钠灯下 α -蒎烯光敏氧化反应中区域选择性的催化调控游奎一¹, 尹笃林^{2,a}, 毛丽秋², 刘平乐¹, 罗和安^{1,b}¹湘潭大学化工学院, 湖南湘潭 411105²湖南师范大学化学化工学院, 湖南长沙 410081

摘要: 发展了一种简单有效的 α -蒎烯光敏催化氧化方法, 该方法以高压钠灯为绿色光源, 内循环氧气作为氧化剂和搅拌气, 自制水浴式光化学反应器。考察了催化剂种类和反应条件对 α -蒎烯转化率和产物选择性的影响。结果表明, α -蒎烯可通过催化一步生成单萜醇、醛和酮, 且通过催化剂的酸碱协同作用可调节产物的区域选择性。当以 *N,N*-二甲基甲酰胺为溶剂时, α -蒎烯的转化率可达 98%, 主产物马鞭草烯酮和马鞭草烯醇的总选择性达到了 84%。此外, 还探讨了 *N,N*-二甲基甲酰胺酸碱协同催化的作用机理, 并利用密度泛函计算结果对 α -蒎烯分子中化学反应活性和产物选择性之间的对应关系进行了合理的解释。

关键词: 光敏氧化; α -蒎烯; 催化调控; 分子氧; *N,N*-二甲基甲酰胺; 密度泛函理论

中图分类号: O643 文献标识码: A

收稿日期: 2011-06-13. 接受日期: 2011-08-20.

^a通讯联系人. 电话: (0731)88872576; 传真: (0731)88872531; 电子信箱: dulinyin@126.com

^b通讯联系人. 电话: (0731)58293545; 传真: (0731)58298267; 电子信箱: hl原因@xtu.edu.cn

基金来源: 国家自然科学基金 (21006081, 20976043); 湖南省自然科学基金 (11JJ3024, 09JJ8002); 湖南省教育厅青年项目 (11B122); 湖南省科技计划项目 (2010JT4051); 新世纪优秀人才支持计划 (NCET-10-0168).

本文的英文电子版(国际版)由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

Catalytic Modulation on the Regioselectivity of the Photosensitized Oxidation of α -Pinene with Molecular Oxygen under Sodium Lamp IrradiationYOU Kuiyi¹, YIN Dulin^{2,a}, MAO Liqiu², LIU Pingle¹, LUO He'an^{1,b}¹College of Chemical Engineering, Xiangtan University, Xiangtan 411105, Hunan, China²College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, Hunan, China

Abstract: A simple and efficient photosensitized catalytic oxidation approach for α -pinene with molecular oxygen in a temperature-controlled reactor with sparged dioxygen as oxidant and an immersed high-pressure sodium lamp as a green irradiation light source was developed. The effects of various catalysts and reaction parameters on reaction performance were studied. The results indicated that 98% conversion with 84% total selectivity for verbenone and verbenol was obtained when *N,N*-dimethylformamide (DMF) was used as a solvent. The product distributions were remarkably affected by the reaction media and DMF was found to especially modulate the regioselectivity of the products. Moreover, a possible photosensitized catalytic oxidation reaction mechanism in DMF is proposed and a clear acid-base synergistic catalysis effect was evident. The relationship between chemical reactivity and selectivity was modeled using density functional theory at the B3LYP/6-311+G(d) level from optimized molecular configurations.

Key words: photosensitized oxidation; α -pinene; catalytic modulation; molecular oxygen; *N,N*-dimethylformamide; density functional theory

Received 13 June 2011. Accepted 20 August 2011.

^aCorresponding author. Tel: +86-731-88872576; Fax: +86-731-88872531; E-mail: dulinyin@126.com

^bCorresponding author. Tel: +86-731-58293545; Fax: +86-731-58298267; E-mail: hl原因@xtu.edu.cn

This work was supported by the National Natural Science Foundation of China (21006081, 20976043), Natural Science Foundation of Hunan Province (11JJ3024, 09JJ8002), Scientific Research Fund of Hunan Provincial Education Department (11B122), Scientific and Technological Plan Project of Hunan Province (2010JT4051), and Program for New Century Excellent Talents in University (NCET-10-0168).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

α -Pinene is the main component of turpentine oil and is an inexpensive, readily available, and renewable starting material for the production of a wide variety of valuable products such as various flavors, fragrances, agrochemicals, and therapeutically active substances [1,2]. The oxyfunctionalization of α -pinene is of special interest since its oxygenated products (verbenol, verbenone, myrtenal, myrtenol, and epoxide etc.) are used in the synthesis of intermediates in fine and specialty chemicals including citral, menthol, taxol, and vitamins A and E [3].

