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자체증감작용으로 인한 옥소디피로메텐의 광산소화반응

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Self-Sensitized Photooxygenation of Oxodipyrromethene

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요 약. 빌리루빈의 경우와 같이 옥소디피로메텐도 자체증감작용으로 생긴 단일상태 산소와 반응하여 광분해 하였다. 단일상태 산소의 수명이 각각 다른 용매에서 시험한 결과, 수명이 더 긴 용매에서 옥소디피로메텐의 광산화반응이 빨랐으며, 단일상태 산소의 퀜칭제가 존재하는데서는 광반응이 느렸다. 더우기, 증감제를 사용하지 않은 반응에서 생성물이 증감제를 사용한 반응에서 생성물과 같았다.

ABSTRACTS. Oxodipyrromethene was degraded by a self-photosensitized reaction, similar to the degradation of bilirubin by other investigators. Photodegradation of oxodipyrromethene was faster in methanol-d_4, in which the life time of singlet oxygen is longer, than in methanol. It was slower in a solvent which contained a singlet oxygen quencher. Moreover, the products from sensitized and unsensitized reactions are same.

INTRODUCTION

Bilirubin is known to undergo a self-sensitized photooxygenation. In 1971 McDonagh[1] postulated that bilirubin photooxygenation is a self-sensitized reaction involving singlet oxygen, $^1O_2$

$$BR \xrightarrow{h\nu} BR^* \xrightarrow{^3O_2} BR + {}^1O_2$$
$$^1O_2 + BR \longrightarrow \text{Products}$$

More evidence[2] for the self-sensitizing reaction of bilirubin was provided by the following: First, photooxidation of 2, 5-dimethylfuran in methanolic 0.05 *M* NH_3 (100 m*l*) was sensitized by the addition of bilirubin (155 μmole); second, when bilirubin was irradiated in 0.05 *M* NH_3 in CD_3OD, a five-fold increase in photo degradation over that found for the methanol control was observed. We would like to report the self-sensitizing action of oxodipyrromethene.

RESULTS AND DISCUSSION

To observe the self-sensitizing action for oxodipyrromethene **1**, an appropriate concentration of the oxodipyrromethene **1** ($2.7\times10^{-5}M$) with added radical inhibitor (DBP), singlet oxygen quencher (DABCO), or spin trapping agent (PBN) was prepared in methanol (2 m*l*)

Table 1. Percentage of oxodipyrromethene **1** transformed with or without quencher *vs.* irradiation period.

Condition Solvents	% Transformed*			% Transformed**	
	10 min	60 min	140 min	40 min	130 min
MeOH (Control)	23.7	26.7	37.5	3.9	18
Methanol-d_4	32.8	87.8***	.....	81.8	.....
PBN^+ (4.5×10^{-4} *M*) MeOH	22.0	25.0	33.0	3.5	14.5
DBP^+ (1.5×10^{-3} *M*) MoOH	23.0	27.0	36.3	3.6	17.4
DBP^+ (1.5×10^{-2} *M*) MeOH	23.0	27.0	36.0	4.1	17.1
$DABCO^+$ (1.5×10^{-3} *M*)	23.0	26.0	31.2	3.5	10.7

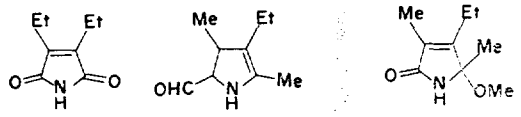
*Absorbancy differences. **% Transformed beginning after 10min irradiation (after photoisomerization probably). ***50 min irradiation. †PBN (phenyl-*t*-butyl nitrone), DBP (di-*t*-butylphenol), DABCO (1, 4-diazabicyclo 2, 2, 2-octane).

and **1** was irradiated by monochromatic light (at 417 nm, λ_{max} of **1**, Hg-lamp, 100 W). The appropriate results are summarized in *Table* 1.

