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Solvent Effect on Photooxidation of Triphenylphosphine Selenide Sensitized by Polymer-supported Rose Bengal

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Synopsis. Solvent effect on the photooxygenation of triphenylphosphine selenide was examined by using cross-linked polystyrene- or silica gel-anchored Rose Bengal as sensitizers. Different types of solvent dependency of the product yields were observed in each case.

Recently, polymer-supported photosensitizers have been extensively utilized for synthetic photochemistry.[1] For instance, Rose Bengal anchored to 1%-crosslinked polystyrene beads have been successfully applied to the photogeneration of singlet oxygen.[2]

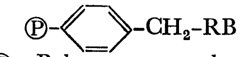
As part of our continuing interest in the photosensitized oxidation of thione compounds,[3] we have examined the photosensitized oxidation of triphenylphosphine selenide which has not yet been studied thus far, and shed light on the properties of Rose Bengal bound to different types of supports.

Results and Discussion

First, the efficiency of Rose Bengal itself as a sensitizer was examined in various solvents. Triphenylphosphine selenide was irradiated under oxygen bubbling for 5 h in the presence of Rose Bengal in $Me_2C{=}O$, MeCN, MeOH, and $CHCl_3$–MeOH (1:1 V/V) affording the corresponding oxide in 3, 11, 78, and 92% of isolated yields, respectively, but no product was obtained in nonpolar solvents such as benzene, $CHCl_3$, and CS_2, because Rose Bengal is not soluble in these solvents.

$$Ph_3P{=}Se + O_2 \xrightarrow[\text{5 h, Rose Bengal}]{\text{CHCl}_3\text{-MeOH, } h\nu} \underset{(92\%)}{Ph_3P{=}O} + \underset{(75\%)}{Se}$$

Meanwhile, the effect of solvent on product yields for the reaction with styrene–1%-divinylbenzene copolymer-bound Rose Bengal (Ⓟ-RB: **1**) as a sensitizer was compared with that with silica gel-bound Rose Bengal (Ⓢ-RB: **2**).[4] Tables 1 and 2 list the yields for **1** and **2**, respectively. Inspection of these tables reveals that the yield is solvent dependent in both cases.



(**1**) Ⓢ-$(CH_2)_3$-RB (**2**)

Ⓟ = Polystyrene copolymer; RB = Rose Bengal; Ⓢ = silica gel.

When **1** was employed, the yield of the product decreased in the order: CH_2Cl_2–MeOH (1:1) > $CHCl_3$ > CH_2Cl_2 > benzene–MeOH (1:1) > CCl_4 > benzene > MeCN > MeOH. Apparently, **1** did not act as a sensitizer in MeOH because of the hydrophobicity of the polystyrene copolymer bead. The lifetime of singlet oxygen in single component solvents was reported to decrease in the following order: CCl_4 > $CHCl_3$ > benzene ≥ MeCN > MeOH,[5] whereas the degree of swelling of the bead decreases in the order: benzene > $CHCl_3$ > CH_2Cl_2 > CCl_4 > MeCN > MeOH. It is apparent, therefore, that neither the swelling index nor the lifetime of singlet oxygen alone can account for the observed order, but a combination thereof may be a possible explanation for that. The interesting finding is that the photooxidation is more efficient in MeOH-containing solvents such as $CHCl_3$–MeOH and benzene–MeOH than in $CHCl_3$ and benzene, respectively, although MeOH swells the polystyrene bead least and decreases the lifetime of singlet oxygen most of all the solvents examined.[6] This effect of MeOH is best explained if the reaction involves the intermediacy of the zwitterion having a structure like **4** (the peroxyselenide) depicted in Scheme 1 and if MeOH acts as the hydrogen-bonding donor toward **4**, thus promoting the nucleophilic attack on the negative oxygen by the second phosphine selenide. In aprotic solvents the intermediate **4** dissociates readily into the original selenide and ground-state dioxygen.

Table 1. Solvent effect on the photo-sensitized oxygenation of triphenylphosphine selenide by polystyrene-supported Rose Bengal (**1**)[a]

Solvent	$Ph_3P{=}O$ (%)	$Ph_3P{=}Se$ (recovered) (%)	Swelling index[c]	Lifetime of $O_2{}^1$/μs
CH_2Cl_2-MeOH (1:1)	91	5	—	—
CH_2Cl_2-MeOH[b] (1:1)	32	61	—	—
$CHCl_3$	68	20	5.15	60
$CHCl_3$[b]	<1	95	—	—
CH_2Cl_2	55	31	4.46	—
Benzene-MeOH (1:1)	50	21	—	—
CCl_4	43	39	4.30	711
Benzene	5	90	5.54	24
MeCN	2	93	2.77	30
MeOH	<1	96	1.07	7

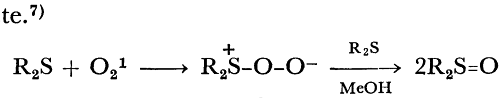
a) **1**: 100 mg; $Ph_3P{=}Se$: 0.5 mmol. Irradiated for 4 h. b) 1 mmol of DABCO was added. c) Swelling indices of 2%-crosslinked polystyrene bead: Swollen volume/dry volume.

