ratio A/B differs markedly the expected value and hence the temperature dependence data may not be used to interpret the NMR chemical shift. We also observe from Table 3 that values of A, B and C depend markedly on the location of the NMR nucleus and the dominant contribution to ΔB/B arises from the $1/T^2$ term but the 1/T term is certainly significant.

At this moment it is required to mention that the NMR chemical shift has already been examined and has derived a general mformula for a $4d^1$ system in a strong crystal field environment of octahedral symmetry.[7] It is however found that this formula is not correct, therefore we reexamine the NMR chemical shift for a $4d^1$ system in a strong crystal field environment of octahedral symmetry and derive the correct expression for ΔB/B. We also study further the temperature dependence of ΔB/B.

Acknowlegement. This work is supported, partly, by the Ministry of Education.

References

1. R.M. Golding, R.O. Pascual and C. Suvanprakorn, "Advances Solution Chemistry, Plenum, 129 (1981).
2. R.M. Golding, R.O. Pascual and S. Ahn, *J. Magn, Recon.*, **46**, 406 (1982).
3. L.C. Stubbs, Unpublished Thesis (Ph. D. The University of New South Wales, (1978).
4. R.M. Golding and L.C. Stubbs, Proc. R. Soc. Lond. A. **354**, 223 (1977).
5. B. Bleaney, *J. Magn, Reson.*, **8**, 91 (1972).
6. J.W.M. DeBoer, P.J.D. Sakkers, C.W. Hilbers and E. DeBoer, *J. Magn. Reson.*, **25**, 455 (1977).
7. S. Ahn, S.W. Oh, and E. Park, *Bull. Korean Chem. Soc.*, **4**, 103 (1983).

A Thermal and a Photochemical Mutarotation of α-(D)-Glucose in Dimethyl Sulfoxide

Sang Don Han, Tae Young Lee, and Woo Ki Chae*

Department of Chemistry Education, Seoul National University, Seoul 151. *Received February 28, 1986*

Mutarotation of glucose in aqueous solvent has been extensively investigated,[1] but in nonaqueous solvents a few research works have been reported.[2] Recently, Pincock[3] *et al.* have reported the kinetic study of heterogeneous catalysis of glucose mutarotation by standard alumina suspended in dimethyl sulfoxide. In the alumina catalyzed mutarotation, of course, a thermal mutarotation was assumed to be negligiblle at room temperature. This led us to investigate a thermal and a photochemical mutarotation of α-(D)-glucose in dimethyl sulfoxide. Although the mechanisms of glucose mutarotation in DMSO are not thoroughly understood at present, we wish to report the mechanism including thermodynamic parameters, temperature dependence of quantum yield and the relationship between the rate constants and the quantum yields.

Table 1. Thermodynamic Constants for Mutarotation of α-(D)-Glucose in DMSO and H_2O at 30°C. (a) reference (1) data, (b) this work except ΔH

Solvent	ΔH cal. mol^{-1} deg^{-1}	ΔG cal. mol^{-1}	ΔS e.s.u.
H_2O (a)	-270	-327	0.19
DMSO (b)	-270	-315	0.15

Table 2. Activation Energies for Mutarotation of α(D)-Glucose in DMSO and H_2O at 30°C. (a) Kcal. mol^{-1} (b) cal. mol^{-1}. deg^{-1}. (c) references 7 and 8. (d) this work

Solvent	$E_a{}^a$	$\Delta G^{\neq a}$	$\Delta H^{\neq a}$	$\Delta S^{\neq b}$
H_2O (c)	17.24	24.66	17.24	-24.9
	16.09	22.08	16.09	-19.8
DMSO (d) (thermal)	21.28	23.20	20.0	-10.55
DMSO (d) (photo.)	10.28	22.44	9.62	-42.3

Irradiation[4] of α-(D)-glucose in DMSO causes the photomutarotation and the reaction mixture reaches equilibrium at the optical rotation, [α] = 51°. During the irradiation, a thermal mutarotation was also observed especially at the elevated temperature and the equilibrium mixture showed optical rotation, [α] = 54°.

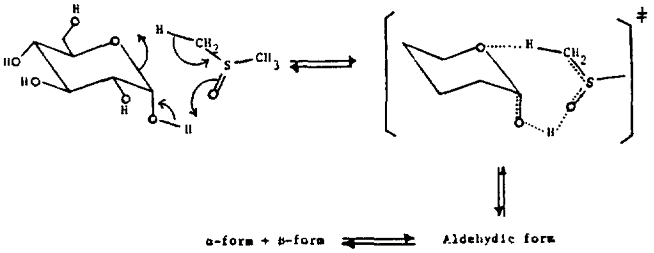
While the thermal mutarotation was reversible, the photomutarotation was irreversible,[5] so that the two different rate equations[6] were used to evaluate the rate constants (Figure 1 and 2). Although the photo-mutarotation is irreversible, photo-mutarotation reaches equilibrium at the optical rotation, [α] = 51°. This equilibrium state may come from that the thermal equilibrium control overrides the irreversible

Table 3. Temperature Dependence of Quantum Yields. (a) Calculated Values Using k_r (photo). (b) Mmol Disappearance vs. Milli Einstein Absorbed

Temp(°C)	k_r (min^{-1}) thermal	k_r (min^{-1}) photo	ϕ^a_{mut} (b)
30	1.06×10^{-4}	3.75×10^{-4}	0.21 (0.20)
40	2.91×10^{-4}	8.69×10^{-4}	0.48 (0.48)
50	1.05×10^{-3}	1.55×10^{-3}	0.86 (0.84)
60	2.09×10^{-3}	2.21×10^{-3}	1.28 (1.25)
70	5.75×10^{-3}	3.30×10^{-3}	1.83 (1.91)

photo-mutarotation.