The reaction rate was 3.3 times faster in methanol-d_4 than that in methanol. (It was 21 times faster in methanol-d_4 than in methanol when measuring the rates after 10 minutes of photoisomerization. The *Z*-oxodipyrromethene **1** was photoisomerized to the *E*-isomer at the early stage of the reaction[3]. These data indicate that $^1O_2$ from self-sensitizing by the oxodipyrromethene **1** was involved at the late stage in the reactions, since the life time of $^1O_2$ is longer in methanol-d_4.[4,5] The self-sensitized reaction was inhibited by 1, 4-diazabicyclo 2, 2, 2-octane (DABCO), a $^1O_2$ quencher[6] in the latter stage of the reaction. At the beginning of the reaction, the rate was the same as in the control experiment, presumably because DABCO did not interfere with the initial photoisomerization. This behavior is consistent with the conclusion that the reaction is a self-sensitizing reaction. Davidson and Trethewey[7] recently reported that high concentration of DABCO ($5\times10^{-2}M$) quenches the excited singlet states of the dyes (RB, methylene blue). Thus, the concentration of DABCO should be lower than 5×10^{-2} *M*. No appreciable effects of DBP (di-*t*-butylphenol), a radical inhibitor,[8] and PBN (phenyl-*t*-butylnitrone), a spin trapping agent, were observed. Therefore, no radical intermediate appears to be involved.

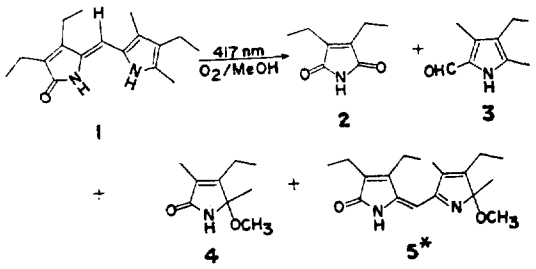
For comparison of the product distribution of dye-sensitized and self-sensitized reactions, the following experiment was done. A sample of the stock solution of **1** (17 m*l* from 0.1 mg/100 m*l* MeOH) was diluted to 25 m*l* with methanol. The solution was irradiated with monochromatic light (at 417 nm, Hg-lamp) in long quartz cell (2 cm diameter, 10 cm long) for 50 hrs (90 % reacted).

After evaporation of the solvent, analytical TLC gave *Rf* values in chloroform/ether (6:4) of 0.82, 0.79, 0.72, 0.65, 0.29, 0.16 and 0.09. The *Rf* values of **2**, **3** and **4** are 0.65, 0.29 and 0.16 respectively.



2 **3** **4**

The same pattern was observed for other developing solvents (*e. g.* ethylacetate). The products with *Rf* values of 0.82, 0.79, 0.72 and 0.09 have not yet been identified. The identified products, except **3**, were also obtained from broad spectrum light irradiation of **1**[9]. The results are depicted as follows.



*Not identified here, but from Quisted's[9].

The stock solution of **1** (17 m*l*) containing 1 m*l* of rose bengal (RB) stock solution (2 mg/10 m*l* MeOH) was diluted to 25 m*l* with methanol. The solution was irradiated at 557 nm (monochromatic litht, tungsten lamp, λ_{max} of RB) in a long quartz cell (2 cm diameter, 10 cm long) for 30min (90 % reacted). Analytical TLC gave *Rf* values of 0.83, 0.63, 0.31 and 0.16 in $CHCl_3/Et_2^0$) (6:4). The *Rf* values of **2**, **3** and **4** are 0.63, 0.31 and 0.16 respectively. The same pattern was observed in other developing solvents (*e.g.* AcOEt). The compound of *Rf*=0.83 has not yet been identified. The product distribution was simpler than that in the unsensitized reaction. However, the products (*e.g.* **2**, **3** and **4**) were the same as those in self-sensitized reaction.

