Isoprene–Maleic Anhydride Reaction Rate in Hexane–Nitrobenzene Mixture near Critical Points

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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. Recently, it was recognized that supercritical fluids offer a unique environment for reaction processes and also provide advantages for carrying out reactions (Savage et al., 1995). Furthermore, the enhanced reaction rate can be expected in the vicinity of the critical point (Eckert and Chandler, 1997). For the reaction near the vapor–liquid critical point, a pioneering work was reported by Toriumi et al. (1946), who found a maximum conversion for the oxidation of ammonia around the critical point of ammonia. Simmons and Mason (1972) investigated the reaction rate of the dimerization of chlorotrifluoroethylene and observed a marked curvature of the reaction rate and a sharp anomaly in the activation volume near the critical point of reactant. Recently, Ikushima et al. (1996) reported that the esterification, catalyzed by *Candida cylundracea* lipase, of *n*-valeric acid and citronellol showed a maximal reaction rate near the critical point of carbon dioxide.

On the other hand, for the reaction at a liquid–liquid critical point, Snyder and Eckert (1973a) reported that the reaction rate of the Diels–Alder reaction of isoprene with maleic anhydride was increased by 30–40% at the critical solution point of the hexane–nitrobenzene mixture. It seems that no other studies have been reported for chemical reactions near the critical point of liquid solution.

The comparison of reaction rates near the critical points of both vapor–liquid and liquid–liquid systems is very interesting and important from the scientific point of view. In order to clarify the reaction mechanism around the critical point, it is important to measure the reaction rate of the same reaction system at both vapor–liquid and liquid–liquid critical points and compare the extent of their solvent effect. Therefore, we plan to compare the reaction rates near the liquid–liquid critical point and the vapor–liquid critical point for the Diels–Alder addition of isoprene with maleic anhydride. The Diels–Alder reaction is excellent for fundamental studies because it is a well-characterized reaction system with no significant side reactions (Paulaitis and Alexander, 1987; Wong and Eckert, 1969). First of all, we reexamined the reaction rate near the liquid–liquid critical point according to Snyder and Eckert (1973a). However, unusual or anomalous behavior of the Diels–Alder reaction rate near the liquid–liquid critical point was not observed in our experiment.

Experimental Studies

Measurement of liquid – liquid equilibria

The liquid–liquid equilibria, including the critical point of the hexane–nitrobenzene binary mixture, was measured by two methods. First, a hexane–nitrobenzene mixture was put into a flask that was kept within ±0.01 K in a temperature-controlled bath. The mixture was stirred by a magnetic stirrer for 20–25 min, and then maintained for 20 min to achieve the phase separation. Samples were taken from both the top and bottom phases and were analyzed by a gas chromatograph. The chromatograph used was a Shimazu GC-353 equipped with an FID detector and a GL-science (Dimethyl Polysiloxane TC-1) capillary column (30 m × 0.32 mm ID, 1.0-μm film).

Further, the phase-separation temperature was determined by observing a meniscus. A liquid mixture of known composition was sealed into the flask, which was placed in a temperature-controlled bath. Then the temperature of the bath was set higher than the phase-separation temperature of the mixture. The temperature of the bath was lowered in increments of 0.1 K with intermittent stirring. The bath was maintained at each temperature for 15–30 min to achieve equilibrium. The highest temperature at which a meniscus was observed was defined as the phase-separation temperature.

Reaction

The reaction of isoprene and maleic anhydride was carried out in a dilute condition (isoprene 0.01 mol/L, maleic anhydride 0.015 mol/L) by the conventional batch method. The hexane and nitrobenzene binary solution was used as the reaction solvent. The reaction was run in a flask. The flask was placed in a bath at constant temperature, which could be held within ±0.01 K. Samples were withdrawn from the flask every 60 min for 6–8 h. The half-life time of the Diels–Alder reaction generally exceeds 24 h. Samples were analyzed by gas chromatography as mentioned earlier.

