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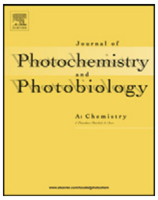

Selective photosensitized oxidation and its catalytic regulation of monoterpene with molecular oxygen in different reaction media

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ABSTRACT

The photo-catalytic oxidation of α-pinene, β-pinene and limonene with molecular oxygen sensitized by tetrachlorotetraiodo-fluorescein sodium salt (RB) has been studied in different reaction media under green light irradiation. Simple and efficient photosensitized oxidation equipment was employed successfully to improve the efficiency of the photosensitized reaction. The results indicate that the photosensitized oxidation products can be directly obtained without after-treatment by reductive reagent. Furthermore, it was found that the product distributions are remarkably affected by reaction media, and that N,N-dimethylformamide (DMF) can regulate the selectivity to products. In particular, the good selectivity (85%) to the main product (myrtenal) and the excellent conversion (99%) were obtained in the absence of any other catalysts when DMF was used as reaction solvent in the photosensitized oxidation of β-pinene. Moreover, the possible photosensitized oxidation reaction mechanism in different media was suggested in the present work.

1. Introduction

Selective oxidation of alkenes by molecular oxygen is one of the current challenges in the manufacture of organic building blocks and industrial intermediates [1–7], and photosensitized oxidation holds special promise for yielding product specificity [8,9]. There are two well-established paths of dye-sensitized photo-oxidation: the energy-transfer pathway and the electron-transfer pathway [10,11]. Unfortunately, in many cases, the two paths of photo-oxidation occur simultaneously. Although the photosensitized oxidation has been found many applications in the field of synthesis, control of regio- and stereo selectivity are still difficult issues and the selectivity of oxidation reactions is not high [12]. To gain excellent selectivity in these reactions, various efforts have been made in the past decades, and remarkable control of the reaction pathway by the use of organized and constrained media [13–20]. In previous works, Tung et al. [21] used *trans*-stilbene as a substrate and successfully demonstrated that a good control of the selectivity in the photo-oxidation process might be achieved by isolation of the substrate within Na-ZSM-5 zeolites from the sensitizer 9,10-dicyanoanthracene (DCA) in the surrounding solution. The photo-oxidation yields the endoperoxide as an intermediate of 1,4-cycloaddition of $^1O_2$, which would decompose to give benzaldehyde at 100% yield as the final product. Li et al. [22] reported the photo oxidation of pinene sensitized by DCA under ultraviolet light irradiation (with a 450-W medium pressure Hg lamp as light source) in homogeneous solution, followed by reduction of the reaction mixture with sodium sulfite solution, giving the '*ene*' products and '*non-ene*' products. Recently, Maldotti et al. [23] have found that a composite palladium porphyrin photo-catalyst is an excellent sensitizer in photo-oxidation of cyclohexene by molecular oxygen. The reaction gives cyclohexene hydroperoxide as the major product with a high selectivity up to 90%, whereas cyclohexenol and cyclohexenone are only formed in a trace amount. Sehlotho and Nyokong have employed zinc phthalocyanine as the sensitizer [24]. This complex, as compared to palladium porphyrin, can utilize a larger portion of solar light. The sensitized reaction, however, results in several products with low selectivity. The catalyst itself also suffers a serious bleaching during the reaction. In addition, such undesirable degradation is also found with other phthalocyanines of iron, cobalt and manganese, during the thermally catalytic oxidation of alkenes [25–28].