The thermodynamic constants of mutarotation in water and DMSO are not quite different (Table 1) and the large negative values for the entropies of activation (Table 2) are ascribed to the participation of solvent molecules in the transition state as shown.



The photo-mutarotation is irreversible that the rate constants k_r (Table 3) were used to calculate the quantum yield by the following equation

$$\phi_{mut.} = \frac{C_o}{mE} \cdot k_r t$$

where C_0, initial concentration; t, irradiation time; mE, total absorbed milli Einstein (0.56 mE per hour).[10] As shown in Table 3, the marked increase in quantum yields with temperature may suggest that appreciable energy barriers wil be encountered where the photo-mutarotation is involved. Although it is too early to mention about the energy barriers, it seems likely that the excited species might be in thermal equilibirum or in complexed states with its solvent environment and(or) thermally activated glucose molecules to produce reponsible excited states for the photo-mutarotation whose quantum yields are over unity. Detailed mechanism including the responsible excited state, irreversibility of photo-mutarotation, and temperature dependence of quantum yields are under investigation.

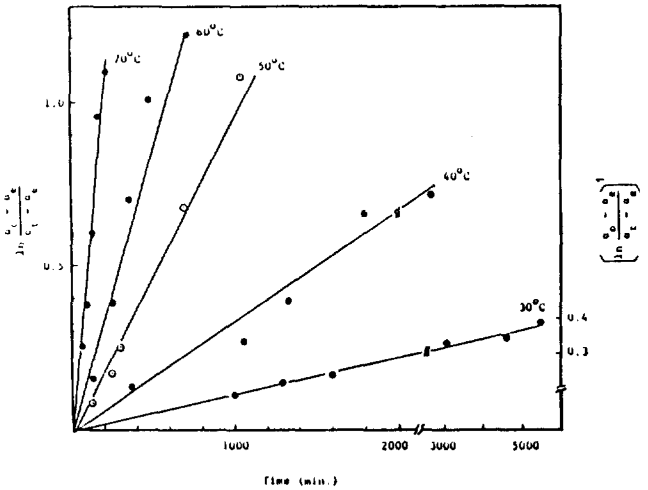


Figure 1. Plots of $\ln \frac{\alpha_0-\alpha_e}{\alpha_t-\alpha_e}$ vs. time (min.) under various temperature: (1), last three points for 30°C.

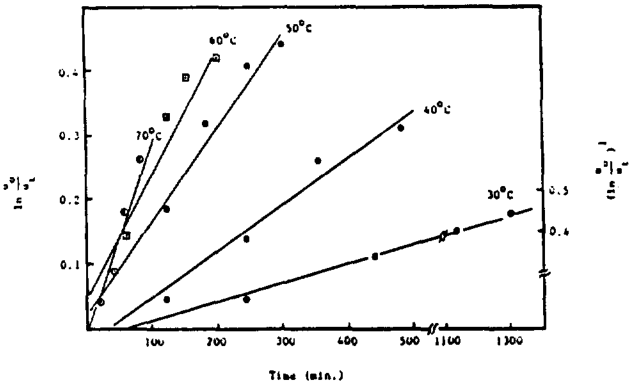


Figure 2. Plots of $\ln \frac{\alpha_0}{\alpha_t}$ vs. time (min.) under various temperature: (1) last two points for 30°C.

Acknowledgement. This work was supported by the Basic Science Research Institute Program (1985), Ministry of Education.

References

1. W. Pigman and H.S. Isbell, *Advan. Carbohyd. Chem.*, **23,** 13 (1968).
2. Brian Capon, *Chem. Rev.*, **69,** 407 (1969).
3. T.D.J. Dustan and R.E. Pincock, *J. Phys. Chem.*, **88,** 5684 (1984).
4. A soslution of 1.0 g (5.55 mmol) of glucose in 10 ml of DMSO was placed in a quartz tube and degassed with purified N_2 gas. Irradiation was carried out with 450 W. medium pressure Hg arc lamp using 7 - 54 corning glass filter (transmission range, 230 - 400 nm). Optical rotation values were obtained by Polarax-ATAGO polarimeter.
5. β-(D)-glucose in DMSO at 47°C mutarotates with k_r of 1.0×10^{-3} min^{-1}. Under irradiation condition, however, the mutarotation of β-form is much slower than that of thermal condition.
6. $\ln \frac{\alpha_0-\alpha_e}{\alpha_t-\alpha_e} = k_r t$ for thermal mutarotation.

   $\ln \frac{\alpha_0}{\alpha_t} = k_r t$ for photo-mutarotation.
7. a) H. Schmid, *Monatsch.*, **94,** 1206 (1963). b) H. Schmid and G. Bauer, **95,** 1781 (1964); **97,** 866 (1966).
8. C.Y. Lee and T.E. Acree, *Carbohyd. Res.*, **1,** 495 (1966).
9. a) R.S. Givens and W.K. Chae, *J. Amer. Chem. Soc.*, **104,** 2456 (1982). b) W.K. Chae, *J. Kor. Chem. Soc.*, **27,** 302 (1983).
10. Light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker, *Proc. Roy. Soc.*, Ser. A, **235,** 518 (1956).