The selective oxidation of alkenes by molecular oxygen is one of the current challenges in the manufacture of organic building blocks and industrial intermediates [4]. The non-catalytic oxidation of terpenes generally takes place with poor reproducibility, low yields, and low selectivities [5–7]. Therefore, the development of catalytic methods for the selective oxidation of α -pinene by “green” oxidants is a challenging goal in fine chemistry. Recently, photosensitized catalytic oxidation has found many applications in the synthesis field and it holds special promise for product specificity [8–10]. Unfortunately, controlling regio- and stereoselectivity are still difficult issues [11].

For excellent selectivity in these reactions various efforts have been made over the past few decades and remarkable control of the reaction pathway has been achieved by the use of organized and constrained media [12–14]. In previous work, Murphy et al. [15] reported the allylic oxyfunctionalization of cyclic olefins and a broad range of homogeneous catalysts were tested and some of them afforded a yield of more than 90% of the desired α,β -unsaturated ketones. Guo et al. [16] reported the catalytic selectivity of metalloporphyrins for the aerobic oxidation of double bonds and the allylic C–H of α -pinene. The results indicated that TPPMnCl afforded the largest selectivity for the oxidation of C=C bonds and TPPFeCl gave the largest selectivity for the oxidation of allylic C–H bonds. Li et al. [17] reported controllable selectivity during the photooxidation of olefins sensitized by 9,10-dicyanoanthracene under ultraviolet light irradiation (with a 450 W medium pressure Hg lamp as a light source). These were included in vesicles giving ‘ene’ products and ‘non-ene’ products. These results indicate that the organized semirigid environment in vesicles prevents the olefin molecules from conformational change. Allal et al. [18] systematically investigated the nature of the catalyst, the oxidizing agent and the reaction conditions for the allylic oxidation of α -pinene catalyzed by a transition metal using *t*-butyl hydroperoxide (TBHP) and hydrogen peroxide. The results showed high selectivity for verbenone was achieved under mild conditions when using copper salts as catalysts and TBHP as an oxidant. Yang et al. [19] reported the catalytic selectivity of TiO₂ for the epoxidation of double bonds of α -pinene, and the good selectivity of epoxida-

tion product was obtained.

The primary results of our investigation into the photosensitized oxidation of three monoterpenes with molecular oxygen sensitized by tetrachloro tetraiodo-fluorescein sodium salt (RB) under visible light irradiation have been reported previously [20]. Herein, we report detailed results from an investigation into the photosensitized oxidation of α -pinene with molecule oxygen in the presence of various catalytic systems. Moreover, the relationship between chemical reactivity and selectivity was modeled by density functional theory (DFT) calculations.

1 Experimental

1.1 Photosensitized oxidation experiment

All the photosensitized oxidation reactions were performed according previous work [20]. α -Pinene was distilled under reduced pressure from turpentine oil. All the other chemicals were of analytical grade and used as purchased. A 110 W high-pressure sodium lamp was used as the green irradiation source. The final products were identified by GC-MS and quantitatively analyzed by the internal standard method. Gas chromatography (GC) was performed on an Agilent 6890 equipped with an FID detector. Mass spectra (MS) were obtained from an America Varian Saturn 2100T GC-MS instrument.

