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Implications of a Transition State in a Diels–Alder Reaction in Supercritical Carbon Dioxide

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Synopsis. For the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide at 323 K, the solubility parameter of the activated complex was determined as a function of the pressure, ranging from 7 to 20 MPa, in order to study the nature of the complex and the effect of the solvent on the reaction. The relation between the solubility parameter and the $E_T(30)$-scale was examined as well.

Supercritical fluids (SCFs) have recently been attracting much attention for controlling chemical reaction processes.[1,2] Several studies show that the use of SCFs as reaction media leads to significant increases in the reaction rates and the variations in the product distributions.[3—5] Although solvent effects on the chemical reactions in SCFs were previously reported in several articles,[6,7] the effects have been only little discussed regarding the microscopic levels.

In a previous study,[8] we considered the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide (SC-CO_2) at changing pressures and a constant temperature of 323 K. It was found that the rate of the reaction changes drastically with the pressure at around the critical point of SC-CO_2. Moreover, the activation volume was estimated to have a markedly large negative value near to the critical point.[9] We therefore assumed that strong interactions occur between an activated complex and solvent molecules, and that this is closely related to the great change in the product distribution observed at that pressure region. The nature of the SC-CO_2 solvent was previously evaluated using an $E_T(30)$ value corresponding to the magnitude of the polar solvent–solute interactions.[9] The observed pressure effect was discussed in terms of the relation between the $E_T(30)$ parameter and the activation volume of the reaction.

For a further study it would be informative to evaluate the solvent properties of SC-CO_2 using various other parameters. The solubility parameter concept was thus applied in order to further study the same Diels–Alder reaction in SC-CO_2 in the present work. The solubility parameter is useful for evaluating the solvent properties of SC-CO_2, as well as the mutual affinity among the chemical species present in the reaction mixture, i.e., the solvent (SC-CO_2), the reactants (isoprene and methyl acrylate), and the activated complex. We have tried to estimate the value of the solubility parameter for the activated complex through transition-state theory. We also examined its pressure dependence, and compared it with those of the solvent and the reactants in order to inspect the SC-CO_2 solvent effect as well as the nature of the activated complex. In addition, the relation between the solubility parameter of the activated complex and the $E_T(30)$ value of the solvent was examined.

Experimental

Details concerning the experimental apparatus and the procedures have been described elsewhere.[10,11] Liquid carbon dioxide was charged into a high-pressure syringe pump and then compressed to the desired pressures. Pressure control was achieved by a back-pressure regulator; the fluctuations were less than ±0.01 MPa at below 20 MPa. The Diels–Alder reaction between isoprene and methyl acrylate was conducted at 323±0.1 K and 6.86—19.12 MPa. The initial concentrations of the reactants in the solvent were below 1%. After the reaction, the effluent was sampled and analyzed using gas chromatography.

Calculation of Solubility Parameter

According to transition-state theory, a chemical reaction proceeds via a transition state with an activated complex **X**, which is assumed to be in equilibrium with the reactants. Now consider such a simple reaction as the Diels–Alder reaction concerned in the present work:

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathbf{X} \rightarrow \text{product}. \tag{1}$$

Since the reaction rate is assumed to be proportional to the concentration of X, the rate constant (k) can be expressed as

$$k = s(k_B T/h)K_a(\gamma_A\gamma_B/\gamma_X) = k_o(\gamma_A\gamma_B/\gamma_X), \tag{2}$$

where k is the overall rate constant, k_B Boltzmann's constant, h Planck's constant, T the absolute temperature, K_a the equilibrium constant, γ the activity coefficient, and k_o the reaction rate constant in an ideal solution. s is the transition coefficient, and is usually assumed to be unity.

To consider the solution properties of the reaction mixture, we invoke the solubility parameter concept. The solubility parameter (δ_i) of species i is associated with its activity coefficient (γ_i) as follows:

$$RT\ \ln\gamma_i = V_i(\delta_i - \delta_M)^2, \tag{3}$$

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where V_i is the molar volume of solute i, R the gas constant, and δ_{M} the solubility parameter of the mixture. For the reaction of (1), Eqs. 2 and 3 give

$$RT\ \ln(k/k_{\circ}) = V_{\mathrm{A}}(\delta_{\mathrm{A}}-\delta_{\mathrm{M}})^2 + V_{\mathrm{B}}(\delta_{\mathrm{B}}-\delta_{\mathrm{M}})^2 - V_{\mathrm{X}}(\delta_{\mathrm{X}}-\delta_{\mathrm{M}})^2. \tag{4}$$

The solubility parameter of the mixture (δ_{M}) is estimated by a simple mixing rule:[12,13]

$$\delta_{\mathrm{M}} = \sum \phi_i \delta_i, \tag{5}$$

where

$$\phi_i = x_i V_i / \sum x_j V_j. \tag{6}$$

Here, ϕ_i is the volume fraction of solute i.

The solubility parameter and molar volume of SC-CO_2 significantly change with pressure, as way reported previously,[14] while those of the reactants, isoprene and methyl acrylate are assumed to be pressure-independent. The rate constant and the molar volume of the activated complex of the Diels–Alder reaction between them were previously determined at different pressures.[8,9] The rate constant in an ideal reference solvent can be estimated from the following linear relationship with the $E_{\mathrm{T}}(30)$-value with a correlation coefficient r=0.9993:[9]

$$\ln k = 1.364\ E_{\mathrm{T}}(30) - 46.160. \tag{7}$$

Using the $E_{\mathrm{T}}(30)$ value at low density at which the solvent–solute interactions are assumed to be low, $k_{\circ}$ may be estimated from the above equation; an extrapolation of the $E_{\mathrm{T}}(30)$ vs. density plot[9] to the intercept yields an $E_{\mathrm{T}}(30)$ value of 28.4 kcal mol^{-1}, from which $\ln k_{\circ}$ is determined to be -7.40.