TABLE 2. SOLVENT EFFECT ON THE PHOTOSENSITIZED OXYGENATION USING SILICA GEL-BOUND ROSE BENGAL (**2**)[a)]

Sovent	$Ph_3P=O$ (%)	$Ph_3P=Se$ (%)
CCl_4	84	3
CH_2Cl_2	76	16
CH_2Cl_2[b)]	28	c
$CHCl_3$	71	10
CH_2Cl_2-MeOH (1:1)	67	20
Benzene	43	43
MeCN	43	39
MeOH	39	34

a) **1**: 200 mg; $Ph_3P=Se$: 0.5 mmol: irradiated for 2 h. b) $Ph_3P=Se$: 0.167 mmol. c) Not determined.

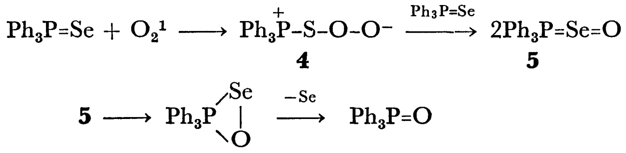
A similar rate-enhancement due to hydrogen-bonding interaction between a zwitterion and MeOH was reported in the singlet oxygenation of sulfide in which the persulfoxide **3** is involved as a reactive intermediate.[7)]



$$R_2S + O_2^1 \longrightarrow R_2\overset{+}{S}\text{-}O\text{-}O^- \xrightarrow[\text{MeOH}]{R_2S} 2R_2S{=}O$$

3

Addition of 1,4-diazabicyclo[2.2.2]octane (DABCo), a typical singlet oxygen quencher, significantly inhibits the formation of the phosphine oxide especially in nonpolar solvents, implying that singlet oxygen is the only oxidizing species.[8)] Thus, one of the tentative mechanisms of the oxidation may be visualized as follows: The initial pre-equilibrium formation of the peroxyselenide **4**, followed by attack of another selenide on it, yields the oxyselenide **5**, which rearranges and then eliminates selenium, eventually giving the phosphine oxide.



Scheme 1.

On the other hand, when Ⓢ-RB (**2**) was employed,[9)] the sequence of the solvent effect on the yield was quite similar to that expected from the lifetime of singlet oxygen (Table 2). In contrast to the case with Ⓟ-RB (**1**) or Rose Bengal itself, no rate-enhancement by MeOH was observed. This is due to the fact that singlet oxygen, photogenerated in a silica particle, does not have sufficient lifetime to diffuse out of the particle with a diameter of 10^{-2} cm, since singlet oxygen has a short mean radius of diffusion of less than 10^{-4} cm during the lifetime.[10)] The singlet oxygen would then react with triphenylphosphine selenide predominantly in the solvent channel of the same particle, giving **4**, which is then strongly adsorbed at the silica gel through hydrogen-bonding to react with another selenide. Even in MeOH solvent, **4** may hydrogen-bond effectively to silica rather than to MeOH. Accordingly, the main factor to determine the solvent effect is to be the lifetime or concentration of singlet oxygen in the solvent in question.

In conclusion, with Ⓟ-RB as a sensitizer, the yield of the phosphine oxide is remarkably increased by addition of MeOH, while with Ⓢ-RB, the solvent dependency of the yield just parallels the lifetime or concentration of singlet oxygen and thus the yield is the lowest in MeOH.

Experimental

Materials. Chloromethylated 1%-crosslinked polystyrene beads (0.75 meq CH_2Cl/g resin; 300 mesh) were purchased from Bio Rad Laboratories, Richmond, Cal. and Silica gel (Wakogel C-300) from Wako Pure Chemical Industry, Tokyo. Polystyrene-supported Rose Bengal (**1**: 2 mg of Rose Bengal per g of the polymer) was prepared according to the method of Blossey and Neckers.[2)] Silica gel-supported Rose Bengal (**2**) was prepared by heating a DMF solution of Rose Bengal and silica gel modified with (3-chloropropyl)trichlorosilane at 120 °C for 20 h.[4)] The resultant reddish silica gel was filtered and washed successively with H_2O, acetone, and $CHCl_3$ and then continuously extracted with $CHCl_3$–MeOH (1:1) until the color due to Rose Bengal did not come out into the eluent. The silica gel thus obtained (**2**: 0.3 mg of Rose Bengal per g of silica gel) was dried in a vacuum oven at 60 °C for 5 h.

Photooxidation of Triphenylphosphine Selenide Using Rose Bengal. Triphenylphosphine selenide (0.5 mmol) and 5 mg of Rose Bengal dissolved in 25 cm^3 of $CHCl_3$–MeOH (1:1) were placed in a Pyrex tube and irradiated with a tungsten-halogen lamp (500 W) under O_2 bubbling for 5 h until the selenide disappeared completely. The filtrate was concentrated to 0.5 cm^3 and the residue was chromatographed on TLC (Kieselgel 60, benzene) giving 92% of triphenylphosphine oxide.

General Procedure for Photooxygenation with Polymer-supported Rose Bengal. The selenide (0.5 mmol) and **1** (100 mg) or **2** (200 mg) in 25 cm^3 of a solvent were placed in a Pyrex tube with a magnetic stir bar and irradiated under O_2 bubbling with the tungsten lamp. After the irradiation, the polymer was filtered off and the filtrate was concentrated to 0.5 cm^3. The residue was subjected to TLC analysis. The results are summarized in Tables 1 and 2.

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