SHORT COMMUNICATION

SOLVENT EFFECTS ON THERMAL *cis-to-trans* ISOMERIZATION OF AZOBENZENE : UV/VIS SPECTROSCOPIC STUDIES

KHURSHIDA KHAYER*

Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh

AND

WOLFRAM SANDER

Fakultät für Chemie, Ruhr-Universität, Bochum, Germany

INTRODUCTION

Nowadays, azobenzene and its derivatives are considered as useful materials[1-3] for liquid crystals, light-driven switches and image storage devices having fast response time. Thus, such types of compounds are important not only from the view of fundamental photochemistry, but also for their potential role in industrial applications. The heart of these compounds, *trans↔cis* isomerization (Fig. 1), controls their chemistry.
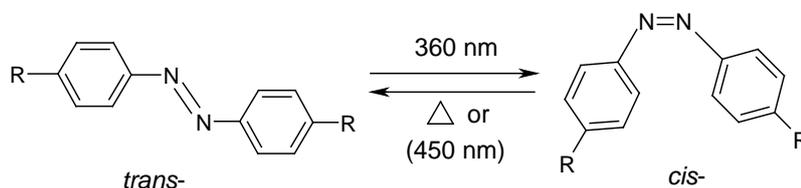
Fig. 1. *Trans↔cis* isomerization of azo compounds.

But till now both the photo- and thermal isomerization of azobenzene compounds have been a subject of some controversy due to the possible alternative conversion routes, viz. rotation[4,5] and inversion[6-9]. Asano *et al.*[5] investigated the solvent effect on push-pull azobenzene derivative and found that the rate enhancement on changing from n-hexane to formamide is ca.10^5. Such a significant solvent effect is an idication of the dipolar character of the activated complex. This strongly supports the rotation mechanism. A complete π-bond rupture of the N=N bond produces highly dipolar rotational transition state, and rotation occurs around the remaining single bond. On the other hand, facile isomerization of the azobenzene unit, even though it is fixed as a part of a ring system[7], strongly supports inversion mechanism, where the N=N double bond remains intact. Some theoretical work[8-10] calculated by *ab initio* variation-perturbation[9,11] and CASSCF method[12] provides support for inversion. Therefore, a further investigation of the isomerization of azobenzene is still necessary. The aim of the present work is to investigate the solvent effect on thermal *cis-to-trans* isomerization of azobenzene.

RESULTS AND DISCUSSION

Upon irradiation, *trans*-azobenzene is converted to a photostationary state (PSS), which contains the maximum *cis/trans*-azo-isomer ratio of ca. 80:20 in different solvents. When PSS was reached, irradiation of *trans*-isomer was discontinued and immediately starts kinetic measurement in dark.
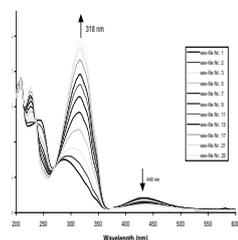
Fig. 2. UV-Vis spectra of thermal decay of *cis*-azobenzene in n-propanol at 56 °C. Time interval: 0 min, 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, 10 h and 13 h, respectively, from bottom to top.

To study the thermal *cis-to-trans* isomerization of azobenzene, this method is well established, and is widely used by many authors.[13, 14] The PSS solution (bottomest spectra in Fig. 2) in different solvents (enriched in *cis* form obtained by irradiation of *trans* form) was used in each case to study the thermal *cis-to-trans* isomerization of azobenzene. This investigation was made by UV/Vis spectrophotometrically between 29 °C and 64.8 °C. The spectral variation for the thermal decay of *cis*-azobenzene at 56 °C in n-propanol were recorded at every 30 min interval and shown in Fig. 2. The observation was continued until the original spectrum of *trans*-form was reached. The spectral variations at different temperatures in different solvents are measured, but not shown in this paper.

