Cosolvent Effect on the Tautomerism of Ethyl Acetoacetate in Supercritical CO_2

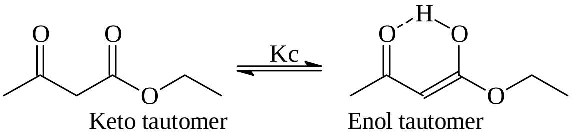
Hong Ping LI, Hai Fei ZHANG, Jun LIU, Bu Xing HAN*

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080

Abstract: The effect of cosolvent cyclohexane, chloroform, and acetonitrile on the keto-enol tautomeric equilibrium of ethyl acetoacetate in supercritical CO_2 was studied by UV-Vis spectroscopy over the pressure range from 76 to 110 bar at 308.15 K. It was found that the equilibrium constant decreases with increasing polarity of the cosolvents.

Keywords: Supercritical CO_2 , cosolvent effect, ethyl acetoacetate, tautomerism.

There are some unique advantages for chemical reactions in SCFs. For example, reaction rates, yields, and selectivity can be tuned by pressure or small amount of cosolvent. SCFs can be used to replace environmentally undesirable solvents. It is not surprised that in recent years the use of SCFs as solvents for chemical reaction media has received much attention. However, mechanism for the effect of pressure and cosolvents on chemical reactions is not very clear. Tautomeric reactions are ideal reversal reactions for studying the mechanism. The tautomerism of ethyl acetoacetate (EAA) in liquid solvents[1] and in SCFs[2,3] has been studied. The tautomerism reaction can be expressed as following



In this work, we studied the effect of cyclohexane, chloroform, and acetonitrile on the tautomerism of EAA in SC CO_2. The total concentration of the two isomers was 1.7×10^{-4} mol/L and that of the cosolvents was 0.05 mol.L^{-1}. A UV-vis spectrometer (TU-1201, Beijing General Instrument Factory) was used to determine the concentration of enol isomer at 240 nm. The temperature-controlled high pressure cell and the experimental procedures were the same as that described previously[3]. The values of equilibrium constants K_c defined by the ratio of the concentration of enol isomer to that of keto isomer are listed in **Table 1.** The data in **Table 1** indicate that the Kc in different mixtures follows the order, K_C(SC CO_2 + cyclohexane) > K_C(SC CO_2 + $CHCl_3$)

> K_C(SC CO_2 + ACN). It is reasonable that Kc in SC CO_2 + cyclohexane is larger than that in SC CO_2 + $CHCl_3$ and in K_C(SC CO_2 + ACN) because the dipole moment of enol tautomer (3.0D) is less than that of keto tautomer (4.0D), and a polar cosolvent should stabilize the keto form. It can be expected that $CHCl_3$ can form hydrogen bond with the keto tautomer, while ACN can not form hydrogen bond with the keto tautomer. The Kc in SC CO_2 + $CHCl_3$ should be smaller than that in SC CO_2 + ACN if the hydrogen bonding was a dominant factor for affecting the equilibrium. Thus, we can conclude that the hydrogen bonding is not dominant because the Kc in SC CO_2 + $CHCl_3$ is larger than that in SC CO_2 + ACN. The data in **Table 1** also show that Kc decreases with pressure at the lower pressures, but is nearly independent of pressure at the higher pressures. This can be explained by the fact that the properties of SCFs are very sensitive to pressure in near critical region.

Table 1 Equilibrium constants K_c at 308.15K

CO_2+Cyclohexane			CO_2+$CHCl_3$			CO_2+ACN		
P/bar	K_c	P_E(%)	P/bar	K_c	P_E(%)	P/bar	K_c	P_E(%)
78.1	0.204	16.9	78.9	0.176	15.0	76.8	0.149	12.9
78.9	0.186	15.7	80.0	0.158	13.6	77.3	0.130	11.5
80.0	0.180	15.3	81.2	0.148	12.9	79.3	0.127	11.3
82.0	0.172	14.7	83.1	0.148	12.9	80.2	0.121	10.8
83.9	0.168	14.4	84.3	0.149	13.0	81.3	0.120	10.7
88.2	0.169	14.5	86.3	0.149	13.0	83.3	0.119	10.6
93.7	0.168	14.4	89.2	0.148	12.9	84.4	0.117	10.5
98.9	0.167	14.3	94.5	0.146	12.8	89.2	0.116	10.4
104.0	0.166	14.2	99.5	0.148	12.9	93.8	0.115	10.3
111.2	0.166	14.2	105.4	0.148	12.9	106.2	0.115	10.3

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