The First Unequivocal Observation of Dynamic Solvent Effects in the Thermal Geometrical Isomerization of 3,3'-Diethyloxadicarbocyanine Iodide (DODCI)

Jong Chul Kim, Yasushi Ohga, and Tsutomu Asano*
Department of Applied Chemistry, Faculty of Engineering, Oita University, Oita 870-1192

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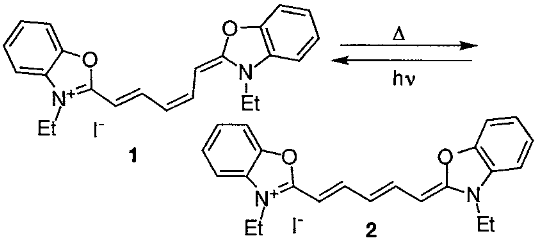
Pressure dependence of the rate of thermal geometrical isomerization of 3,3'-diethyloxadicarbocyanine iodide (DODCI) was studied in ethanol and in a highly viscous hydroxylic solvent, 2-methyl-2,4-pentanediol. The kinetic effects of pressure in the two solvents are qualitatively different and the results strongly suggest that the stochastic analysis of the kinetic results in 1-alkanols reported earlier needs to be renounced.

Influence of the solvent thermal fluctuations, i.e., dynamic solvent effects, on the isomerization where a bulky atomic group makes a large amplitude motion have been studied extensively both experimentally and theoretically.[1] Most of the experimental works were performed with molecules in their electronic excited state. A typical example is the photo-induced geometrical isomerization of stilbene.[2] In such reactions, the loss of the reactant to the product takes place in such a short time that the thermal equilibrium can hardly be maintained between the reactant and the activated complex and the effects of solvent thermal fluctuations could be observed in liquids with low viscosities such as straight chain alkanes.

On the other hand, by doing kinetic measurements in viscous media realized under high pressure, we demonstrated that effects of slow solvent thermal fluctuations could be observed only at viscosities higher than 10 Pa s (= 1×10^4 cP) in the *Z*/*E* isomerization of azobenzenes and *N*-benzylideneanilines in their electronic ground state.[3-5] The activation energies of these reactions were 50 kJ mol^{-1} or higher and kinetic effects of pressure on these isomerizations in common solvents with low viscosities were fully understood within the framework of the transition state theory (TST).[6,7] In other words, all of the pressure effects could be rationalized in terms of the activation volume, i.e., partial molar volume differences between the reactant and the activated complex.

It has been known for many years that a similar relatively slow *Z*/*E*-type thermal isomerization takes place in 3,3'-diethyloxadicarbocyanine iodide (DODCI) following the photo-induced formation of an unstable conformer **1** as shown in eq 1.



(1)

The activation energy for the thermal process is ca. 60 kJ mol^{-1} and the half life of the unstable isomer is in milliseconds. The rates of the reaction was measured in various 1-alkanols both at atmospheric[8] and high[9] pressures. Fleming and his co-workers[8] did kinetic measurements at various temperatures in seven 1-alkanols and Hara and Akimoto[9] studied the effects of pressure on the isomerization in four 1-alkanols, from methanol to 1-butanol, at 30 °C and up to 500 MPa. In the former, the viscosity (η) range was $1\times10^{-3} < \eta < 2\times10^{-2}$ Pa s and in the latter, it was $5\times10^{-4} < \eta < 3\times10^{-2}$ Pa s. Despite the relatively low viscosity ranges, the rate constant k_{obs} seemingly decreased with increasing viscosity and both Fleming and Hara assumed that the apparent viscosity dependence was a manifestation of the dynamic solvent effect. However, considering our results on the azobenzenes and the *N*-benzylideneanilines, it could hardly be believed that dynamic solvent effects appeared at such low viscosities in the slow thermal isomerization of DODC cation. Therefore, we decided to study kinetic effects of pressure on the reaction in ethanol and 2-methyl-2,4-pentanediol (MPD) at various temperatures (5 °C $\le T \le$ 35 °C). The dielectric constants of these solvents are similar (24.55 for EtOH at 25 °C and 25.86 for MPD at 20 °C), however, MPD is much more viscous because of its branched molecular structure especially at high pressures.