1.2 Theoretical background and computational details

DFT local descriptors are useful in describing chemical reactivity. A well-known example is the Fukui function [21–24]. For a system with electron gain $f^+(r)$ is used as the index for nucleophilic attack. For electron donation $f(r)$ is used as the index for electrophilic attack. The average of the two, $f^0(r) = (f^+(r) + f(r))/2$, represents the radical attack ability. The condensed Fukui functions are based on a population analysis under the finite difference approximation, e.g., natural bond orbital (NBO) analysis. For atom k in a molecule, for example, the condensed Fukui functions f_k are:

$$\begin{aligned} f_k^+ &= q_k(N+1) - q_k(N) \\ f_k^- &= q_k(N) - q_k(N-1) \\ f_k^0 &= (q_k(N+1) - q_k(N-1))/2 \end{aligned}$$

where $q_k(N+1)$, $q_k(N)$, and $q_k(N-1)$ are the gross NBO charges on atom k in a molecule with $N+1$, N , and $N-1$ electrons, respectively. In this work the Fukui function value of a typical carbon atom in the molecular structure of α -pinene was calculated by the above-mentioned method.

All the geometrical optimizations for α -pinene and hydroperoxide intermediates were carried out using a DFT hybrid exchange-correlation energy density functional con-

sisting of the Becke's three parameterized exchange energy density functional and the Lee-Yang-Parr correlation functional [25–29]. All calculations were carried out at the DFT B3LYP/6-311+G(d) level with the GAUSSIAN-03 package, version E02, with tight SCF convergence and ultrafine integration grids.

2 Results and discussion

2.1 Photosensitized catalytic oxidation of α -pinene in different media

The RB-sensitized photooxidation reaction of α -pinene with molecular oxygen was examined in different reaction media. After irradiation by a high pressure sodium lamp the 'ene' products verbenol (**2**), myrtenol (**5**), and the 'non-ene' products myrtenal (**4**), verbenone (**3**), 4-hydroxy-2, 3-epioxypinane (**6**), and 1-hydroxy-2, 3-epioxypinane (**7**) were obtained (see Scheme 1). The products selectivity distributions in various catalytic systems are given in Table 1.

From Table 1 it is obvious that the various catalysts catalyze the photosensitized oxidation reaction of α -pinene to some extent. The oxidation reaction hardly occurred in the absence of light irradiation. This indicates that the high pressure sodium lamp plays an extraordinarily important role in the photosensitized oxidation reaction. Singlet oxy-

gen is generated by an energy transfer process during a collision of the excited sensitizer with triplet molecular oxygen. However, sensitizer excitation is generally achieved by a one photon transition ($h\nu$) between the ground state and a singlet excited state [30]. Therefore, the light source is essential to photosensitized oxidation. Among these catalysts 2,6-dimethylpyridine combined with acetic anhydride gives the best results with 97% conversion, 42% selectivity for verbenone (**3**), and 36% selectivity for verbenol (**2**) in a methyl alcohol solution. A special photosensitized oxidation reaction effect was observed when DMF was used as a solvent as the conversion of material and selectivity for the main product improved significantly. The best results of 98% conversion with 51% selectivity for verbenone and 33% selectivity for verbenol was obtained in the absence of any catalysts while only low amounts of residue was obtained. A possible reason is that DMF can convert to a zwitterion resonance structure with a N positive ion and an O negative ion. Therefore, DMF possesses the characteristics of acids and bases, which promotes the decomposition of the hydroperoxide intermediates to the corresponding aldehydes and ketones or a reduction to alcohols. Therefore, the conversion of material and selectivity for the product is higher under acid-base synergetic catalysis. The formation mechanism of the photosensitized oxidation products in DMF has been reported in our previous work [20].

Scheme 1. Photosensitized catalytic oxidation of α -pinene with molecular oxygen.

Table 1 Product distributions for the RB-sensitized photocatalytic oxidation in different media

Solvent	Catalyst	Conversion ^a (%)	Selectivity ^a (%)						Residues ^b
			2	3	4	5	6	7	
CH ₃ OH	none	86	13	32	7	7	5	1	35
CH ₃ OH	2,6-dimethylpyridine ^c	0	0	0	0	0	0	0	0
CH ₃ OH	acetic anhydride	94	13	36	5	2	1	0	43
CH ₃ OH	2,6-dimethylpyridine	94	17	35	5	10	3	5	25
CH ₃ OH	pyridine	89	5	45	22	4	2	1	21
CH ₃ OH	quinoline	87	8	42	16	3	3	2	26
CH ₃ OH	2,3,5-trimethylpyrazine	85	10	26	15	1	2	1	45
CH ₃ OH	composites ^d	89	28	36	8	4	6	2	16
CH ₃ OH	composites	97	36	42	13	5	2	1	1
DMF	composites	96	26	50	14	2	1	0	7
DMF	none	98	33	51	8	6	2	0	0

Reaction conditions: reaction temperature 300 K, reaction time 4 h.

