} \tag{6}$$

The quasi-thermodynamic equilibrium assumption is that $X^\ddagger$ is in equilibrium with the reactants. The quasi-equilibrium constant $K^\ddagger$ is defined in terms of activity, a, as

$$K^\ddagger = a_x{}^\ddagger/(a_A a_B) = (\gamma_X{}^\ddagger/\gamma_A\gamma_B)([X]^\ddagger/([A][B])) \tag{7}$$

where γ is activity coefficient and [A] is the concentration of component A. Using the assumption that the reaction rate is proportional to the concentration of the activated complex, the rate constant can be expressed as

$$k = s(k_BT/h)K^\ddagger(\gamma_X{}^\ddagger/\gamma_A\gamma_B) \tag{8}$$

where k_B is Boltzmann's constant and h is Planck's constant. s is the transmission coefficient and usually assumed equal to unity. The connection between the quasi-thermodynamic equilibrium constant and the activation Gibbs free energy, $\Delta G^\ddagger$, is made

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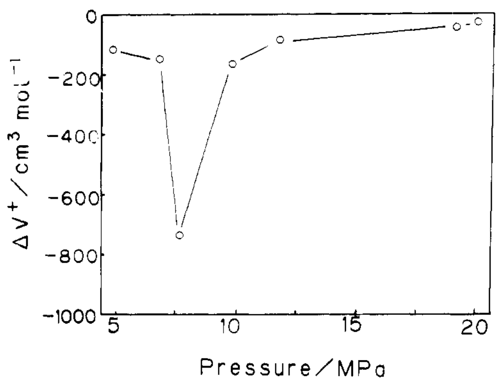

Figure 5. Relationship between the transition activation volume of the Diels–Alder reaction between isoprene and methyl acrylate and pressure at 323 K.

through the standard relation from equilibrium thermodynamics as follows.

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{9}$$

The general definition of the activation volume for reactions is

$$\Delta V^{\ddagger} = V_{\mathrm{M}} - \sum u_i V_i \tag{10}$$

where V_{M} is the partial molar volume of activated complex, V_i is the partial molar volume of reactant i, and u_i is the stoichiometric coefficient of reactant i. From thermodynamic relations the following equation is obtained as

$$(\partial \Delta G^{\ddagger}/\partial P)_T = \Delta V^{\ddagger} \tag{11}$$

and then, from eqs 8, 9, and 11, the following relation is given,

$$(\partial \ln k_x/\partial P)_T = -\Delta V^{\ddagger}/RT \tag{12}$$

where k_x is the rate constant on the mole fraction scale, R is the gas constant, and T is the temperature.

From eqs 5 and 12, the transition activation volume for the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide is estimated by

$$\Delta V^{\ddagger} = 1.364RT(\partial E_{\mathrm{T}}(30)/\partial d)_T d\beta \tag{13}$$

where d is the density of supercritical carbon dioxide and β (= $-(\partial V/\partial P)_T/V$) is the isothermal compressibility. Figure 5 shows the transition activation volume of the Diels–Alder reaction in supercritical carbon dioxide as a function of pressure at 323 K in supercritical carbon dioxide. It was found that the volume very greatly decreased and became much negative in the neighborhood of the critical point. This result strongly suggests that great intermolecular forces between the activated complex and solvent molecules occur in the complex-organized cybotactic region as the compressibility increases near the critical point, where aggregation could be formed in the solvation shell about the activated complex.

3. Estimation of the Cluster Size about the Activated Complex. The Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide has the strong possibility of the aggregation of solvent molecules about the activated complex in the near-critical region. We will examine the aggregation phenomenon through the estimation of the excess number of aggregating molecules at the transition state, which is called the cluster size.

Debenedetti derived the relation between the partial molar volume of solute and the cluster size based on the application of fluctuation theories[40] and calculated the cluster size of solutes such as naphthalene and tetrabromomethane in dilute supercritical mixtures.[41] The cluster size in dilute supercritical mixtures is increased as the compressibility of solvent increases.