The unstable isomer was formed by irradiation from a xenon flash lamp, and its decay was followed

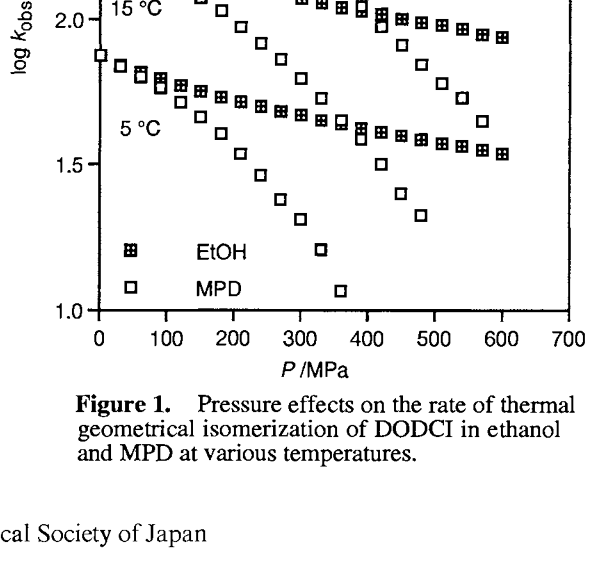


Figure 1. Pressure effects on the rate of thermal geometrical isomerization of DODCI in ethanol and MPD at various temperatures.

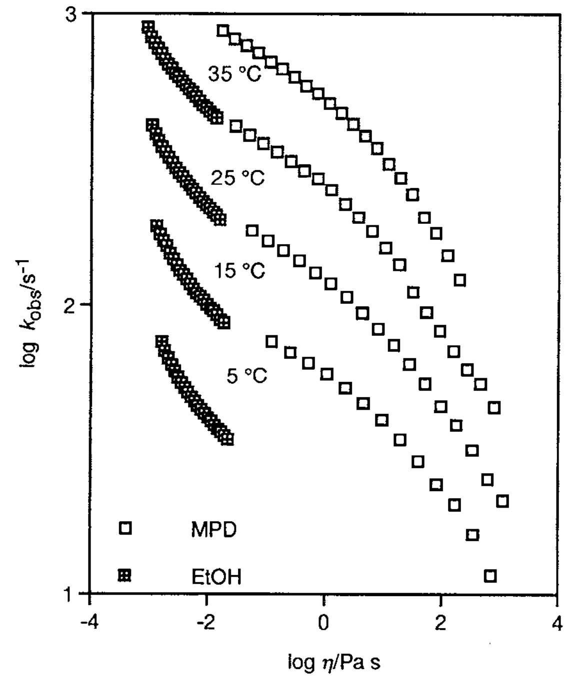


Figure 2. log k_{obs} - log η plots for the isomerization of DODCI in ethanol and MPD at various temperatures.

spectrophotometrically. The reaction followed the first-order kinetics at all of the conditions studied. A high-pressure optical vessel similar to the one described previously[10] was used.

The pressure and viscosity dependence of k_{obs} are illustrated in Figures 1 and 2, respectively. The rate constants in the two solvents were very close to each other at 0.1 MPa, strongly suggesting the validity of TST in MPD at atmospheric pressure. However, the pressure effects were qualitatively different in the two solvents. Although the reaction was retarded by an increase in pressure in both solvents, the magnitude of the retarding effect decreased with increasing pressure in ethanol as observed in other reactions with a positive activation volume.[11] This tendency is generally observed because an increase in the volume is, at least partly, a result of a larger free volume created by thermal fluctuations and it, in turn, results in a larger isothermal compressibility. On the other hand, the magnitude of the pressure effect increased with increasing pressure in MPD. Considering the high viscosities of MPD[4] under high pressure (see Figure 2) and similar tendencies observed for other isomerizations in the same solvent,[4] this difference would best be rationalized by assuming that TST stays valid in ethanol but the reaction shifts from the TST-valid region to the TST-invalid one with increasing viscosity in MPD. The rationalization of the retarding pressure effects in ethanol on the basis of TST is further supported by a recent observation of a volume decrease during the photo-induced *E*/*Z* (**2** to **1**) isomerization of DODCI by Braslavsky and her co-workers.[12] The measurement was made by Laser-Induced Optoacoustic Spectroscopy. The estimated volume change in the photo-isomerization was -29±12 cm^3 mol^{-1} in 30% ethanol, i.e., the partial molar volume of the reactant would increase in ethanol along the reaction coordinate of the thermal isomerization from **1** to **2**. The observed positive activation volumes in ethanol, 5-6.5 cm^3 mol^{-1} at 0.1 MPa, are in accordance with this expectation.

The results presented here strongly suggest that the analyses of the solvent and pressure effects on the rate of thermal *Z*/*E* isomerization of DODCI by Fleming[6] and Hara[7] on the basis of a stochastic model needs to be renounced. Further measurements on a related cyanine dye, 3,3'-diethyloxacarbocyanine iodide (DOCI) are in progress and the full analysis of the results will be presented when they are completed.

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References and Notes

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