Kinetics of Isoprene-Maleic Anhydride Diels-Alder Reaction in Supercritical Carbon Dioxide

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Kinetics of Isoprene-Maleic Anhydride Diels-Alder Reaction in Supercritical Carbon Dioxide

by

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(Received May 28, 2004)

Abstract

The rate constants for the Diels-Alder reaction of isoprene with maleic anhydride in supercritical carbon dioxide were measured. The temperatures of the measurement were at 308.2, 313.2 and 318.2 K and the pressure range was from 7.5 to 14.1 MPa. A batch reactor used was connected to the Fourier transform infrared (FT-IR) spectroscopy, so that the amount of product can be measured without sampling. The concentrations of product were measured for about 30 to 40 hours at interval of several hours. The reaction rate constants were determined based on the second order reaction relationship. The reaction rate constants at high pressure region coincide with the literature data. The rate constants near the critical pressure of carbon dioxide are several times higher than those in high pressure region at each temperature. It is considered that reaction rate enhancement near the critical pressure is resulted from the local composition enhancement due to density fluctuation because molecular collision would be more frequently. The rate constants obtained were correlated using the transition-state theory coupled with a local composition model by using the Peng-Robinson (PR) equation of state. The correlated results showed a good agreement with the experimental results.

Keywords: Supercritical carbon dioxide, Diels-Alder reaction, Reaction rate, Critical region

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1. Introduction

Supercritical fluid technology has received much attention in many fields. To date, it has been actively applied and used commercially in extraction, fractionation and purification processes. Particularly, supercritical carbon dioxide (critical pressure p_c = 7.38 MPa and critical temperature T_c = 304.2 K) is often used because it can be used under relatively mild condition. Recently, it has been recognized that supercritical fluids offer unique environment for reaction processes and also provide advantages for carrying out chemical reactions (Savage *et al.*, 1995). Furthermore, the enhanced reaction rate can be expected in the vicinity of critical point. The authors selected the Diels-Alder reaction as a model reaction to examine the reaction mechanism in the vicinity of the critical point. The following Diels-Alder reaction of isoprene with maleic anhydride in supercritical carbon dioxide was considered.

$$\text{(reaction scheme)} \tag{1}$$
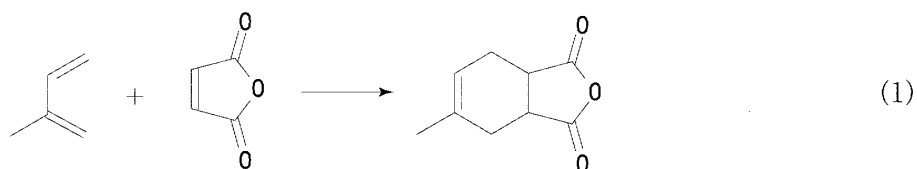
This reaction is suitable for fundamental studies because it is a well-characterized reaction system with no significant side reactions. The rate constants obtained were correlated by the transition-state theory coupled with a local composition model.
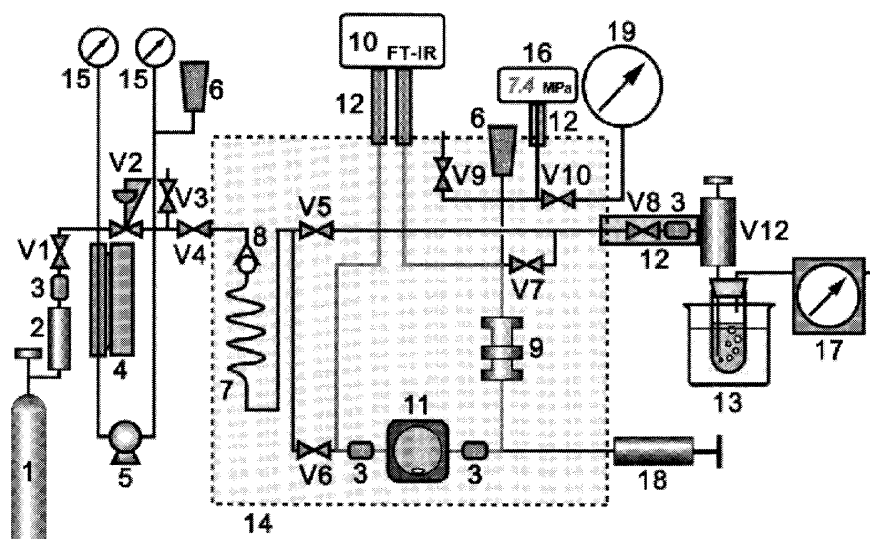
2. Experimental