In this work, a novel photosensitized catalytic oxidation for monoterpene with molecular oxygen sensitized by tetrachlorotetraiodo fluorescein sodium salt (RB) under high pressure sodium lamp irradiation was studied. The catalyst was added into the reaction system and the photosensitized oxidation products were directly obtained without after-treatment by reductive reagent. Furthermore, a special effect on the photosensitized oxidation reac-

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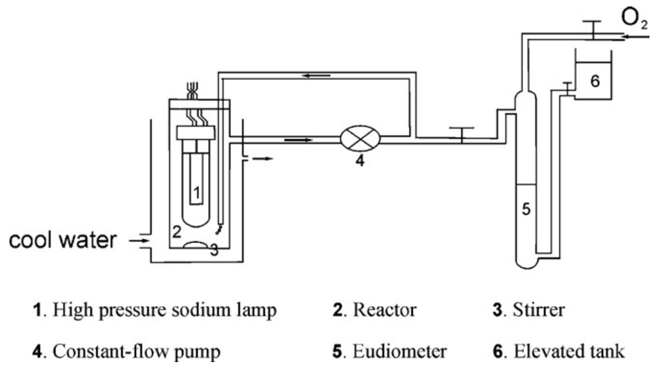


Fig. 1. Experimental equipment for photosensitized oxidation.

tion was observed when N,N-dimethylformamide (DMF) was used as solvent, and the selectivity to the main product can be efficiently improved. This finding may be very significant to establish a new synthesis process in organic photochemistry fields.

2. Experimental

2.1. Reagents and instrument

α-Pinene, β-pinene and limonene were distilled under reduced pressure from turpentine oil; 2,6-lutidine was purchased from BDH Chemicals Ltd., Poole, England; acetic anhydride (AR), tetrachlorotetraiodo-fluorescein sodium salt (RB), methyl alcohol (AR), DMF (AR) and decalin (AR) were purchased from chemical reagent factory of Shanghai. A 110 W high-pressure sodium lamp was used as the green irradiation source. Gas chromatography (GC) analysis was performed on an Agilent 6890 equipped with an FID detector and a quartz capillary column (DB-5, 30 m × 0.25 mm × 0.25 μm). Mass spectra (MS) were run on an America Varian Saturn 2100T GC–MS instrument.

2.2. Experiment process of photosensitized oxidation

All the photosensitized oxidation reactions were carried out in a water-bathed reactor with the inner-circulated molecular oxygen as oxidant and the immersed high-pressure sodium lamp as the green irradiation light source (see Fig. 1). Firstly, the methyl alcohol or DMF solution of 0.5 mol/L substrate concentration was prepared; then, the sensitizer (RB) and catalyst (5 wt.% of substrate) were added into the reactor. After the photosensitized oxidation was performed for 4 h at room temperature, the final products were identified by GC–MS and the products were quantitatively analyzed by the internal standard method (decalin was used as internal standard sample).

3. Results and discussion

3.1. Photosensitized oxidation of α-pinene

The RB-sensitized photooxidation reaction of α-pinene with molecular oxygen was examined in different reaction media. After irradiation by the high-pressure sodium lamp, the '*ene*' products verbenol (**2**), myrtenol (**5**), and the '*non-ene*' products myrental (**4**), verbenone (**3**), 4-Hydroxy-2,3-epioxypinane (**6**) and 1-Hydroxy-2,3-epioxypinane (**7**) have been obtained, as is shown in Scheme 1(a). The product selectivity distributions in various different reaction media are given in Table 1. The most probable photosensitized oxidation reaction path may be described as through a hydroperoxide intermediate process.

In Table 1, it is clearly shown that the 2,6-lutidine and acetic anhydride can efficiently catalyze the photosensitized oxidation reaction of α-pinene in Table 1. It is worth mentioning that the photosensitized oxidation products can be directly obtained in the absence of any other catalysts and the residues (non-volatile substances) are minimal when DMF is used as solvent. Furthermore, the selectivity to the main product verbenone is remarkably improved also, and the selectivity to verbenone is up to 51% with 98% conversion in DMF solution. However, 97% conversion with 42% selectivity to verbenone is only afforded under the catalysis of 2,6-lutidine combined with acetic anhydride in methyl alcohol solution. The possible reason is that DMF itself possesses a zwitterion resonance structure with characteristics of acidity and basicity, which prompts decomposition or reduction of the hydroperoxide intermediate to the corresponding aldehyde, ketone and alcohols. In addition, the selectivity to the main product and conversion of material are affected by the method of addition of the catalysts. The selectivity and conversion are much higher when the composite catalysts are directly added before the reaction than after the reaction. The results indicate that the selectivity and conversion strongly depend on the reaction media.