Table 1. Liquid–Liquid Equilibria of the Hexane(1)–Nitrobenzene(2) Binary Mixture

T [K]	x_2^T	x_2^B
283.23	0.177	0.686
286.15	—	0.662
288.15	0.217	0.628
291.15	—	0.550
291.65	0.285	0.562
292.21	0.268	0.545
292.74*	0.500	—
292.75*	0.349	—
293.15*	0.430	—

*Determined by observing a meniscus.

The reaction-rate constant was determined by measuring the concentration of the product, C_P. Based on the first-order reaction relationship, the reaction-rate constant k is given by

$$k = \frac{1}{t(C_{B0} - C_{A0})} \ln \frac{C_{A0}(C_{B0} - C_P)}{C_{B0}(C_{A0} - C_P)},$$

where C_{A0} and C_{B0} are the initial concentrations of isoprene and maleic anhydride. The reaction experiments were run in both a series of several hexane–nitrobenzene mixtures near the critical solution temperature and a series of temperatures at the critical composition. It should be noted that the critical point of the mixture containing reactants and product is a little higher or lower than the critical temperature of the hexane–nitrobenzene binary mixture because of the existing reactants and product. Therefore, all reactions were carefully run slightly above the critical solution temperature of the binary solvent mixture. All reagents are of high-purity reagent grade and were used as received.

Results and Discussion

Liquid–liquid equilibria

The experimental results of the liquid–liquid equilibria for the hexane(1)–nitrobenzene(2) mixture are given in Table 1 and illustrated in Figure 1. The results show good agreement with those of Snyder and Eckert (1973b). The critical solution temperature and composition (mole fraction) are determined to be $T_c = 293.15$ K and $x_{c2} = 0.430$, respectively.

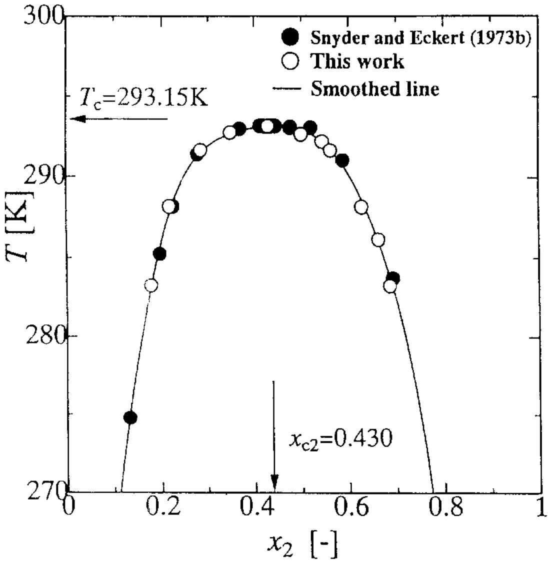

Figure 1. Liquid–liquid equilibria of the hexane(1)–nitrobenzene(2) binary mixture.

Table 2. Rate Constants for Isoprene–Maleic Anhydride Reaction at $T = 293.88$ K in Dilute Solution of the Hexane(1)–Nitrobenzene(2) Mixture

x_2	k [L·mol^{-1}·s^{-1}]×10^{-4}
1.00	2.88
0.915	2.47
0.910	2.47
0.817	2.13
0.610	1.50
0.711	1.73
0.710	1.75
0.520	1.35
0.431	1.24
0.429	1.26
0.350	1.11
0.267	0.963
0.126	0.698
0.050	0.484
0.010	0.325
0.0090	0.355

Reaction rate near critical point

The Diels–Alder reaction-rate constants in a series of several hexane–nitrobenzene mixtures in the vicinity of the critical-solution temperature of 293.88 K, which is slightly higher than T_c, are presented in Table 2 and shown in Figure 2. Snyder and Eckert (1973a) reported that the reaction rate of this system increased by 30–40%, as shown in Figure 2. They thought that the increase of the reaction rate was due to large fluctuations of concentration at the critical point. However, the results in this work are different from those of Snyder