2.1 Materials

Reagent-grade isoprene (more than 95.0 % supplied by Wako Pure Chem. Ind.) and reagant-grade maleic anhydride (more than 99.0 % supplied by Wako Pure Chem. Ind.) were used. High-purity carbon dioxide (more than 99.9 % supplied by Sumitomo Seika Co.) was used as received. High-purity nitrogen (more than 99.9 % supplied by Sumitomo Seika Co.) was used as purge gas.

2.2 Apparatus

A conventional batch-type apparatus was constructed to measure the rate constants of isoprene-maleic anhydride Diels-Alder reaction. The schematic diagram of the apparatus is shown in **Fig. 1**. The apparatus consisted of a gas cylinder (1), a cooling unit (4), a feed pump (5), a preheating coil (7), a circulation pump (9), a water bath (14: controlled within ± 0.1 K), a digital pressure meter (16: HPO precision transducer, Dresser Industries Inc. Heise Plant), an injector (18), a precision Bourdon gauge (19: NKS type, Nagano Keiki Co.), and a back pressure regulator (V2). A reaction cell (11: Taiatsu Techno Co.) was made of SUS316, and equipped with two sapphire windows. The inner diameter, length, and volume of the cell were 18.0 mm, 102.2 mm, and 26.0 mL, respectively. A FT-IR (10: Fourier transform infrared: FTIR-8300, Shimadzu Co.) spectroscope was equipped with a MCT (mercury-cadmium-telluride) detector and a high-pressure optical cell (Shimadzu Co.). The optical path length of the optical cell was 5.0 mm. The windows of the optical cell were made of ZnSe. The diameter and thickness were 8.0 mm, respectively. The temperature of the

1. Gas cylinder
2. Dryer
3. Filter
4. Cooling unit
5. Feed pump
6. Safety valve
7. Preheating coil
8. Check valve
9. Circulation pump
10. FT-IR
11. Cell with glass window

12. Flexible heater
13. Trap
14. Water bath
15. Pressure meter
16. Digital pressure meter
17. Flow meter
18. Injector
V2. Back pressure regulator
V12. Expansion valve
V1, V3-V10. Stop valve

Fig. 1 Experimental apparatus for measurement of reaction rate in supercritical carbon dioxide.

optical cell was maintained by water pumped from the water bath (14). The FT-IR was connected with the reactor directly. The IR spectra of product can be measured without sampling.

2.3 Procedure

The rate constants of the Diels-Alder reaction were measured at 308.2 K under 7.5-14.1 MPa, at 313.2 K under 8.0-14.1 MPa, and at 318.2 K under 10.0-14.1 MPa. The experiment was carried out as follows. Carbon dioxide supplied from the gas cylinder (1) was liquefied through the cooling unit (4) and directed to the feed pump (5). The back pressure regulator (V2) was used to maintain a constant pressure inside the system. The liquefied carbon dioxide was sent to the preheating coil (7), and it became a supercritical fluid. The valve (V6) was opened and supercritical carbon dioxide was introduced to a fluid circulation part. The part consisted of the circulation pump (9), the cell with sapphire windows (11), and the FT-IR spectroscope (10). The pressure of the circulation part was measured by the digital pressure meter (16) and the precision Bourdon gauge (19). The uncertainty on pressure measurements was estimated to be less than ±0.025 MPa. The circulation pump (9) was used to mix a supercritical fluid in the circulation part. The volume of the circulation part was 0.109 L.

A known amount of maleic anhydride was placed in the cell (11). Air in the cell was purged with carbon dioxide under atmospheric pressure. Pressurized carbon dioxide was then charged into the cell, and the pressure was monitored by the digital pressure meter (16).