^a Determined by the internal standard method.

^b Refers to nonvolatile substances that have no GC peaks.

^c No irradiation light source.

^d Composites (the mixture of 2,6-dimethylpyridine and acetic anhydride) were added into the system after the reaction.

The selectivity and conversion are affected by the catalyst addition method. The selectivity and conversion was found to be far higher when the composite catalysts were added directly to the system before the reaction compared to after the reaction. The obtained results show that the selectivity and conversion strongly depend on the reaction media.

In this work, the composite of 2,6-dimethylpyridine and acetic anhydride possesses acid and base characteristics and can, therefore, promote the decomposition of the hydroperoxide intermediate to the corresponding products. Therefore, 2,6-dimethylpyridine combined with acetic anhydride, as a composite, was selected as a typical catalyst to investigate the reaction conditions of the photosensitized oxidation.

2.2 Effects of 2,6-dimethylpyridine with different amounts of acetic anhydride on the photosensitized oxidation of α -pinene

The experimental results from the photosensitized oxidation of α -pinene upon catalysis by 2,6-dimethylpyridine combined with different amounts of acetic anhydride are summarized in Table 2. The conversion of α -pinene increased initially and then decreased gradually because of the higher amount of acetic anhydride. However, the selectivity for verbenone decreased gradually and the amount of residue decreased initially and then increased. The conversion of α -pinene was 97% with 42% selectivity for verbenone and 36% selectivity for verbenol at a 1:1 molar ratio of 2,6-dimethylpyridine to acetic anhydride. However, the conversion and selectivity had a declining trend and the amounts of residue increased gradually when the molar ratio exceeded 1:1. A possible reason is that the excess acetic anhydride aggravated the polymerization of allylic peroxide free radicals and, thus, the selectivity for residues increased and the selectivity for the main product decreased. Therefore, a suitable amount of acetic anhydride can efficiently catalyze the photosensitized oxidation of α -pinene. These results confirm that the acid-base synergistic catalytic properties of 2,6-dimethylpyridine and acetic anhydride have an

important influence on the conversion and selectivity in the photosensitized oxidation of α -pinene.

2.3 Effects of reaction time on the photosensitized oxidation of α -pinene

The effect of reaction time on the conversion of α -pinene and selectivity for verbenone and the residues was examined at 300 K. The results are shown in Fig. 1. In the first 4 h the conversion of α -pinene and the selectivity for verbenone increased dramatically to 97% and 42%, respectively, while the selectivity for the residues decreased gradually to 1%. The reaction rate then gradually slowed and the conversion of α -pinene gradually increased to 98% at 5 h. Moreover, the selectivity for verbenone decreased slightly while the selectivity for the residues increased rapidly from 1% to 12% when the reaction time exceeded 4 h. A possible reason is that the polymerization of the allylic peroxide free radical was aggravated with an increase in the reaction time and, thus, selectivity for the residues increased and selectivity for the main product decreased. Therefore, selecting the appropriate reaction time is essential in the photosensitized oxidation of α -pinene.

Fig. 1. Effects of reaction time on the photosensitized oxidation upon catalysis by 2,6-dimethylpyridine and acetic anhydride. Reaction conditions: molar ratio of 2,6-dimethylpyridine to acetic anhydride 1:1, reaction temperature 300 K.

