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Photo-Sensitized Mutarotation of α-(D)-Glucose in Dimethyl Sulfoxide (DMSO)

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Mutarotation of glucose in aqueous solvent has been extensively investigated, but in nonaqueous, aprotic solvent, effort to study both thermal and photochemical mutarotations have been severely limited because of poor solubility of glucose in the solvents.

We have first reported[1] the kinetics of photo-mutarotation of α-(D)-glucose including thermodynamic parameters and temperature dependence of quantum yields. In the previous paper, however, the photons and the photochemical effect of DMSO on the photo-mutarotation were not mentioned in detail.

Table 1. Change of Specific Rotations of α-(D)-Glucose on Irradiation at 350 nm. (temp: 34 ± 2 °C)

Time (min.)	Specific Rotations					
	$[\alpha]^W$	$[\alpha]^D$	$[\alpha]^a$	$[\alpha]^{ac}$	$[\alpha]^b$	$[\alpha]^{bc}$
0	106.9	106.9	105.6	105.6	105.8	105.8
514	106.9	106.9	102.5	101.1	101.7	100.6
1224	105.0	105.0	96.9	97.3	93.9	94.2
1562	102.8	102.8	87.2	91.5	86.1	89.3
2752	84.4	84.4	63.3	84.7	62.2	83.3
7200	54.0	54.0	53.9	53.9	54.4	54.0

^{W}wrapped. ^{D}DMSO only. ^{a}acetophenone and DMSO. ^{b}benzophenone and DMSO. ^{ac}acetophenone effect only (corrected for the thermal effect). ^{bc}benzophenone effect only (corrected for the thermal effect).

Table 2. Stern-Volmer Quenching of the Sensitizer's Phosphorescence by Glucose

Sensitizer	kq τ	τ (sec)[3]	kq
Benzophenone	0.409	4.7×10^{-3}	0.1×10^{10}
Acetophenone	0.037	2.3×10^{-3}	1.6×10^{10}

[3] V. L. Ermolaev, Soviet Physics, p. 333 (1963).

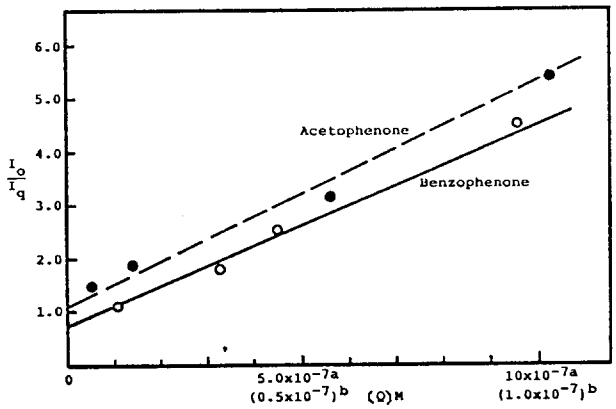

Figure 1. Stern-Volmer Quenching of Acetophenone and Benzophenone Phosphorescence by Glucose. (I_q and I_o represent the phosphorescence intensity with and without quencher respectively. *a* and *b* represent the Concentration of Quencher for Benzophenone and Acetophenone respectively).

In this paper, we wish to discuss the photochemical mechanism including the roles of DMSO, benzophenone and acetophenone.

Since the glucose molecule does not have any UV absorbing chromophores, the photo-mutarotations were not expected. However, irradiation of α-(D)-glucose in DMSO at 254 nm caused glucose molecule to mutarotate. To investigate the roles of DMSO, some classical sensitizers such as benzophenone and acetophenone were chosen for the sensitized mutarotations.

Irradiation[2] of α-(D)-glucose in DMSO with benzophenone or acetophenone at 350 nm showed mutarotations and the reaction mixtures reached equilibrium at the optical rotation, $[\alpha] = 53.9°$.

The phosphorescence of benzophenone and acetophenone were quenched efficiently by glucose molecules and showed linear Stern-Volmer relations (Table 2 and Figure 1).

Irradiation of α-(D)-glucose in DMSO without benzophenone or acetophenone at 350 nm showed no mutarotation (Table 1), however, irradiation at 254 and 300 nm caused an efficient mutarotation (Table 3).

The mutarotation at 254 nm in DMSO is not an unexpected result since DMSO molecule has a chromophore absorbing at 250-260 nm.

α-(D)-Glucose in water did not mutarotate at any wavelength of irradiation. This is an understandable fact considering the absence of UV-absorbing chromophores both in water and glucose. α-(D)-Glucose in DMSO, however, showed a chromophores absorbing at 285-290 nm, which would be

Table 3. Efficiency of the Photo-mutarotation by some Sensitizers at Different Wavelengths

Solvent	Sensitizers	Quantum Yields		
		254 nm	300 nm	350 nm
DMSO	DMSO	0.48[1]	0.031	0.00
DMSO	Benzophenone			0.005
DMSO	Acetophenone			0.004

[1]previous work, ref. (1).