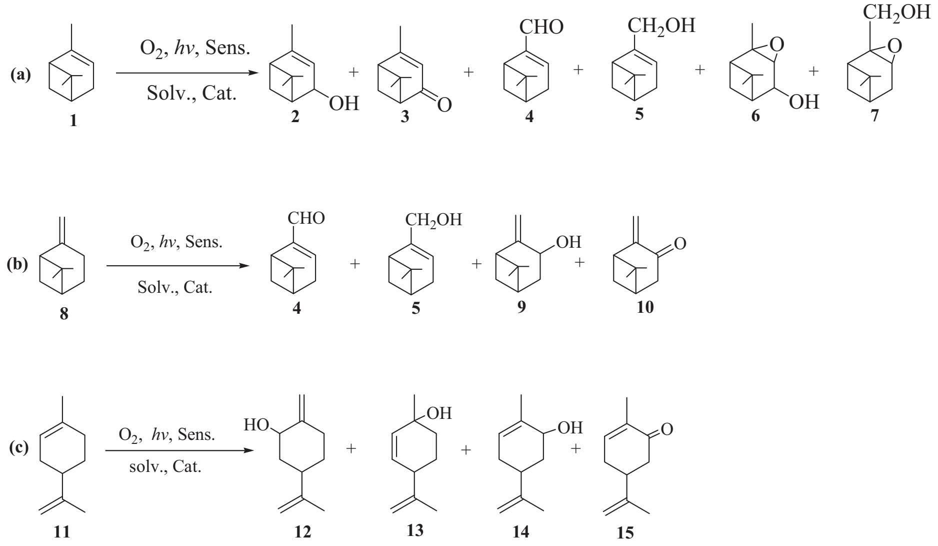
3.2. Photosensitized oxidation of β-pinene

As observed in the case of α-pinene, the RB-sensitized photooxidation of β-pinene (**8**) was investigated by the same method. There may be two probable reaction paths in photosensitized oxidation of β-pinene. Firstly, the singlet oxygen reacts with the double bond carbon atom to form a peroxide radical, and then the peroxide radical abstracts the hydrogen to generate a hydroperoxide intermediate. Finally, the intermediate is decomposed to myrtenal (**4**) or reduced to myrtenol (**5**) under the action of catalysts. The second probable path involves the allylic oxidation of β-pinene, and affords pinocarveol (**9**) and pinocarvone (**10**), as is shown in Scheme 1(b). The product distributions in methyl alcohol and DMF are given in Table 2.

Table 1
Product distributions in the RB-sensitized photooxidation of α-pinene.[a]

Solvent	Catalyst	Conversion (%)	Selectivity (%)						
			2	3	4	5	6	7	Residues[b]
CH_3OH	None	86	13	32	7	7	5	1	35
CH_3OH	2,6-lutidine	94	17	35	5	10	3	5	25
CH_3OH	Acetic anhydride	94	13	36	5	2	1	tr[e]	43
CH_3OH	Composites[c]	89	28	36	8	4	6	2	16
CH_3OH	Composites[d]	97	36	42	13	5	2	1	1
DMF	None	98	33	51	8	6	2	tr	0

[a] Conversion and selectivity were determined by the internal standard method.
[b] Residues refers to non-volatile substances in gas chromatography.
[c] Composite catalyst stands for added 2,6-lutidine and acetic anhydride after the reaction.
[d] Composite catalyst stands for added 2,6-lutidine and acetic anhydride before the reaction.
[e] Trace amounts.



Scheme 1. The photosensitized oxidation of three monoterpenes.

Table 2
Product distributions in the RB-sensitized photo oxidation of β-pinene.

Solvent	Catalyst	Conversion (%)	Selectivity (%)				
			4	**5**	**9**	**10**	Residues
CH_3OH	None	63	33	26	2	2	37
CH_3OH	2,6-Lutidine	78	49	11	2	2	36
CH_3OH	Acetic anhydride	75	41	4	tr[b]	2	53
CH_3OH	Composites[a]	92	74	9	9	tr	8
DMF	None	99	85	6	4	2	3

[a] Composite catalyst stands for 2,6-lutidine and acetic anhydride.
[b] Trace amounts.