The decay of *cis*-azobenzene in n-propanol is associated with the increase in intensity of the π-π^* transition band at 318 nm. The decrease in intensity of the n-π^* transition band at 440 nm was also observed. The isomerization to *trans*-form was found quantitative at all temperatures and in all solvents mentioned above. The decay pattern of *cis*-azobenzene in benzene, n-propanol, acetonitrile and DMSO at 38.2 °C and 64.8 °C are shown in Fig. 3.
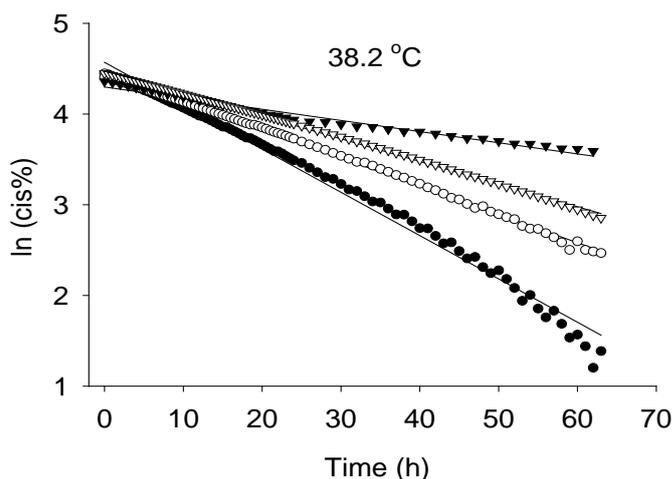
Fig. 3A. Plots showing the thermal decay of *cis*-azobenzene at 38.2 °C temperature in different solvents. . ● Benzene ($r^2 = 0.989$), ○ 1-Propanol ($r^2 = 0.979$), ▼ Acetonitrile ($r^2 = 0.994$), Δ DMSO ($r^2 = 0.990$), —Regression plot.
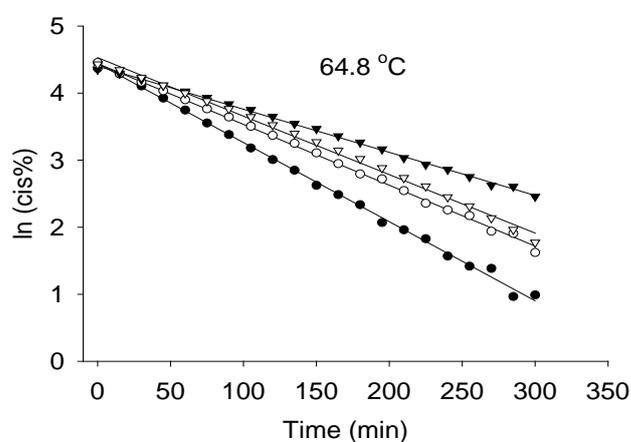
Fig. 3B. Plots showing the thermal decay of *cis*-azobenzene at 64.8 °C temperature in different solvents. ● Benzene ($r^2 = 0.992$), ○ 1-Propanol ($r^2 = 0.969$), ▼ Acetonitrile ($r^2 = 0.938$), Δ DMSO ($r^2 = 0.973$), —Regression plot.

The rate constants at different temperatures and the activation energies, E_a, are shown in Table 1. The decay rate studies in different solvents indicate that there was no significant solvent effect. The rate is slightly faster in non polar solvent (e.g., in benzene), but slower in polar solvents (e.g., in n-propanol or DMSO). This effect is consistent with the work of Halpern *et al.*[15] We have found that the rate at 38.2 °C varies from 9.85×10^{-6} s^{-1} (in benzene) to 5.68×10^{-6} s^{-1} (in DMSO), an approximately, 2-fold variation. The plots shown in Figure 3 as ln (*cis* %) against time in each solvent indicate that the reaction is consistently first order. Nice straight lines were obtained for each of the solvents. The regression co-efficients (r^2) of these straight lines are greater

than 0.98 except in only few cases where these are still greater than 0.93. When ln k was plotted against 1/T, excellent Arrhenius lines were obtained for each of the solvents (Fig. 4). The activation energies, E_a, and the pre-exponential factors, A, of the reaction in different solvents, were calculated from the slopes of these lines, using the Arrhenius equation, $k = A \exp(-E_a/RT)$. We note that in these studies the pre-exponential values obtained in each solvent were found in the same order ($\sim 10^{11}$ s^{-1}). The regression co-efficients (r^2) of these Arrhenius lines are greater than 0.99. The value of E_a obtained in benzene (23.8 kcal/mol) agrees well with the value (E_a=23.7 kcal/mol) reported by Le Fevre and Northcott.[16] The value of E_a in acetonitrile (23.9 kcal/mol) also agrees with the value reported by Halpern *et al.*[15]

Table 1

The rate constants, k_{ct} (s^{-1})^a of *cis*-azobenzene in different solvents

Solvent	Temperature (°C)					E_a (kcal/mol)
	29	38.2	47.2	56.0	64.8	
Benzene	2.95×10^{-6}	9.85×10^{-6}	2.87×10^{-5}	7.65×10^{-5}	2.02×10^{-4}	23.8
1-Propanol		7.28×10^{-6}	1.97×10^{-5}	5.38×10^{-5}	1.39×10^{-4}	23.2
Acetonitrile		4.55×10^{-6}	1.43×10^{-5}	3.72×10^{-5}	9.53×10^{-5}	23.9
DMSO	1.85×10^{-6}	5.68×10^{-6}	1.57×10^{-5}	4.55×10^{-5}	1.18×10^{-4}	23.6

^{a} Error in thermal rate constant, k_{ct} 2-5 %

If a reaction takes place in solution, then the initial reactant as well as the activated complex will be solvated to a different extent, according to the solvating power of the solvent used. This differential solvation can reduce or accelerate the reaction.

