Investigations of the Thermal Inversion Rates of Azobenzenes in Supercritical and Gaseous CO_2: A Shift from the Energy-Transfer-Limited to the TST-Valid Region at Low Densities

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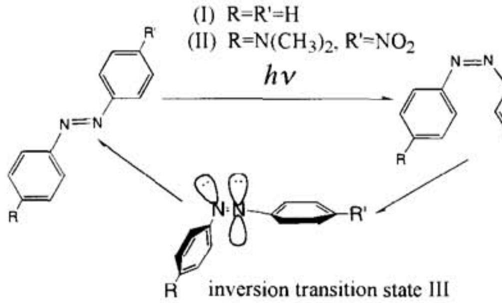
(Received August 13, 1998; CL-980622)

Studies of slow thermal Z/E isomerization reactions around the N=N double bond of azobenzenes in supercritical and gaseous carbon dioxide revealed that a shift from the energy-transfer-limited to the TST-valid region predicted by Kramers takes place at relatively low densities.

In recent years, a growing number of scientific applications of supercritical fluids (SCFs) have been reported.[1-4] Supercritical carbon dioxide is considered to be one of the most versatile fluids, as one can easily control its density and fluidity by varying the pressure and the temperature. In this study, we utilized such characteristics of CO_2 for the purpose of examining the application limit of the transition state theory (TST) in low density CO_2.

In 1940, Kramers predicted the application limit of TST, by solving the mass transfer equation as a function of viscosity η of the reaction medium.[5] His theory implies that TST fails both at high and low viscosity / density region of the medium. Namely, at high viscosities, the movement of the reactant along the reaction coordinate is retarded by slow thermal fluctuations of the solvent molecules (fluctuation-limited region) and at low densities, energy transfer from the medium to the reactant limits the reaction rate (energy-transfer-limited region). Several studies[2,6-8] involving very rapid reactions, such as photo-induced Z/E isomerization of stilbene, have been carried out to examine the turnover phenomena and the results qualitatively supported the prediction. However, in slow reactions, only the deviations from TST at high viscosity region have been reported.[9-11] Sigman and Leffler[4] investigated the isomerization rate of 4-(diethylamino)-4'-nitroazobenzene in relatively high-density CO_2, and found that the rate constant was linearly dependent on the Kamlet-Taft π^* parameter, which indicates that TST is valid in their region. In this study, we have examined the thermal Z/E isomerization of azobenzene (**I**) and 4-(dimethylamino)-4'-nitroazobenzene (**II**) in relatively low-density CO_2 in order to confirm the existence of the energy-transfer-limited region.

Scheme 1.



Thermal Z/E isomerization of azobenzenes proceeds through the inversion of one of the nitrogen atoms in nonpolar media[12] and the transition state (**III** in Scheme 1) is expected to have a slightly lower polarity compared with the parent Z-isomer.[13] The reaction of **I** was studied in low density gaseous CO_2 ($0.0035 < \rho$ / g cm^{-3} < 0.111), while **II** was studied in supercritical CO_2 at higher densities ($0.7 < \rho$ / g cm^{-3} < 0.9). The reaction was monitored by a Jasco V-570 spectrophotometer at 300 and 420 nm for **I** and **II**, respectively, after irradiation of the reaction mixture by a 150 W xenon lamp (Unisoku Co. Ltd.). An ISCO 100DX syringe pump connected to a Jasco UV-VIS cell with a temperature controller (Neslab Ltd.) was used to achieve desired pressure and temperature. The low solubility of **II** prevented us from measurements at lower densities while slow dissolution of **I** at higher densities made reliable measurements extremely difficult and limited the highest density in the reaction of **I**. The densities and viscosities at experimental conditions could be reliably estimated according to the literature method.[14-16]

The observed rate constants for **I** at 70 °C and for **II** at 40 °C are plotted against the solvent density in Figures 1 and 2, respectively. The estimated rate constants calculated from the reported kinetic parameters for the gas phase reactions are also included in Figures 1 and 2.[17,18] The gas phase rate constants