Table 2 summarizes representative results for the photosensitized oxidation reaction of β-pinene, and clearly shows that the 2,6-lutidine, acetic anhydride and DMF can catalyze the photosensitized oxidation reaction to some degree. In particular, the photosensitized oxidation products can be directly obtained without need for any other catalysts and the residues (non-volatile substances) are minimal when DMF is used as solvent. Moreover, the special effect is clearly observed that the selectivity to the main product is remarkably improved in the DMF solution. The excellent result of 99% conversion with 85% selectivity to myrtenal was obtained in the DMF solution.

3.3. Photosensitized oxidation of limonene

According to the above-mentioned experimental process, the photosensitized oxidation of limonene (**11**) was likewise examined in the different reaction media. In this case, the oxidation products carveol (**14**) and carveone (**15**), as well as 2,8-p-menthadiene-1-ol (**13**) and 2-methylene-5-(1-methylethenyl) cyclohexanol (**12**), have been obtained, as is shown in Scheme 1(c). The product distributions in methyl alcohol and DMF are listed in Table 3. From Table 3, the strong effect of the monoterpene structure on the conversion and selectivity has been observed in the photosensitized oxidation of limonene. The conversion of limonene is also obviously much lower than α-pinene and β-pinene under the same reaction conditions. Generally, the photosensitized oxidation of limonene takes place on its intra-cyclic double bond, while the external-cyclic double bond is comparatively steady under the reaction conditions. Maybe the reactivity is determined to itself molecular structure.

It is worth noting that the product distributions in DMF solution are also different from those in methyl alcohol solution in the photosensitized oxidation reaction of limonene. In spite of the fact that the conversion of limonene changes a little, the selectivity to the main product 2,8-p-menthadiene-1-ol is remarkably improved in DMF solution. The possible reason relates to the procedure of decomposition or reduction of the hydroperoxide intermediate.