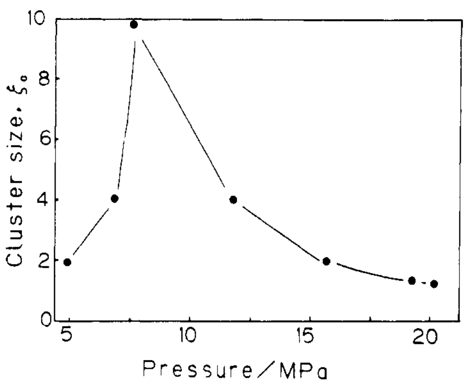

Figure 6. Cluster size for the Diels–Alder reaction between isoprene and methyl acrylate in carbon dioxide as a function of pressure at 323 K.

SCHEME I

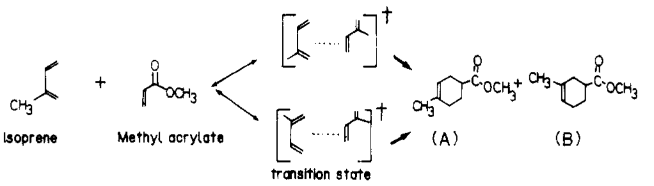

TABLE I: Isomer Distribution for the Diels–Alder Reaction between Isoprene and Methyl Acrylate

press., MPa	temp, K	distribution, % A	distribution, % B
atmospheric	308	99.5	0.5
atmospheric	313	99.5	0.5
atmospheric	320	99.6	0.5
atmospheric	333	98.3	1.7
atmospheric	423	99.6	0.4
4.90	323	67.1	32.9
7.45	323	38.9	61.1
11.77	323	71.3	28.7
15.69	323	75.5	24.5
19.12	323	81.0	19.0
20.60	323	85.9	14.1

According to Debenedetti,[41] the cluster size at infinite dilution can be calculated by

$$\xi_{\mathrm{c}} = dN_{\mathrm{av}}k_{\mathrm{B}}T\beta - \bar{V}_1^{\infty} dN_{\mathrm{av}} \tag{14}$$

where ξ_{c} is the cluster size and N_{av} is Avogadro's number. $\bar{V}_1^{\infty}$ is the partial molar volume of solute. In the present Diels–Alder reaction, $\bar{V}_1^{\infty} = V_{\mathrm{m}} = \Delta V^{\ddagger} + \sum u_i V_i$ from eq 10. We assume that the partial molar volumes of the reactants even at supercritical conditions are less comparable to the volume of $\Delta V^{\ddagger}$ observed, and we calculate the cluster size about the complex by using $\Delta V^{\ddagger}$ for $\bar{V}_1^{\infty}$ in eq 14. The transition activation volume of the present Diels–Alder reaction in supercritical carbon dioxide at infinite dilution has been determined using the $E_{\mathrm{T}}(30)$ value as described above.

Figure 6 shows the cluster size in the Diels–Alder reaction as a function of pressure at 323 K. The magnitude rapidly increases in the near-critical region. The values near the critical point reach ca. 10 times those at higher pressures above 15 MPa. The cluster size calculation for tetrabromomethane–carbon dioxide system by Debenedetti reaches above 100 in the critical region,[41] larger than our values, but the pressure dependence is very similar to that of Figure 6. In addition, the pressure dependence of the transition activation volume of the Diels–Alder reaction determined above is indicated in Figure 5. As shown in Figures 5 and 6, the relationships of the cluster size and of the activation volume with pressure are very analogous. That is, the great activated complex–solvent intermolecular forces due to the aggregations of solvent molecules about the complexes are found to occur in the

