

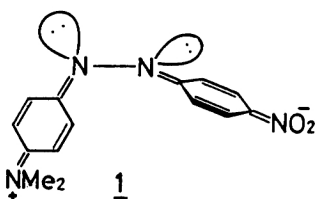
Reversal of Pressure Effect on Thermal Z-E Isomerization
of 4-(Dimethylamino)-4'-nitroazobenzene

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It has been discovered that the kinetic effect of pressure on Z-E isomerization of 4-(dimethylamino)-4'-nitroazobenzene reverses at about 500 MPa in glycerol triacetate at 25 °C. At lower pressures, the rate increases with increasing pressure, but at higher pressures, it decreases rapidly with increasing pressure. The most probable reason for this reversed pressure effect is retardation of the intramolecular rotational movements by viscous interactions between the reactant and the solvent molecules.

In previous communications,^{1,2)} it was established that thermal Z-E isomerization of 4-(dimethylamino)-4'-nitroazobenzene, hereafter referred to as NMe₂-NO₂-AB, proceeds via dipolar rotational transition state (1) in solvents with medium and high polarities. Since the polarity of the activated complex is much higher than that of the Z-isomer, the extent of the electrostatic solute-solvent interactions is expected to increase during activation. The large acceleration of the reaction by the increase in the solvent polarity and external pressure gave strong support for this mechanism. For example, in acetone at 25 °C, the rate constant increases from 9.57 s⁻¹ at 0.1 MPa to 45.4 s⁻¹ at 210 MPa.³⁾ However, the rotational movement of the aryl ring(s) will be retarded by viscous interactions with the solvent molecules in solvents with high viscosities. Because viscosity of liquids generally increases with the application of external pressure, it may be expected that the pressure effect is reversed at some point in such solvents. If this expectation is met, such systems will provide valuable data about the effect of viscosity on the intramolecular rotational movement in molecules at their electronic ground state.



The effect of pressure on the isomerization of NMe₂-NO₂-AB was studied in glycerol triacetate (triacetin) and ethanol in the pressure range of 0.1-800 MPa. The viscosities of these solvents at 25 °C and 0.1 MPa are 16.1 and 1.08 mPa s respectively. The results are illustrated in Fig. 1. At relatively low pressures, the pressure increase resulted in a large acceleration of the isomerization in both of the solvents, and this tendency continued to 800 MPa in ethanol. In

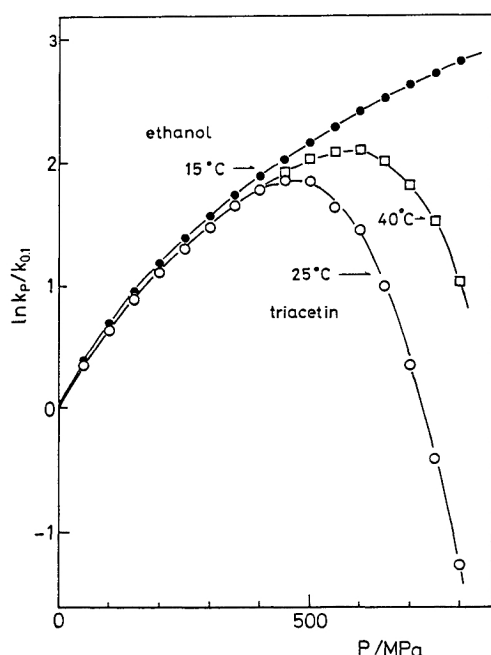


Fig. 1. Kinetic effect of pressure on thermal Z-E isomerization of $\text{NMe}_2\text{-NO}_2\text{-AB}$. Rate constants at 0.1 MPa are as follows; 8.46 (ethanol), 1.29 (triacetin, 25 °C), 3.48 (triacetin, 40 °C) s^{-1} .

triacetin, however, the rate constant reached the maximum value at around 500 MPa at 25 °C and then started to decrease rapidly with increasing pressure as can be seen clearly in Fig. 1. The fact that this reversal of pressure effect is observed only in highly viscous triacetin strongly suggests that this is an indication of the retardation of the rotational movement by the increase in the solvent viscosity. There is little reason to expect a new mechanism operating only in triacetin under high pressure. The fact that the maximum pressure shifts to ca. 600 MPa at 40 °C also supports this discussion. The effect of viscosity on intramolecular rotation is now becoming an object of active investigation. However, most of the works are concerned with molecules in their excited states, and the viscosity changes are realized by changing the structures of the solvent molecules and the reaction temperatures.⁴⁾ The

system presented here will provide new possibilities for studying the viscosity effects on the reaction of molecules in their electronic ground state.⁵⁾

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