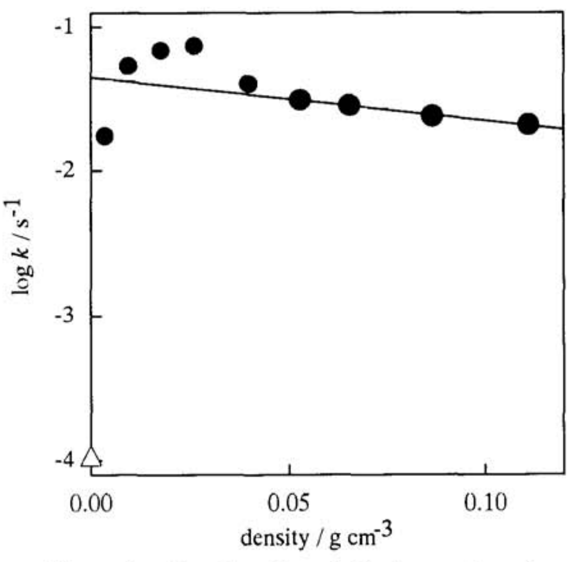


Figure 1. The plot of log *k* for the reaction of compound (I) *vs* the density of CO_2. (●) in gaseous CO_2 ; (Δ) gas phase.

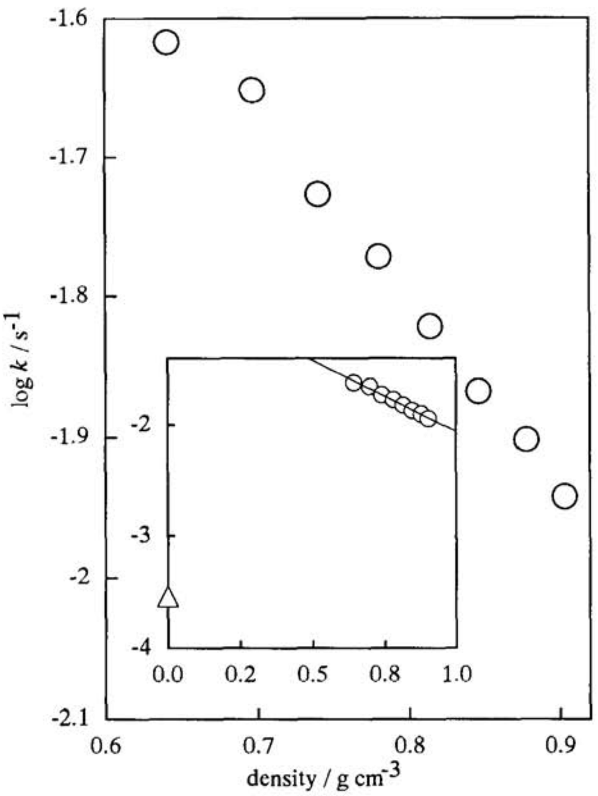


Figure 2. The plot of log$k$ for the reaction of compound (II)*vs* the density of CO_2. (o) in supercritical CO_2. Inset : an enhanced scale. (Δ): reaction in gas phase.

for each compound are very reliable as the kinetic parameters for these reactions were evaluated from the results obtained in the wide temperature range. As expected from the small polarity decrease during the activation, a slight decrease in the rate with the increasing density ρ was observed in **I** at $\rho > 0.05$ / gcm^{-3}. This tendency coincides with the one reported for the liquid phase,[19] strongly suggesting the validity of TST in this region. However, at lower densities ($\rho < 0.02$ / gcm^{-3}), the rate constant increased with increasing medium density as predicted by Kramers: the results in Figure 1 unequivocally demonstrate a shift of the reaction from the energy-transfer-limited to the TST-valid region. Although similar negative density / polarity dependence was observed for II, it was not possible to confirm the existence of the energy-transfer-limited region directly because of the reason stated above. However, a much smaller rate constant in the gas phase than that expected from the extrapolation can be taken as indirect evidence for the existence of such a region. In other words, the present results, together with the previously reported viscosity-induced retardations,[9,10] complete the first observation of the Kramers turnover in a slow thermal reaction. It is interesting to note that the densities where the shift to the TST-valid region takes place in the present reactions are in the same (for **II**) or lower (for **I**) order of magnitude with that in photo-induced isomerization of (*E*)-stilbene (~ 0.3 gcm^{-3}), despite the large difference in the activation energy (15 kJmol^{-1} for stilbene, 118 and 102 kJ mol^{-1} for **I** and **II**, respectively).[20] Further experiments are under way and the results will be reported when they are completed.

This research was partly supported by the Grants-in-Aid for Scientific Research (Grant No. 10440193) from the Ministry of Education, Science, Culture and Sports of Japan.

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