The pressure in the cell was regulated to experimental pressure with additional carbon dioxide under experimental temperature. When maleic anhydride was dissolved in carbon dioxide, a known amount of isoprene was added into the cell from the injector (18). Every 0.5 - 4.0 h, the FT-IR spectroscope (10) purged with dry nitrogen was used to obtain all IR spectra. The IR spectra were measured at 1 cm^{-1} wavenumber resolution to obtain the desired signal-to-noise ratio. The molarities of product were determined by the absorption at 1171 cm^{-1}. The reaction was carried out in a single phase throughout the reaction which was confirmed by observation through the sapphire windows of the reaction cell (11).

3. Results and discussion

Based on the second-order reaction relationship, the rate constant k_c is given by

$$k_c t = \frac{1}{(C_{10} - C_{20})} \ln \frac{C_{20}(C_{10} - C_4)}{C_{10}(C_{20} - C_4)} \qquad (2)$$

where C_{10} and C_{20} are the initial molarity of maleic anhydride (1) and isoprene (2), respectively. C_4 is the molarity of the product (4) and t is the reaction time. The right hand side of Eq.(2) was plotted against t and the value of k_c was determined as the slope.

The Diels-Alder reaction rate constants at 308.2, 313.2 and 318.2 K in supercritical carbon dioxide are presented in **Table 1** and **Fig. 2**. As shown in **Table 1**, the rate constants at the same pressure near the critical point were not the same values. The main reason of the results would be the dramatical density change with slight change of pressure, because the density fluctuations of reaction mixtures become large near its critical point. The uncertainty on pressure mearurements of the present apparatus was estimated to be less than ± 0.025 MPa. It was difficult to regulate the same experimental pressure near the critical point. The results reported by Alexander (1985), and Paulaitis and Alexander (1987) are also plotted in **Fig. 2**. The present data are in good agreement with the literature data in the pressure range higher than 7.8 MPa at 308.2 and 318.2 K. As a result, the soundless of the method and the performance of the apparatus were verified. As shown in **Fig. 2**, the rate constants have a tendency to increase near the critical pressure of carbon dioxide. The increases in rate constants near critical pressure of carbon dioxide are also investigated for the other reaction systems by Thompson *et al.* (1999) for the Diels-Alder reaction of anthracene with 4-phenyl-1,2,4-triazoline-3,5-dione and by Ellington *et al.*(1994) for the esterification of phtalic anhydride with methanol. **Figure 3** shows the rate constants for the three reaction systems. The pressure dependences of rate constants near the critical pressure are very similar even if the reaction systems are different.

Table 1 Rate constants for isoprene-maleic anhydride Diels-Alder reaction in supercritical carbon dioxide.

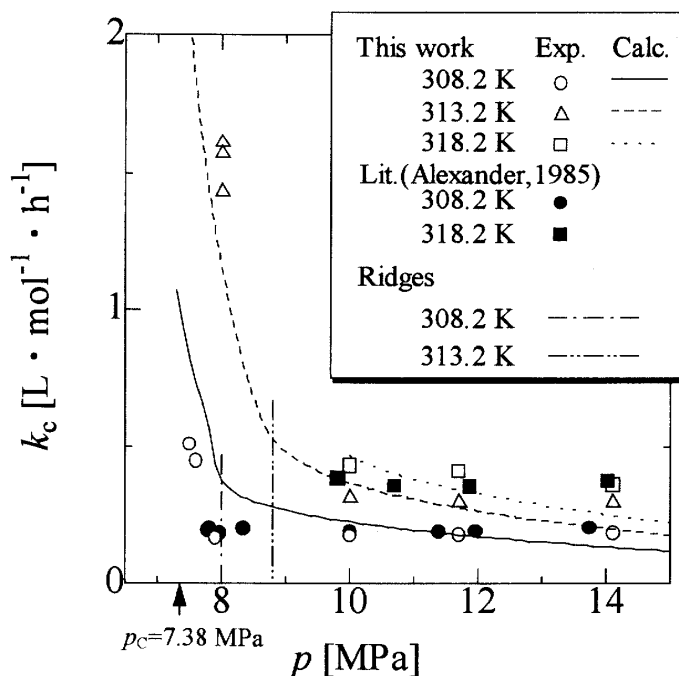| 308.2 K		313.2 K		318.2 K	
p[MPa]	k_c[L·mol^{-1}·h^{-1}]	p[MPa]	k_c[L·mol^{-1}·h^{-1}]	p[MPa]	k_c[L·mol^{-1}·h^{-1}]
7.5	0.51	8.0	1.61	10.0	0.43
7.6	0.43	8.0	1.57	11.7	0.41
8.0	0.17	8.0	1.43	14.1	0.36
10.0	0.18	10.0	0.32		
11.7	0.18	11.7	0.29		
14.1	0.18	14.1	0.30		

