

Evidence for Two Competing Mechanisms in Regeneration of 2-(2,4-Dinitrobenzyl)pyridine from its Enamine Tautomer

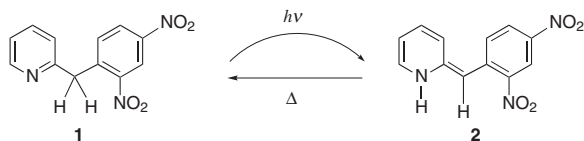
Nobuhiro Kira, Toru Takahashi, Yasushi Ohga,* and Tsutomu Asano*

Department of Applied Chemistry, Faculty of Engineering, Oita University, 700 Dannoharu, Oita 870-1192

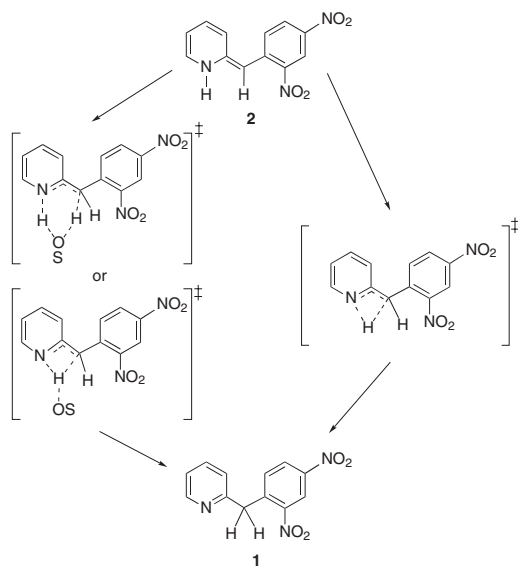
(Received August 27, 2004; CL-041012)

Kinetic effects of pressure on the title reaction were studied. The reaction was insensitive to a change in pressure at 0.1 MPa, however, it was accelerated by an increase in pressure at $P > 100$ MPa, showing the existence of two reaction routes with and without solvent participation. Viscosity-induced retardations observed in highly viscous media supported intervention of solvent molecules at high pressures.

2-(2,4-Dinitrobenzyl)pyridine **1** is widely known for its photochromic behavior.^{1,2} Irradiation of the sample with UV light results in blue-colored species. As a result of various spectroscopic investigations, the colored species is now believed to be an enamine **2** shown in Scheme 1.^{3,4} There have been some reports on the photo-induced and thermal proton transfer processes of intramolecular reaction of dinitrobenzylpyridines.⁵ However, there has been no report on the existence of the solvent participation in thermal regeneration of the pyridine from the enamine. This letter reports experimental results of kinetics which unequivocally demonstrate the existence of two competing reaction mechanisms in the thermal prototropic tautomerization.

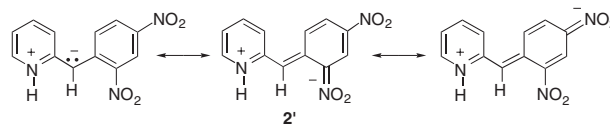


Scheme 1.



Scheme 2.

In the enamine–pyridine isomerization, two mechanisms are conceivable, proton transfer with and without solvent participation (Scheme 2). In this reaction shown in Scheme 1, little intrinsic volume change⁶ is expected because the reaction is a simple movement of a proton from the pyridine nitrogen to the benzyl carbon. The enamine has some zwitter ionic character⁴ **2'** (Scheme 3) and the polarity will decrease slightly during the reaction and this may result in a small volume increase because of desolvation. If a solvent molecule participate in the proton transfer, on the other hand, solute-solvent interactions must be reinforced in the activation step and this, in turn, would result in a negative activation volume. Therefore, high-pressure kinetics seems to be an ideal tool to study the mechanism in the present reaction.



Scheme 3.

