TAUTOMERIZATION OF 2, 4-PENTANEDIONE IN SUPERCRITICAL CO₂

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Introduction

Recently, Johnston *et al.*⁴⁾ studied the tautomeric equilibrium of 4-(phenylazo)-1-naphthol of azo (with a dipole moment of 1.79 D) and hydrazone (5.03 D) in supercritical CO₂, ethane and trifluoromethane, and proposed that the equilibrium ratio between the tautomers could be an indication of the solvency of a supercritical fluid—that, in short, polar fluids favor polar tautomers and vice versa. The present work reports a keto-enol tautomerization of 2, 4-pentanedione (acetylacetone) in supercritical CO₂, in which the solvent affects only the conformational change through intramolecular hydrogen bonding of the molecules. We selected 2, 4-pentanedione for the following reasons. The tautomeric equilibrium of 2, 4-pentanedione has been studied extensively, including gas phase study³⁾. Recently, studies of the tautomerization of 2, 4-pentanedione in a polar supercritical fluid, trifluoromethane, using NMR were reported by Yamasaki and Kajimoto⁶⁾, and Akao and Yoshimura¹⁾. Yamasaki and Kajimoto⁶⁾ reported that the equilibrium constant was almost independent of the fluid density while Akao and Yoshimura¹⁾ reported that the tautomeric equilibrium was shifted to keto form as trifluoromethane density increased. Thus, the density dependence of the tautomeric equilibrium of 2, 4-pentanedione in supercritical fluid has not been elucidated. The purpose of the present work is to study the density dependence of the tautomerism through intramolecular hydrogen bonding by using supercritical CO₂, which is known to be non-polar and is the most widely used supercritical fluid. In this work, the tautomeric equilibrium of 2, 4-pentanedione (**Fig. 1**) in supercritical CO₂ was analyzed with FT-IR spectroscopy.

1. Experiments

CO₂ supplied from Nihon Sanso (purity > 99.9%) was used as a solvent without further purification. 2, 4-

pentanedione (acetylacetone) supplied from Wako Pure Chemicals (purity > 99.0%) was used without further purification.

High-pressure FT-IR equipment used consisted of a FT-IR spectrophotometer (Digilab, FTS-7R), a high-pressure optical cell, a microflow pump (JASCO, 880-PU HPLC pump), a back-pressure regulator, a stainless steel column (i.d. 4.6 mm and 28 mm long) and a magnetic circulation pump. The column and the magnetic circulation pump were immersed in a constant-temperature airbath (MAXALTO, BX-770-B). The high-pressure optical cell was made of SUS 304 stainless steel and its optical windows were made of 5 mm-thick ZnS. The optical path length was 5.25 mm. The cell had an inner volume of 0.103 cm³ and its maximum working pressure and temperature were 40 MPa and 423 K respectively.

IR spectra were obtained with a deuterated triglycine sulfate (DTGS) detector at 2 cm⁻¹ resolution with 16 scans. The spectra of the sample (2, 4-pentanedione) in supercritical CO₂ were obtained by subtracting the background spectra of CO₂ from the spectra of supercritical CO₂ solution containing 2, 4-pentanedione at the same temperature and pressure. We measured the background spectra of CO₂ at 318.15 K and various pressures, and the infrared spectra of 2, 4-pentanedione in supercritical CO₂ at 318.15 K and from 9 MPa to 27 MPa. Among the infrared absorptions of 2, 4-pentanedione, we focused our attention on the carbonyl stretchings of keto (*ca.*1700 cm⁻¹) and enol (*ca.*1600 cm⁻¹, stabilized by hydrogen bonding) forms²⁾.

2. Results and Discussion

Figure 2 shows the fluid density dependence of absorbances of C = O stretchings of keto and enol forms of 2, 4-pentanedione in supercritical CO₂ at 318.15 K. Absorption spectra from both tautomers of 2, 4-pentanedione were observed in supercritical CO₂. The absorbances of the less polar enol form (3D) were larger than

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Fig. 1 Tautomeric equilibrium of 2, 4-pentanedione

Fig. 2 Density dependence of absorbances of keto and enol forms of 2, 4-pentanedione in supercritical CO₂

those of the polar keto form (4D) in supercritical CO₂. Considering the fact that 2, 4-pentanedione exists in enol form in a nonpolar solvent, such as *n*-hexane, it was suspected that supercritical CO₂ was slightly polar such that 2, 4-pentanedione could exist in keto form. This slight polarity was considered to result from the quadrupole moment of CO₂. The absorbances of the enol form of 2, 4-pentanedione tended to decline as fluid density increased, while those of the keto form of 2, 4-pentanedione increased with increase in fluid density. This suggests that the tautomeric equilibrium could be shifted by varying the fluid density. To clarify the shift of tautomeric equilibrium, the absorbance ratios of A(keto)/2A(enol) were evaluated and are plotted against density in Fig. 3. The factor 1/2 in the ratio arises from the correction of double counting of carbonyl stretchings of the keto form in a 2, 4-pentanedione. Since the ratio of absorbances generally represents the ratio of concentration, the plots in Fig. 3 suggest a shift of tautomeric equilibrium from enol to keto with increase in fluid density. In addition, no peculiar behavior near the critical density of CO₂ was observed for the tautomeric equilibria, while, as reported in the previous paper, the dimerization of benzoic acids in supercritical CO₂ was promoted in the critical region of CO₂⁵⁾. The values of molar ratio between the tautomers, ([enol]/[keto]), were estimated to be in the range of 9 to 14 by assuming that the absorption coefficients of keto and enol forms are equal. The values were slightly higher than those reported by Akao and Yoshimura¹⁾ (3 to 10) for the tautomerization of 2, 4-pentanedione in supercritical trifluoromethane, which means that the tautomeric equilibrium in CO₂ was shifted to enol compared with that in a polar solvent, trifluoromethane. The trend of density

Fig. 3 Density dependence of the absorbance ratio of A(keto)/2A(enol)

Fig. 4 Plots of peak wavenumber for C = O stretching of enol form vs. density of CO₂

Fig. 5 Plots of peak wavenumber for C = O stretching of keto form vs. density of CO₂

dependence of tautomeric equilibrium in supercritical CO₂ was also the same as reported by Akao and Yoshimura.

A red shift of carbonyl stretching of enol was observed as fluid density increased, as shown in **Fig. 4**. This means that the vibrational transition of the enol form was stabilized in the higher-density region. A slight blue shift of carbonyl stretching of keto could be observed as the fluid density increased, as shown in **Fig. 5**. This may be because the polar keto form is solvated by CO₂ molecules through entropic, rather than enthalpic, requirement as suggested by Yamasaki and Kajimoto⁶⁾. Namely, CO₂ solvation prefers the linear structure of the keto form to the cyclic structure of the enol form and the vibrational transition of the keto form was destabilized in the higher-density region.

Conclusion

The slight polarity of supercritical CO₂ at higher densities facilitated the formation of polar keto form of 2, 4-pentanedione. Thus, by changing the density of supercritical CO₂ it may be possible to control the tautomeric equilib-

rium of a molecule whose tautomers are different in polarity.

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