Fig. 2   Rate constants for isoprene-maleic anhydride Diels-Alder
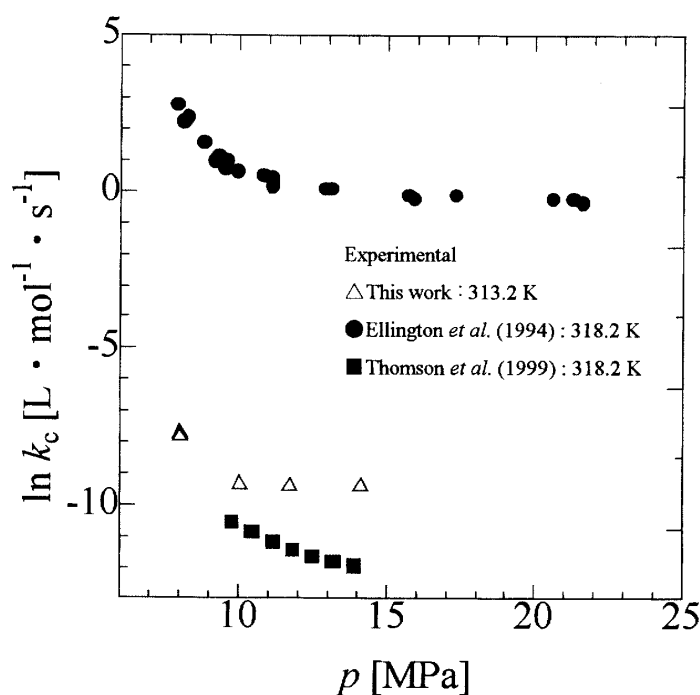reaction in supercritical carbon dioxide.

Fig. 3   Rate constants for the three reaction systems in
supercritical carbon dioxide.

Nishikawa and Tanaka (1995) measured the density fluctuations of supercritical carbon dioxide in the vicinity of critical point. The density fluctuations were found to form a ridge along the extension of coexistence curve of gas and liquid to the supercritical region as shown in **Fig. 4**. The dotted curves represent the contour line of the density fluctuation. The number on the lines represent their values. The ridge shown in **Fig. 4** is the locus of the points where the values of the density fluctuation are at their maximum in isothermal change. The
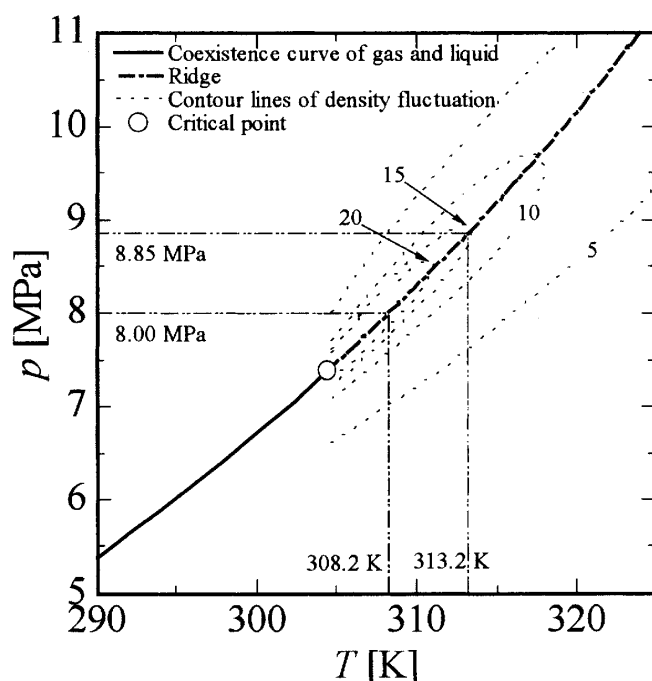
Fig. 4 Phase diagram and contour lines of density fluctuation for carbon dioxide near the critical point (Nishikawa and Tanaka, 1995).

ridges are 8.00 and 8.85 MPa at 308.2 and 313.2 K, respectively. These values are plotted in **Fig. 2**. As shown **Fig. 2**, the points at the beginning of reaction rate enhancements correspond to the ridges. Nishikawa and Morita (2000) also reported that the rate constants of various chemical reaction in supercritical fluids show singular behavior on the ridge. The singularity means maximum, minimum, or inflection point of the rate constants and depends on particular reaction. Ellington *et al.* (1994) attribute the reaction enhancement to the effect of local composition. Local composition would be higher in the high density fluctuation region. In higher local composition region, molecular collisions and interactions seem more frequently. This may be one of the reasons why the reaction rates increase in the vicinity of the critical point.