When 17 m*l* of stock solution of **1**, containing 0.05 m*l* of conc. NH_4OH and 1 m*l* rose bengal stock solution (2 mg/10 m*l*) was diluted to 25 m*l* with methanol and irradiated at 557 nm (monochromatic light, tungsten lamp, 15 W) the above three products were identified in addition to three other products.

These results have three significant aspects. One is that the products of the sensitized photooxygenation of **1** were aslo obtained in the unsensitized photooxidation of **1** (with or with out conc. NH_4OH), indicating self-sensitized reaction. The second is that the aldehyde **3** was isolated (the isolated **3** gave an identical UV spectra to authentic kryptopyrrolealdehyde, λ_{max} =315 nm). The aldehyde **3** could not be detected in broad spectrum light irradiation of **1**,[9] possibly because the aldehyde **3** underwent further oxidation to give **4**. The third is that the sensitizer, rose bengal, when it is irradiated, accelerates the photooxygenation 100 times. (Compare reaction time for 90 % change).

The oxodipyrromethene **1** was photooxygenated by a self-sensitizing $^1O_2$ reaction, since (i) the reaction rate was 21 times faster in methanol-d_4 than in methanol when measuring the rates after 10 min irradiation (isomerization), (ii) DABCO, a singlet oxygen quencher, inhibits the latter stage of the photooxidation reaction, but did not inhibit the early stage of the reaction, (iii) no effect of radical inhibition (DBP) and spin trapping agent (PBN) was observed, and (iv) the product distribution of the sensitized photooxygenation of **1** is similar to that of the unsensitized reaction.

EXPERIMENTAL

Solvents were reagent grade unless otherwise specified. Nuclear magnetic resonance spectra were measured in deuteriochloroform on a Varian A-60 Perkin-Elmer R-24 B. Visible and UV spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were obtained from samples in chloroform with a Beckman IR-8 spectrophotometer. Kinetic photooxygenation studies with quenchers were accomplished in uv cell (1 cm path, 2 m*l*) using 10 nm band pass monochromatic light from a Bausch and Lomb monochromator (Model 33-86-07) equipped with a 100 W super pressure Hg-lamp. Some preparative photochemical reactions were carried out with the above monochromator equipped with 100 W super pressure Hg-lamp or 15 W-tungsten lamp. The plates used for analytical thin layer chromatography (TLC) (20cm×5 cm) were prepared with *ca.* 1g of

absorbent (0.05~0.2 mm silica gel F, M. Woelm, Eschwege) giving a layer thickness of 0.5 mm.

The oxodipyrromethene **1** was prepared by method of Lightner and Quistad[10,11] in 52% yield, m.p 238~240 °C (*lit.*[11]. 238° (*d*)): nmr ($CDCl_3$), δ 1.06 (*t*, 3H, J=7.5 Hz, CH_3), 1.13 (*t*, 3H, J=7.5 Hz, CH_3), 1.20 (*t*, 3H, J=7.5 Hz, CH_3), 2.13 (*s*, 3H, CH_3-C=), 2.38 (*s*, 3H, CH_3-C=), 2.43 (*q*, 4H, J=7.5 Hz, $2CH_2$), 6.10 (*s*, 1H, CH=); UV (methanol), λ_{max}=417 nm, $\varepsilon_{417}=3.6\times10^4$, (chloroform), λ_{max}=408 nm, $\varepsilon_{408}=3.4\times104$; ir ($cm^{-1}$, in CCl_4), 3410 (NH), 3000 (CH), 1670 (C=O), 1640 (C=C); (in KBr), 3400(NH), 3200 (NH hydrogen bonded), 1650 (C=O), 1625 (C=C).

For analytical TLC studies, the authentic samples (*e.g.* **2**, **4**) were prepared by the preparative photooxygenation of **1**.[9] Spectroscopic (nmr, ir, mass spectra) and physical properties were identical with those of the compounds reported. Kryptopyrrole aldehyde (**3**) was also prepared by a Vilsmeier reaction on kryptopyrrole.[12]

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