

## Study on the Tautomerism of an Indoline Spiropyran in Compressed CO<sub>2</sub> and Ethanol Mixture

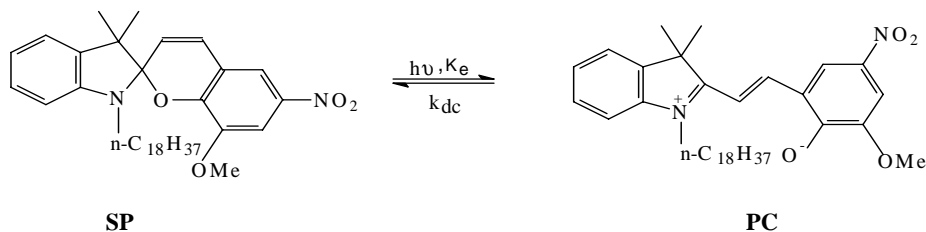
Xi Feng ZHANG, Qiang SUI, Bu Xing HAN\*, Hai Ke YAN, Yan Qiao WANG

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

**Abstract:** Thermodynamic and kinetic properties of the tautomerism of an indoline spiropyran in compressed CO<sub>2</sub>-ethanol mixture were studied by UV-Vis spectroscopy at 298.15 K, 303.15 K, and 308.15 K. It was found that the composition of the mixture affects the equilibrium constant and the rate constant significantly.

**Keywords:** Compressed CO<sub>2</sub>; ethanol; indoline spiropyran; tautomerism.

The solubility of compressed gases in liquids can be very high, which results in the expansion of the liquids. The solubilities of solutes in liquids can be reduced considerably by dissolution of the gases<sup>1</sup> *i.e.*, the gases act as antisolvents. Recently, some compressed gases have been used in many gas antisolvent processes. Understanding of the properties of the compressed gas-liquid mixtures is of great importance to both theoretical study and industrial processes. The tautomerism of spiropyrans and their derivatives has been studied by different authors<sup>2,3</sup>, which indicated that the equilibrium constants  $K_e$  and the decolouration rate constants  $k_{dc}$  are sensitive to the microenvironmental variation. In this work, we studied the tautomerism reaction of an indoline spiropyran (**SP18**) in compressed CO<sub>2</sub>-ethanol mixture. This was not found in a literature survey. The tautomerism reaction is in the following:



In the experiments, the total concentration of the two isomers was from  $10^{-4}$  to  $10^{-5}$  mol/L, which can give measurable intensities of absorption in the visible region. A UV-vis spectrometer was used to determine the concentration of **PC** isomer. The temperature-controlled high pressure cell was the same as that used previously<sup>4</sup>.

The values of equilibrium constants  $K_e$  defined by the ratio of the concentration of **PC** isomer to that of **SP** isomer are listed in **Table 1**. The decolouration process (from **PC** to **SP**) is formulated by first order kinetics in CO<sub>2</sub>-ethanol system, and the rate

constant  $k_{dc}$  determined at 298.15 K is listed in **Table 2**.  $V_o$  and  $V$  in the Tables are respectively the volume of the gas-free solution and that of the expanded solution.  $(V-V_o)/V_o$  is directly related with the expansion of the solution caused by the dissolution of  $CO_2$  in ethanol or the composition of the mixture.

**Table 1.** Equilibrium constants  $K_e$  of **SP18** in  $CO_2$ -ethanol system at different temperatures

$(V-V_o)/V_o$	298.15K		303.15K		308.15K	
	P/bar	$K_e$	P/bar	$K_e$	P/bar	$K_e$
0.0	-----	0.272	-----	0.272	-----	0.268
0.5	55.7	0.181	54.7	0.190	55.7	0.205
1.0	59.3	0.128	63.0	0.136	65.6	0.155
1.5	59.8	0.108	67.2	0.103	71.9	0.120
2.0	61.4	0.085	68.9	0.090	75.0	0.096
2.5	62.3	0.066	69.2	0.066	77.4	0.063
3.0	62.8	0.054	70.4	0.049	78.5	0.059

**Table 2.** Decolouration rate constants  $k_{dc}$  of **SP18** in  $CO_2$ -ethanol system at 298.15K

$(V-V_o)/V_o$	0.0	0.5	1.0	1.5	2.0	2.5	3.0
$k_{dc} \times 10^3 / S^{-1}$	7.74	14.1	18.2	27.4	42.7	50.9	55.0

The results in **Table 1** show that  $K_e$  decreases with the expansion of the solution. It can be concluded that the polarity of the solution is reduced when  $(V-V_o)/V_o$  is increased because  $K_e$  decreases with the polarity of the liquid solvents<sup>2,3</sup>.  $k_{dc}$  increases considerably with  $(V-V_o)/V_o$ , as shown in **Table 2**. It can be expected that  $k_{dc}$  should be increased when the viscosity of the solution is reduced. It can be deduced that the viscosity of the solution decreases with increasing  $(V-V_o)/V_o$ , *i.e.*,  $CO_2$  dissolved in ethanol reduces the viscosity of ethanol. Thus, the tautomerism can be controlled by  $CO_2$  dissolved and the reaction may be used as a probe to detect the properties of the gas-liquid mixtures.

### Acknowledgment

The authors are grateful to the National Natural Science Foundation of China for the financial support(No. 29725308, 29633020).

### References

1. M. A. McHugh, V. J. Krukonsis, *Supercritical Fluid Extraction: Principles and Practice*, 2nd Ed., Butterworth-Heinemann, Boston, **1994**.
2. S. R. Keum, M. S. Hur, P. M. Kazmaier, E. Buncel, *Can. J. Chem.*, **1991**, 69, 1940.
3. X.Q. Song, J. W. Zhou, Y. T. Li, Y. W. Tang, *J. Photochem. Photobiol. A: Chem.*, **1995**, 92, 99.
4. J. Lu, B. X. Han, H. K. Yan, *Ber Bunsenges. Phys. Chem.*, **1998**, 102, 695.

Received 16 February 1999