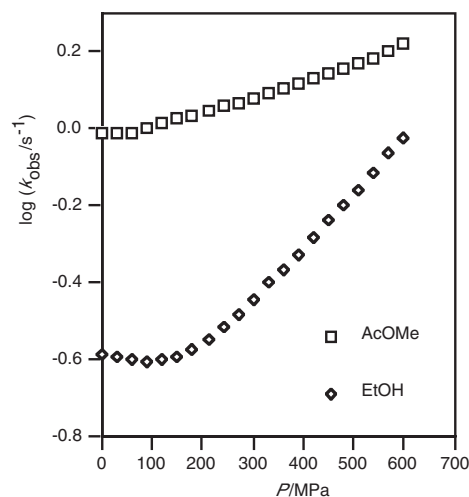


Figure 1. Pressure effects on the thermal tautomerization in Scheme 1 at 25 °C.

We studied pressure effects on this **2** to **1** tautomerization in methyl acetate (AcOMe) and ethanol (EtOH) at 25 °C. The high-pressure kinetics experiment was performed by the procedure which was essentially the same as the previously described method.⁷ The reaction followed the first-order rate law at all of the conditions studied.⁸ The results are illustrated in Figure 1. In both of the solvents, the activation volume ΔV^\ddagger was close to zero at atmospheric pressure (-0.2 ± 0.3 and 3.1 ± 0.8 cm³ mol⁻¹ in AcOMe and EtOH, respectively) clearly indicating

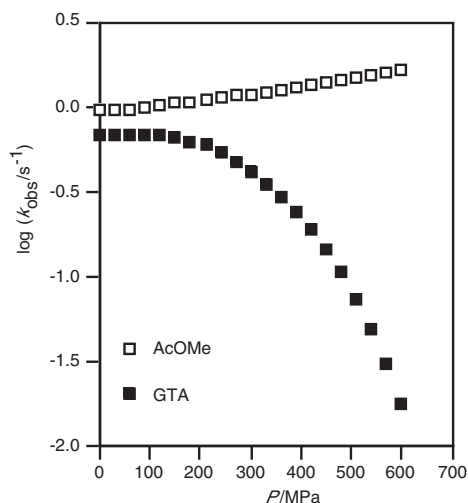


Figure 2. A comparison of pressure effects in methyl acetate and GTA.

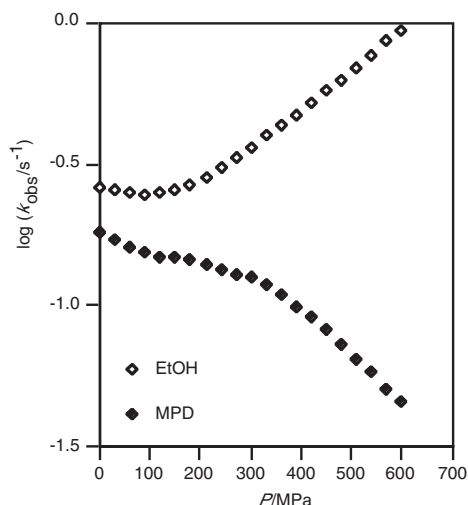


Figure 3. A comparison of pressure effects in ethanol and MPD.

the absence of solvent participation. In ethanol, the reaction was slightly retarded by an increase in pressure suggesting a higher polarity of the reactant in this solvent and its decrease in the activation step. At high pressures, however, the reaction was accelerated both in AcOMe and EtOH. The activation volumes were -2.6 ± 0.1 and $-7.8 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$, respectively. This change in the sign of the activation volume can most reasonably be explained by the intervention of the solvent molecule. Namely, the results in Figure 1 strongly suggest the existence of two competing reaction routes as discussed above.