4. Correlation

By using the transition-state theory (Weinstein *et al.*, 1996), an expression for the pressure dependence of reaction rate constants has been derived as follows (Toh *et al.*, 2001).

$$k_c{}^{\mathrm{TS}}(T, p) = \left(\frac{T}{T^*}\right)^2 \exp\left[-\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right) \right] \frac{(\phi_1 \phi_2/\phi_4{}^{\ddagger})_{T,p}}{(\phi_1 \phi_2/\phi_4{}^{\ddagger})_{T^*,p^*}} \left(\frac{Z_{T,p}}{Z_{T^*,p^*}}\right) k_c{}^{\mathrm{TS}}(T^*, p^*) \tag{3}$$

where $k_c{}^{\mathrm{TS}}(T, p)$ is the reaction rate constant based on the transition-state theory and p^* and T^* are the arbitrary reference pressure and temperature, respectively. In this study, $p^* = 11.7$ MPa and $T^* = 308.2$ K were chosen. The enthalpy of activation $\Delta H^{\ddagger}$ can be evaluated by Arrhenius plot of the experimental data. The value was determined as 65.55 kJ·mol⁻¹. The fugacity coefficients ϕ_i (1: maleic anhydride, 2: isoprene, 4: activated complex) and the compressibility factor Z were calculated by the following Peng-Robinson equation of state (Peng and Robinson, 1976) with the conventional mixing rules.

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+b(v-b)} \tag{4}$$

where

$$a = 0.45724 R^2 T_c^2 / p_c \tag{5}$$

$$b = 0.07780 R T_c / p_c \tag{6}$$

$$\alpha = [1 + m\{1 - (T/T_c)^{0.5}\}]^2 \tag{7}$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{8}$$

and for a mixture of maleic anhydride (1) + isoprene (2) + carbon dioxide (3) + activated complex approximated by product (4).

$$(a\alpha)_m = \sum_i \sum_j y_i y_j (a\alpha)_{ij}, \quad (a\alpha)_{ij} = \sqrt{(a\alpha)_{ii}(a\alpha)_{jj}} \tag{9}$$

$$b_m = \sum_i y_i b_i \tag{10}$$

According to progress of the reaction, the compositions of reactants should be changed. However, the composition changes give no significant effect on the calculated results because the amounts of reactants are extremely small in this experiment. **Table 2** shows the critical constants p_c, T_c and the acentric factor ω. The critical constants and the acentric factors for maleic anhydride and activated complex (approximated by the product) were estimated by the Lydersen's group contribution method (Reid *et al.*, 1987). According to Ellington *et al.* (1994), $k_c^{TS}(T, p)$ was modified as follows by using local properties, because the local compositions are expected to be much different from the bulk compositions near the critical point. It is noted, in this experimental condition, that the concentration of isoprene is much higher than that of maleic anhydride and therefore the local mole fraction of isoprene around maleic anhydride molecules becomes larger than bulk phase mole fraction.

$$k_c(T, p) = k_c^{TS}(T, p) \left[\frac{\rho^{local}}{\rho} \right] \left[\frac{y_2^{local}}{y_2} \right] \tag{11}$$

where ρ means the molar density of mixture which can be evaluated by the following mole fractions (bulk properties).

$$y_1 = y_4 = -7.271 \times 10^{-3} + 1.380 \times 10^{-3} p - 5.076 \times 10^{-5} p^2 \tag{12}$$

$$y_2 = 1.868 \times 10^{-2} + 3.366 \times 10^{-3} p - 9.908 \times 10^{-5} p^2 \tag{13}$$

Table 2 Critical constants p_c, T_c and acentric factors ω(Reid *et al.*, 1987).