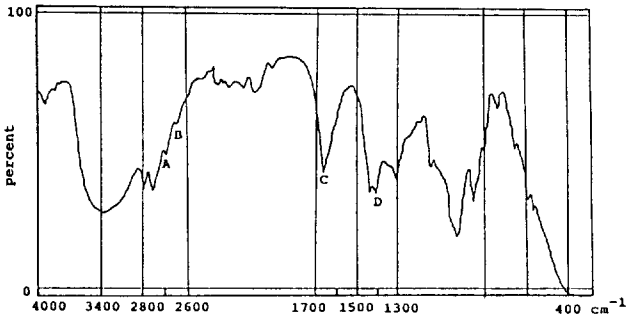

Figure 2. IR Spectrum of Glucose in DMSO. A and B. Aldehydic C-H stretch, 2800 and 2700 cm^{-1}. C. Aldehydic C=O stretch, 1675 cm^{-1}. D. Aldehydic C-H bend, 1390 cm^{-1}.

Table 4. Mutarotation of Glucose with various Sensitizers

Solvent	Sensitizers	Triplet Energy (Kcal/mol)	Mutarotation	
			300 nm	350 nm
DMSO	Fluorene	67.5	Yes	
DMSO	Naphthalene	61	No	
DMSO	2-Acetylnaphthalene	59	No	No
DMSO	1-Acetylnaphthalene	57	No	

responsible for the mutarotation on the direct irradiation at 300 nm in DMSO. The infrared spectrum of glucose in DMSO shows a typical aldehydic absorption characteristics at 1675 cm^{-1}, which is 30 cm^{-1} lower than a normal aldehyde due to the hydrogen bond between an aldehydic group and hydroxyl groups of glucose (Figure 2). The aldehydic group of glucose in DMSO was further confirmed by the doublet absorption at 2700 and 2800 cm^{-1} due to Fermi resonance with overtone of C-H bending band at 1400 cm^{-1}. The UV absorption of glucose in DMSO at 285 nm is ascribed to the aldehydic group which generally appears at 290-295 nm.

This aldehydic form of glucose would quench the phosphorescence of acetophenone and of benzophenone, and undergoes to the triplet excited state. However the possibility of hydrogen abstraction of sensitizers from anomeric hydroxide of glucose cannot be eliminated. Since benzophenone and acetophenone could abstract hydrogen from the anomeric hydroxide of glucose, mutarotations with fluorene, naphthalene, 1-acetylnaphthalene and 2-acetylnaphthalene were investigated and the results were shown in Table 4. Naphthalene (E_T = 61 Kcal), as expected, did not cause glucose to mutarotate but fluorene (E_T = 67.6 Kcal) which does not abstract hydrogen showed mutarotation, and 1-acetylnaphthalene (E_T = 57 Kcal) which could abstract hydrogen[5] also did not show mutarotation of glucose. These results could eliminate the hydrogen abstraction mechanism for the photo-mutarotation.

Based upon the sensitizations, Stern-Volmer quenching study and the wavelength discrepancy, the photochemical mechanism of the mutarotation were suggested as follows:

Sensitizer (Sen.): DMSO, Acetophenone, Benzophenone and Fluorene.

$$\alpha\text{-(D)-Glucose} \xrightarrow{\text{DMSO}} \text{Aldehydic Form (Ald-G)}$$

$$\text{Sen.} \xrightarrow{h\nu} {}^1[\text{Sen.}]^*$$

$${}^1[\text{Sen.}]^* \xrightarrow{\text{isc}} {}^3[\text{Sen.}]^*$$

$${}^3[\text{Sen.}]^* \longrightarrow \text{Sen.} + h\nu_p$$

$$\text{Ald-G} + {}^3[\text{Sen.}]^* \longrightarrow {}^3[\text{Ald-G}]^* + \text{Sen.}$$

$${}^3[\text{Ald-G}]^* \longrightarrow \alpha\text{-(D)-Glucose} + \beta\text{-(D)-Glucose}$$

A conclusion is that an efficient energy transfer occurs from the triplet state of sensitizers to the aldehydic form of glucose molecules, that results sensitized photo-mutarotations of glucose.

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2. A solution of 1.440 g of α-(D)-glucose in 80 m*l* of anhydrous DMSO was equally devided into four portions. Acetophenone, 260 mg, was dissolved in the first portion and benzophenone, 400 mg, was dissolved in the second portion. One of the remaining portions was wrapped by aluminum foil to protect from the irradiation. Each portion was poured into Pyrex tubes and degassed with purified nitrogen. After degassing, the samples were irradiated with 16 RPR-3500 Å lamps. The change in the optical rotation during the photo-mutarotation was determined by Polarax-ATAGO polarimeter.
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4. Light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker, *Proc. Roy. Soc. Ser.*, **A235**, 518 (1956).
5. Configuration of the lowest excited triplet states for 1- and 2-acetylnaphthalene are n, π^*, however, the hydrogen abstraction from glucose is throught not to be eliminated.

α-Chlorination of Ketones Using *m*-Chloroperbenzoic Acid / Hydrogen Chloride / N,N-Dimethylformamide System

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