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Kinetics and Equilibrium of cis-trans Isomers in the Ground State of 4-Amino Azobenzene

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Introduction] Photo-induced studies provide the information regarding the various radiative and non-radiative relaxation processes by which an excited molecule returns to its ground state. For the control on such photo-induced reactions, prior detail information of all deactivation processes is highly vital. In azobenzene (AB) derivatives, trans to cis photoisomerization occurs following irradiation with UV-visible light.¹ Cis to trans thermal isomerization occurs spontaneously in the dark owing to the thermodynamic stability of the trans isomer.^{1, 2} Substitution by different groups at different positions in the parent moiety (AB) can alter spectroscopic properties and dynamics / kinetics of isomerisation.^{3,4} Moreover, mechanism of photoisomerization has also been a subject of debate due to the involvement of more than one higher singlet electronic excited state (i.e, S_1 and /or S_n)². On the other hand, by the virtue of participation of only one state, i.e., the ground state in thermal isomerization, it may become easier to probe the mechanism of isomerization. Therefore, to explore the mechanism of isomerization and to know one of the deactivation processes over a complete photoreaction cycle, we address the kinetics of thermal isomerisation of 4-aminoazobenzene (AAB) and effect of solvent polarity, viscosity and temperature on it.

Experimental] AAB obtained from Wako Pure Chemical Industries, Ltd., Japan (99% pure) was used as such. All the solvents used were of spectroscopic grades. Steady state absorption spectra were recorded by dual beam Shimadzu UV-2400PC spectrophotometer. To generate cis-AAB, cw UV laser (405 nm), ~200 mW was used. To record the shorter ground state decay times, transient time resolved setup was build-up.

Results and Discussion] In diethyl ether (DEE) and acetone (ACTN), AAB exhibits absorption maximum at around 380 nm with long wavelength absorption tail (Fig. 1). To generate cis-AAB, UV laser (405 nm) was irradiated on the sample, until it reached at equilibrium (photo-stationary state). Figure 1b shows the absorption spectrum of photostationary state. Difference absorption spectrum of AAB in DEE is depicted in Fig. 1c. It is clearly shown that prominent photobleaching at 380 nm and the transient absorption peaks of the photostationary state at around 340 nm and 450 nm are observed. The transient absorption peaks can be assigned to the cis-AAB. These curves indicate that most of trans-AAB molecules are converted to the cis-configuration.

As the laser irradiation is stopped, cis-AAB isomers do not remain stable and return towards more stable trans-configuration, and thus one can follow the course of cis to trans conversion (Fig. 2). Rate of thermal isomerization from cis to trans-isomer is mainly governed by activation energy and generally follows a first order kinetics.

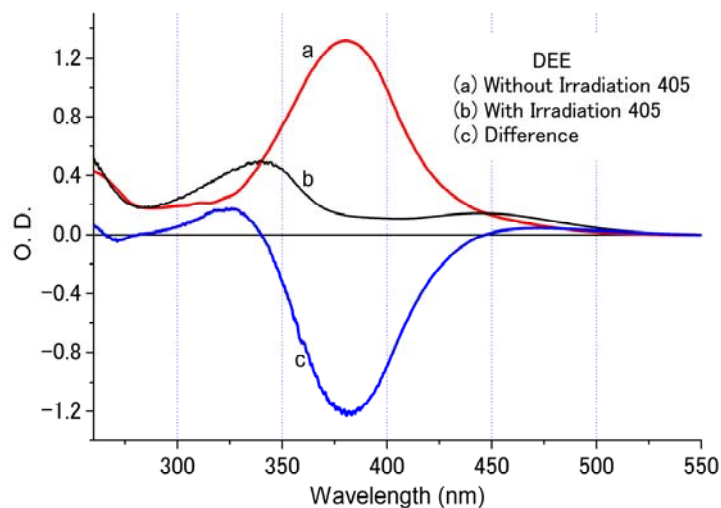


Fig. 1 Absorption spectra of AAB in DEE (298 K)

In order to estimate the activation energy of cis-AAB, we followed the course of isomerization at different temperatures. The uni-molecular thermal cis-to-trans isomerization reaction in dark obeys a single exponential behaviour. For estimation of activation energy, Eyring and Arrhenius equation was employed and the obtained values of barrier height are 0.80 eV and 0.78 eV, respectively. From the temperature dependent measurement on AAB in ACTN and methanol (MeOH) solutions, activation energy was estimated at 0.6 eV and 0.3 eV, respectively.

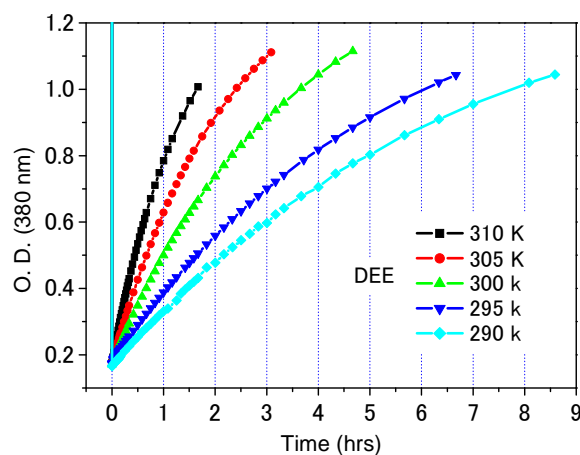


Fig. 2 Temperature dependence of ground state decay of cis-AAB in DEE.

From the above observation, dependence of polarity on activation energy was noticed as it varies from 1.06 eV in gas phase⁵ to 0.3 eV in MeOH. In gas phase, inversion mechanism has been proposed for AAB.^{5,6} DEE being non-polar in character, inversion mechanism can be considered. On the other hand, a polar intermediate can lower the activation energy and favor rotation, and thus accelerate the rate. Therefore, it is worth considering the rotation mechanism in solvents of higher polarity.

References

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