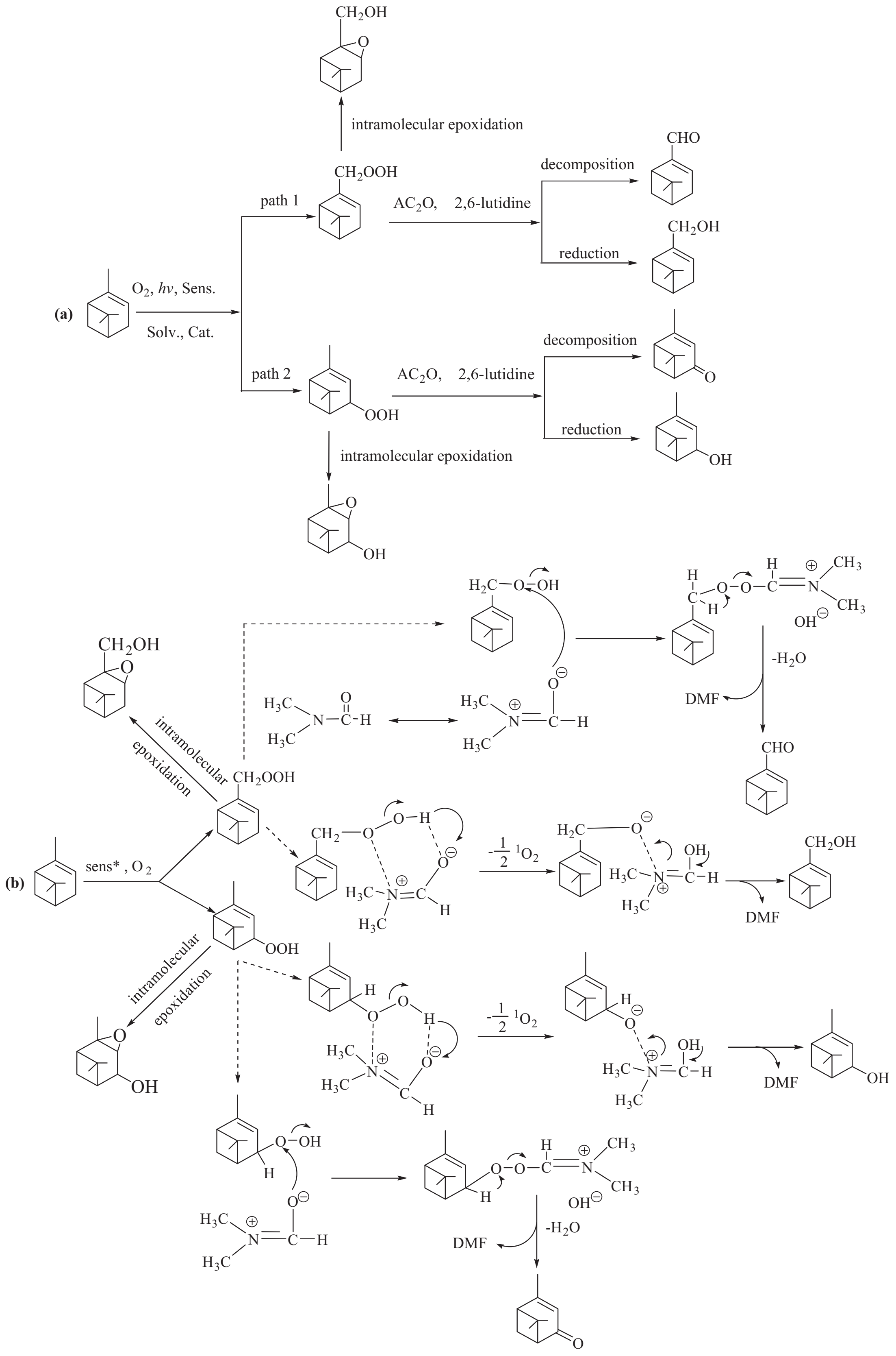
3.4. The possible photosensitized oxidation reaction mechanism of monoterpenes in different reaction media

On the basis of these results in this work, the most probable reaction mechanism of photosensitized oxidation of monoterpenes

Table 3
Product distributions in the RB-sensitized photooxidation of limonene.

Entry	Solvent	Catalyst	Conversion	Selectivity (%)				
			%	**12**	**13**	**14**	**15**	Residues
1	CH_3OH	2,6-Lutidine	25	14	32	24	9	21
2	CH_3OH	Acetic anhydride	21	16	26	22	6	30
3	CH_3OH	Composite[a]	33	13	39	28	9	11
4	DMF	None	34	14	49	24	7	6

[a] Composite catalyst stands for 2,6-lutidine and acetic anhydride.



Scheme 2. The probable reaction path of photosensitized catalytic oxidation of α-pinene in different media.

with molecular oxygen catalyzed by 2,6-lutidine combined with acetic anhydride and DMF was proposed in Scheme 2.

In the present work, 2,6-lutidine combined with acetic anhydride and DMF gives better results in photosensitized oxidation of monoterpenes. The possible reason is as follows. Acetic anhydride and 2,6-lutidine has acidity and basicity respectively, and prompt the hydroperoxide intermediate converting to corresponding oxidation products. Similarly, DMF itself can convert to a zwitterion resonance structure with an N positive ion and O negative ion. In a sense, DMF possesses the characteristics of acidity and basicity (see Scheme 2). Therefore, the conversion of material and selectivity of products are all higher.

4. Conclusions

In summary, photosensitized oxidation of three monoterpenes in homogeneous solution was researched, and efficient photosensitized oxidation equipment had been successfully employed in the present work. The results indicate that the selectivity to products is remarkably controlled by reaction media and that DMF can regulate the selectivity to products. In addition, a probable photo-oxidation reaction mechanism of monoterpene with molecule oxygen sensitized by RB in different reaction media was proposed. This method may also be suitable for photosensitized oxidation of other alkenes with molecular oxygen. It is very significant to establish such a new synthesis approach in the organic photochemistry field.

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