In order to obtain additional evidence for this mechanism, we studied viscosity dependence of the reaction rate. In our previous studies,⁹ we measured effects of viscosity on the rate of various isomerizations. By using viscous liquids such as glycerol triacetate (GTA) or 2-methylpentane-2,4-diol (MPD) as a reac-

tion medium and applying pressures of several hundred megapascals (MPa), we could convert “slow” reactions with a relatively large activation energy, $E_a > 50 \text{ kJ mol}^{-1}$ from “activation-limited” to “fluctuation-limited.” At high viscosities, solvent thermal fluctuations became too slow to maintain the thermodynamic equilibrium between the initial and the transition state and solvent reorganization process became rate-limiting. At such conditions, the reaction rate decreased with increasing medium viscosity and the so-called dynamic solvent effects were observed. If the high-pressure mechanism in the present reaction involves solvent participation, we will find similar viscosity-induced retardations at high pressures in viscous liquids. The results obtained in GTA and MPD are compared with those in nonviscous counterparts in Figures 2 and 3, respectively. Obviously, the pressure dependence was similar at low pressures, however both in GTA and MPD, the reaction was rather strongly retarded by an increase in pressure as observed in our previous studies. These results provide further support to the solvent participation at high pressures in the present tautomerization.

Measurements at different temperatures are in progress and the results will be reported when they are completed.

References and Notes

- 1 A. E. Chichibabin, B. Kuindishi, and S. V. Benewolenskaya, *Ber. Dtsch. Chem. Ges.*, **58B**, 1580 (1925).
- 2 R. Hardwick, H. S. Mosher, and P. Passailaigue, *Trans. Faraday Soc.*, **56**, 44 (1960).
- 3 H. Takahashi, Y. Kobayashi, N. Kaneko, T. Igarashi, and I. Yagi, *J. Raman Spectrosc.*, **12**, 125 (1982).
- 4 A. Corval, K. Kuldova, Y. Eichen, Z. Pikramenou, J. M. Lehn, and H. P. Trommsdorf, *J. Phys. Chem.*, **100**, 19315 (1996).
- 5 D. Ben-Hur and R. Hardwick, *J. Chem. Phys.*, **57**, 2240 (1972); A. G. Turovets and V. I. Danilova, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, **15**, 68 (1972); D. Klemm, E. Klemm, A. Graness, and J. Kleinschmidt, *J. Prakt. Chem.*, **321**, 415 (1979); K. Yokoyama and T. Kobayashi, *Chem. Phys. Lett.*, **85**, 175 (1982); Y. Eichen, J.-M. Lehn, M. Scherl, D. Haarer, J. Fischer, A. DeCian, A. Corval, and H. P. Trommsdorff, *Angew. Chem., Int. Ed. Engl.*, **34**, 2530 (1995); M. Scherl, D. Haarer, J. Fischer, A. DeCian, J.-M. Lehn, and Y. Eichen, *J. Phys. Chem.*, **100**, 16175 (1996); I. Frank, S. Grimme, and S. D. Peyerimhoff, *J. Phys. Chem.*, **100**, 16187 (1996); Y. Eichen, M. Botoshansky, U. Peskin, M. Scherl, D. Haarer, and S. Khatib, *J. Am. Chem. Soc.*, **119**, 7167 (1997); I. Frank, D. Marx, and M. Parrinello, *J. Phys. Chem. A*, **103**, 7341 (1999); S. Khatib, S. Tal, O. Gidsi, U. Peskin, and Y. Eichen, *Tetrahedron*, **56**, 6753 (2000).
- 6 R. van Eldik, T. Asano, and W. J. le Noble, *Chem. Rev.*, **89**, 549 (1989).
- 7 T. Asano and T. Okada, *J. Phys. Chem.*, **88**, 238 (1984).
- 8 The reaction was followed by the absorption decrease at 570 nm. The standard deviation of the rate constant was less than 6%.
- 9 H. Kono, H. Osako, M. Sasaki, T. Takahashi, Y. Ohga, T. Asano, M. Hildebrand, and N. N. Weinberg, *Phys. Chem. Chem. Phys.*, **6**, 2260 (2004) and earlier papers cited therein.