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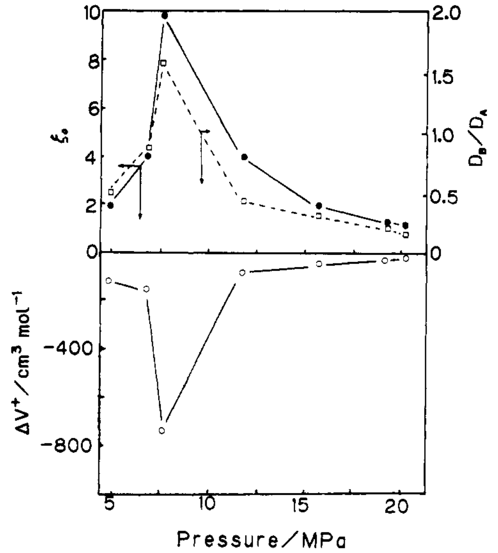

Figure 7. Activation volume, the cluster size, and the isomer distribution ratio as a function of pressure at 323 K.

Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide.

4. Isomer Distribution of the Diels–Alder Reaction in Supercritical Carbon Dioxide. Isomer distribution of the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide are given in Table I.[26] As shown in Scheme I, the two cyclohexene isomers, methyl 4-methyl-3-cyclohexene-1-carboxylate (A) and methyl 3-methyl-3-cyclohexene-1-carboxylate (B) were produced. The chief product is (A) at atmospheric pressure as shown in Table I. The low ratio D_B/D_A at atmopsheric pressure is understandable because the para product (A) is more sterically stable than the meta product (B). However, in supercritical carbon dioxide medium, the isomer distribution varies with pressure. The distribution ratio D_B/D_A is the greatest in the critical region, where supercritical carbon dioxide favors the production of (B). The distribution is density-dependent and such a considerable variation is of great significance.

Figure 7 represents the pressure dependence of the isomer distribution ratio (D_B/D_A) as well as transition activation volume and cluster size at 323 K. Their relationships with respect to pressure are very similar, strongly supporting the participation of great complex–solvent intermolecular forces on the isomer distribution. When the products are formed from activated complexes between isoprene and methyl acrylate near the critical point, the aggregation of the solvent molecules in the critical region would depress the motion of isoprene species, due to the steric constraints by the neighboring solvent molecules. Probably the motion of isoprene species leading to the formation of the sterically stable para product is hindered by such steric constraints, and consequently the ratio meta/para product (D_B/D_A) would significantly increase.

Conclusion

The consequence of the compressible properties of supercritical carbon dioxide on the Diels–Alder reaction between isoprene and methyl acrylate has been explored in microscopic level. The transition activation volume of the reaction was thermodynamically determined using the $E_T(30)$ value of supercritical carbon dioxide measured with IR spectroscopic shift. The activation volume was most negative near the critical point. Furthermore, the excess number of solvent molecules about the reacting species (defined as the cluster size) is statistically calculated using the difference in the $E_T(30)$ value between the cybotactic and bulk regions. The cluster size is significantly increased near the critical point as the compressibility of the solvent is enhanced. The pressure dependence of the isomer distribution ratio is very similar to those of transition activation volume and cluster size, and the change in the isomer distribution in the critical region could be attributed to the aggregation of the solvent molecules leading to the steric constraints to the reacting species.

Note Added in Proof. Very recently, pertinent works have been presented at the Symposium on Spectroscopic Investigations in Supercritical Fluids of 1991 American Chemical Society National Meeting in Atlanta. The group of Eckert and Debenedetti have made experimental and theoretical approaches using fluorescence spectroscopy and a molecular dynamic model to the study of local density augmentation in supercritical fluids. Johnston and coworkers have discussed the effects of pressure and solute-solute clustering on the rate and product distribution for some reactions in supercritical fluids. The group of Bright have studied solvation kinetics in supercritical fluids with dynamic fluorescence spectroscopy. There have been presented some other works investigating the properties of supercritical fluids on molecular level with spectroscopic techniques.

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Registry No. $CH_2{=}C(CH_3)CH{=}CH_2$, 78-79-5; $CH_2{=}CHCO_2Me$, 96-33-3; CO_2, 124-38-9.