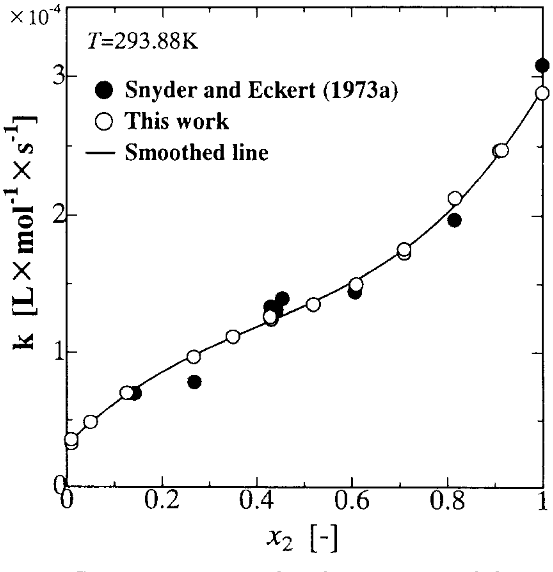

Figure 2. Rate constants for isoprene–maleic anhydride reaction in dilute solution of the hexane(1)–nitrobenzene(2) mixtures near the critical solution temperature.

Table 3. Rate Constants for Isoprene–Maleic Anhydride Reaction at $x_{c2} = 0.430$ in Dilute Solution of the Hexane(1)–Nitrobenzene(2) Mixture

T [K]	k [$\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$]$\times 10^{-4}$
308.15	3.21
306.15	2.74
303.15	2.30
300.15	1.84
298.15	1.58
298.15	1.63
296.15	1.48
293.88	1.24
293.88	1.26

and Eckert (1973a). The reaction rate does not show anomalous enhancement near the critical point, although the relation between the rate constant and mole fraction of nitrobenzene is S shaped.

An Arrhenius plot of the reaction rate constants in a series of temperatures (see Table 3), higher than the critical solution temperature, at the critical composition are shown in Figure 3. The plot shows good linearity and the rate constant at the critical solution temperature, 293.88 K, does not deviate from the linearity. Furthermore, the plot gives a very reasonable value of 53.14 kJ/mol for the activation energy, which is in good agreement with the values of 50.2 to 58.6 kJ/mol found in various solvents (Grieger and Eckert, 1970) and the values of 52.72 kJ/mol found in the nitroethane–hexane solvent system (Snyder and Eckert, 1973a).

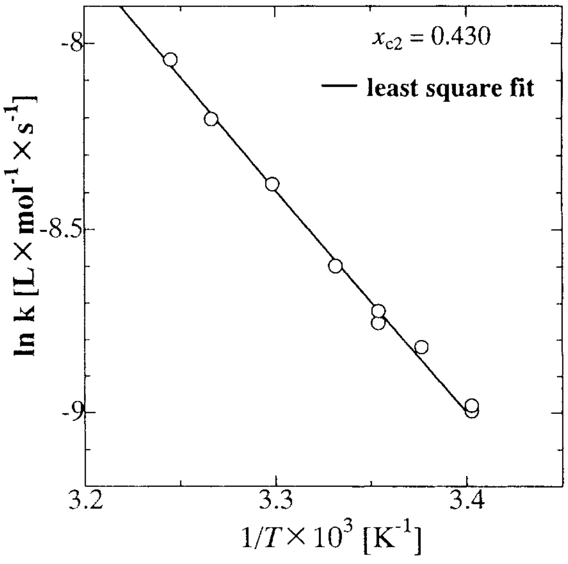

Figure 3. Arrhenius plot for the Diels–Alder reaction of isoprene and maleic anhydride at the critical composition, $x_{c2} = 0.430$, of the hexane(1)–nitrobenzene(2) binary mixture.

As shown above, an anomalous enhancement of reaction rate near the liquid–liquid critical point is difficult to recognize for an isoprene–maleic anhydride reaction in a dilute solution of the hexane–nitrobenzene mixture, although the present experimental technique was not strictly the same as that adopted by Snyder and Eckert (1973a). This discrepancy may arise from the fact that the scaling effect at the liquid–liquid critical point is smaller than that at the vapor–liquid critical point.

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