The value of δ_{X} was determined using Eqs. 4, 5, and 6. Of several quantities included in these equations, the values of V_{A}, V_{B}, δ_{A}, δ_{B}, and $k_{\circ}$ are known and assumed to be pressure-independent, and those of k and V_{x} have been experimentally obtained as a function of the pressure. Thus, using these quantities, the value of δ_{X} was determined as a function of the pressure.

Results and Discussion

Figure 1 shows the solubility parameters (δ_{X} and δ_{CO_2}) of the activated complex and SC-CO_2 as a function of the pressure. The δ_{X} increases greatly with pressure near to the critical point, while it increases only slightly at higher pressures. Although it is similar to δ_{CO_2} at 7 MPa, it becomes much greater than δ_{CO_2} as the pressure increases. From these results, we think that the influence of the solvent on the activated complex is stronger near to the critical point, and is more pronounced than expected from the pressure-dependence of δ_{CO_2}. Furthermore, we can point out that when the pressure increases up to the critical point δ_{X} becomes closer to the solubility parameters of the reactants: 7.2 for isoprene and 8.9 (cal$^{1/2}$ cm$^{-3/2}$) for methyl acrylate.[15] This suggests that the state of the activated complex becomes more similar to that of the reactants, so that the energy needed for the formation of a complex becomes smaller near to the critical point; in other words, the complex is easier to form, resulting in an enhancement of the reaction rate.

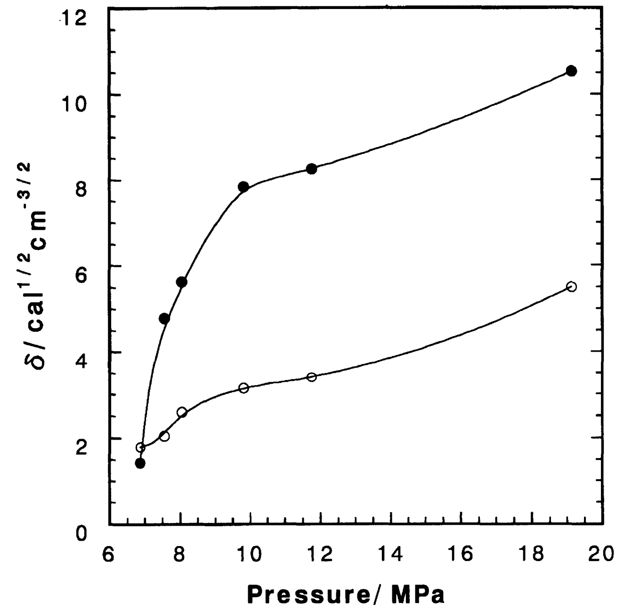

Fig. 1. Pressure-dependence of the δ_{CO_2}-value (○) and the δ_{X}-value (●) for the Diels–Alder reaction between isoprene and methyl acrylate in SC-CO_2 at 323 K.

We examined the relation between δ_{X} and the $E_{\mathrm{T}}(30)$ scale, which is known to correspond to the magnitude of solute-solvent interactions.[16—18] Figure 2 depicts the relationship between the $\delta_{\mathrm{X}}{}^2$ values and the $E_{\mathrm{T}}(30)$ values of SC-CO_2 at pressure of 6.86—19.12 MPa and 323 K. We obtained a good linear relationship between

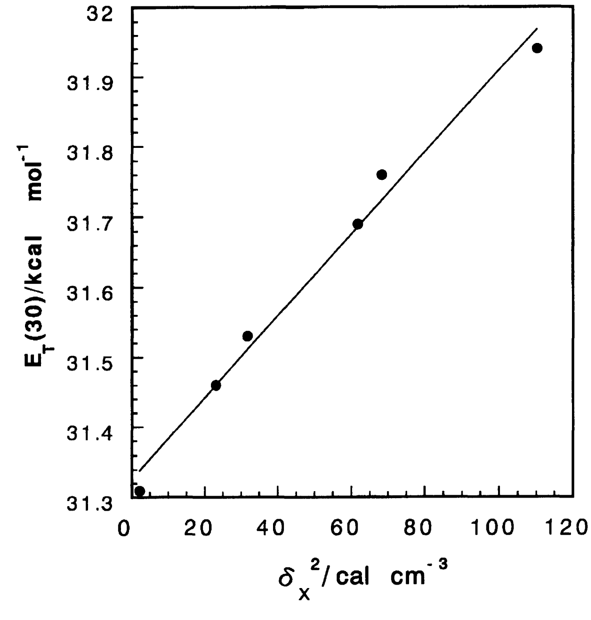

Fig. 2. Relationship between the $\delta_{\mathrm{X}}{}^2$ and the $E_{\mathrm{T}}(30)$-value of SC-CO_2 at 323 K.

them,

$$E_T(30) = 5.832 \times 10^{-3}\delta_X{}^2 + 31.327, \qquad (8)$$

which has a correlation coefficient of $r=0.9935$. Since an excellent straight-line relationship exists between the rate constant (k) and the $E_T(30)$-value for SC-CO$_2$ (Eq. 7), the following relationship between k and $\delta_X{}^2$ is obtained from Eqs. 7 and 8:

$$\ln k = 7.955 \times 10^{-3}\delta_X{}^2 - 3.430. \qquad (9)$$

This linear relationship between $\ln k$ and $\delta_X{}^2$ could reflect a great participation of activated complex–solvent intermolecular forces on the reaction rate for the Diels–Alder reaction in SC-CO$_2$.

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