Component	p_c[MPa]	T_c[K]	ω[-]
1) Maleic anhydride*	5.99	723.1	0.454
2) Isoprene	3.85	484.0	0.164
4) Carbon dioxide	7.38	304.1	0.239
5) Activated complex**	3.61	849.1	0.589

*Estimaled by the Lyderson's group contribution method (Reid *et al.*, 1987).

**Activated complex was approximated by the reaction product and its properties were estimated by the Lydersen's group contribution method.

$$y_3 = 1 - y_1 - y_2 - y_4 \tag{14}$$

Eqs.(12)-(14) are empirical expressions given by curve fitting for the mole fractions obtained with assumption of 50 % conversion at each pressure and they are adopted as the representative mole fractions of the mixture. Ellington *et al.*(1994) observed the local compositions of methanol around phenol blue in supercritical carbon dioxide by using a solvatochromic technique. Their data suggest the following empirical expression for the local composition.

$$\frac{y_2^{\text{local}}}{y_2} = \exp\left[-\beta Z \left(1 - \frac{p^{\infty}}{p} \right) \right] \tag{15}$$

where β and p^{∞} are the empirical parameters. The parameter p^{∞} should be adjusted as y_2^{local} $\rightarrow y_2$ when $p(p > p_c) \rightarrow p^{\infty}$. In the present correlation, p^{∞} is assumed to be equal to p^{*} for simplicity. Therefore, the experimental k_c (11.7 MPa and 308.2 K) datum was adopted. Using y_2^{local} calculated by the Eq.(15), ρ^{local} can be obtained by the PR equation of state with the conventional mixing rules and the following local mole fractions.

$$y_1^{\text{local}} = y_1 \tag{16}$$

$$y_3^{\text{local}} = 1 - y_1^{\text{local}} - y_2^{\text{local}} - y_4^{\text{local}} \tag{17}$$

$$y_4^{\text{local}} = y_4 \tag{18}$$

The value of β was determined to give good representations of k_c, and was found to be 7.0.

As shown in **Fig. 2**, the correlated results are in good agreement with the experimental data. It is noted that the effect of local mole fraction is important to represent the marked enhancement of rate constants near the critical point.

Conclusions

The rate constants for Diels-Alder reaction of isoprene with maleic anhydride in supercritical carbon dioxide were measured at 308.2, 313.2 and 318.2 K including critical regions by using a batch reactor equipped with FT-IR spectroscopic detector. The reaction rate constants obtained are almost independent of pressure at high pressure region higher than 10 MPa. However, it is noted that the rate constants show a tendency to increase near the critical pressure of carbon dioxide. The pressures at the beginning of reaction rate constant enhancement correspond to the ridges which are the locus of the points where the density fluctuations are at their maximum in isothermal change. Further, the rate constants obtained could be correlated by the transition-state theory coupled with a local composition model.

Acknowledgements

Nomenclatures

a	= energy parameter in PR equation of state	$[Pa \cdot m^6 \cdot mol^{-2}]$
b	= size parameter in PR equation of state	$[m^3 \cdot mol^{-1}]$
C	= molarity	$[mol \cdot L^{-1}]$
$\Delta H^{\ddagger}$	= enthalpy of activation	$[J \cdot mol^{-1}]$
k_c	= rate constant (molar concentration basis)	$[L \cdot mol^{-1} \cdot h^{-1}]$
m	= parameter given by Eq.(8)	$[-]$
p	= pressure	$[Pa]$
R	= gas constant	$[J \cdot mol^{-1} \cdot K^{-1}]$
T	= temperature	$[K]$
t	= reaction time	$[h]$
y	= mole fraction	$[-]$
Z	= compressibility factor	$[-]$
α	= parameter given by Eq.(7)	$[-]$
β	= empirical parameter in Eq.(15)	$[-]$
ρ	= molar density	$[mol \cdot m^{-3}]$
ϕ	= fugacity coefficient	$[-]$
ω	= acentric factor	$[-]$

Subscripts

0	= initial condition $(t=0)$
1	= maleic anhydride
2	= isoprene
3	= carbon dioxide
4	= activated complex (approximated by product)
C	= critical property
i, j	= components i and j
m	= property of mixture

Superscripts

*	= reference state (arbitrary)
∞	= high pressure region where local property approaches bulk property
local	= local property
TS	= transition theory

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