According to the Hughes-Ingold rules[17] a change in solvent polarity will have a negligible effect on the rates of the reaction that involve a little or no change in the charge density on going from reactant to the activated complex. During *cis-to-trans* isomerization of azobenzene, on going from polar reactant, *cis*-azobenzene ($\mu = 3.20$ D)[18] to isopolar transition state (neither dipolar nor radical in nature) only small solvent effect can be observed as in our case. This result reasonably explained that the isomerization proceeds via an inversional (isopolar) transition state. The activation
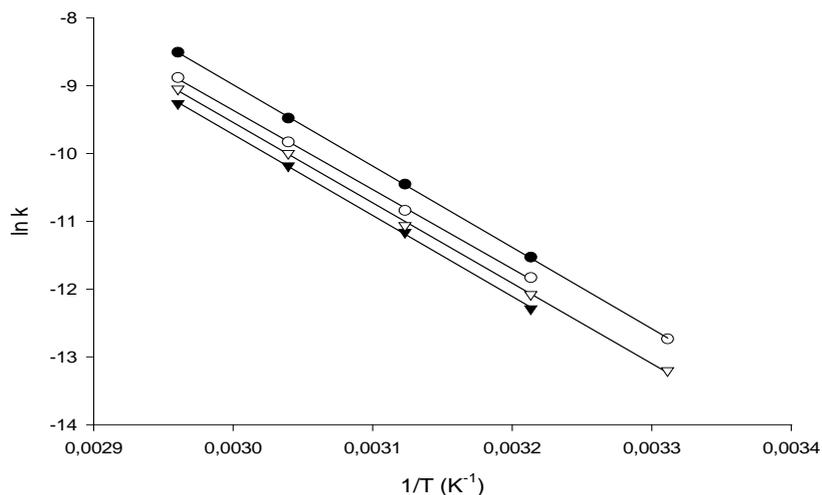
Fig. 4. Arrhenius plot of *cis*-azobenzene in different solvents. ● Benzene ($r^2 = 0.9999$), ○ 1 - Propanol ($r^2 = 0.9994$), ▼ Acetonitrile ($r^2 = 0.9996$), Δ DMSO ($r^2 = 0.9995$),—Regression plot. The temperature range of benzene and DMSO: 302 K–337.8K, n-propanol and acetonitrile: 311.2 K- 337.8 K.

barriers (~23 kcal/mol) obtained in our present work agrees with the activation barriers reported by the theoretical work[9] which supports inversion mechanism.

REFERENCES

1. Z. F. Liu, K. Hashimoto, A. Fujishima, *Nature*, **347,** 658, 1990.

2. Z. Sekkat and M. Dummont, *Appl. Phys., B*, **54**, 486, 1992.

3. T. Ikeda and O. Tsutsumi, *Science*, **268**, 1873, 1995.

4. P. D. Wildes, J. G. Pacifici, G. Irick and D.G. Whitten, *J. Am. Chem. Soc.,* **93**, 2004, 1971.

5. T. Asano, and T. Okada, *J. Org. Chem.*, **49**, 4387, 1984.

6. G. S. Hartly, *J. Chem. Soc.*, 633, 1938.

7. H. Rau and E. Lüddecke, *J. Am. Chem. Soc.,* **104**, 1616, 1982.

8. R. N. Camp, I. R. Epstein and C. Steel, *J. Am. Chem. Soc.*, **99**, 2453, 1977.

9. R. Cimiraglia, T. Asano and H. J. Hofmann, *Gazz. Chim. Ital.*, **126**, 679, 1996.

10. B. M. Gimarc, *J Chem. Soc.,* **92**, 266, 1970.

11. R. Cimiraglia, H. -J., Hofmann, *Chem. Phys. Lett.*, **217**, 430, 1994.

12. P. Cattaneo, and M. Persico, *Phys. Chem. Chem. Phys.*, **1,** 4739, 1999.

13. P. S. Zacharias, S. Ameerunisha and S. R. Korupoju, *J. Chem. Soc., Perkin Trans. 2,* 2055 -2059, 1998.

14. N. Nishimura *et. al*, *J. Chem. Soc., Perkin. Trans. 2,* 1839, 1986.

15. J. HALPERN, G. W. BRADY AND C. A. WINKLER, *Canad. J. Res.*, ***28 B***, 140,   1950.

16. R. J. W. LE FEVRE and J. O. NORTHCOTT, *J. Chem. Soc.*, 867, 1953.

17. C. REICHARDT, "Solvents and Solvent Effects in Organic chemistry"; Verlagsgesellschaft mbH, Germany, 1988.

18. A. L. McCLELLAN,   "Tables of Experimental Dipole moments", W. H. Freeman, San Francisco, Calif. 1963.