2.4 Effects of reaction temperature on the photosensitized oxidation of α -pinene

The effect of reaction temperature on the photosensitized oxidation of α -pinene catalyzed by 2,6-dimethylpyridine combined with acetic anhydride was examined. The results are listed in Table 3. The reaction temperature significantly influences the conversion of α -pinene and the selectivity for the residues. The conversion increased rapidly with an increase in the reaction temperature from 34% at 273 K to 98% at 310 K. The selectivity for verbenone and verbenol

Table 2 Product distributions for the RB-sensitized photooxidation catalyzed by 2,6-dimethylpyridine combined with acetic anhydride

Molar ratio ^a	Conversion (%)	Selectivity (%)							
		2	3	4	5	6	7	Residues	
1:0	85	6	32	15	1	3	2	41	
1:1	97	36	42	13	5	2	1	1	
1:2	94	35	34	9	4	1	2	15	
1:3	88	31	31	7	3	1	1	26	

Reaction conditions: methanol as solvent, reaction temperature 300 K, reaction time 4 h.

^aThe molar ratio of 2,6-dimethylpyridine to acetic anhydride.

Table 3 Influence of reaction temperature on the photosensitized oxidation of α -pinene upon catalysis by 2,6-dimethylpyridine and acetic anhydride

Temperature (K)	Conversion (%)	Selectivity (%)						
		2	3	4	5	6	7	Residues
273	34	17	28	3	0	0	0	52
284	59	22	30	10	4	0	0	34
293	83	25	34	13	4	1	2	21
300	97	36	42	13	5	2	1	1
310	98	25	31	15	9	3	2	15

Reaction conditions: methanol as solvent, the molar ratio of 2,6-dimethylpyridine to acetic anhydride 1:1, reaction time 4 h.

increased gradually with temperature between 273 and 300 K. However, the selectivity for verbenone and verbenol showed a decreasing trend and the amount of residue increased rapidly when the reaction temperature exceeded 300 K. A possible reason is that a higher temperature accelerates the polymerization of the allylic hydroperoxide intermediate and thus the content of nonvolatile substances that have no gas chromatography peaks increased. Therefore, the optimal reaction temperature was 300 K according to the data of the selectivity for verbenone. These results indicate that a proper temperature might favor the synthesis of verbenone and verbenol during the photosensitized oxidation of α -pinene.

2.5 Effects of different additives on the photosensitized oxidation of α -pinene

In previous work, the most probable reaction mechanism for the photosensitized oxidation of α -pinene with molecular oxygen was proposed [20]. To further speculate on the reaction pathway the following experiment was designed. First, a methyl alcohol solution of 0.5 mol/L α -pinene was prepared and then the sensitizer (RB) was added into the reactor. After the photosensitized oxidation was performed over 4 h in the absence of a catalyst the resulting mixture was equally divided into ten portions. Finally, different additives were added to every portion and the obtained results are shown in Table 4.

From Table 4 the selectivity for the oxidation products evidently improves when various additives are added to the mixture. The selectivity for verbenol improves remarkably

Table 4 Effects of different additives on the photosensitized oxidation of α -pinene

Additive ^a	Selectivity (%)						
	2	3	4	5	6	7	Residues
None	13	32	7	7	5	1	35
Acetic acid	14	40	6	5	2	0	33
Acetic anhydride	15	41	7	4	2	2	29
L-phenylalanine	14	43	7	4	9	1	22
Triethylamine	22	44	11	6	0	1	16
2,6-Dimethylpyridine	20	46	8	6	4	1	15
Composites ^b	23	46	8	4	6	2	11
DMF	24	48	13	4	5	0	6
NaHSO ₃	26	42	6	5	4	3	14
Zinc powder	31	42	6	12	3	1	5

^aAdded into the system after the reaction.

^bA mixture of acetic anhydride and 2,6-lutidine.

and the amount of residue is the lowest when zinc powder is added to the reaction system. A possible reason is that the formed hydroperoxide intermediate is easily reduced to the corresponding alcohol products in the presence of a reductant. Selectivity for the main product verbenone improves significantly in DMF.

2.6 Possible theoretical interpretation of the selectivity distribution in the photosensitized oxidation of α -pinene with molecular oxygen

We used well-known DFT computational methods to explain the relationship between chemical reactivity and selectivity during the photosensitized oxidation of α -pinene with molecular oxygen. All the geometrical optimizations of α -pinene and hydroperoxide intermediates were carried out using DFT calculations at the B3LYP/6-311+G(d) level (see Fig. 2).

Table 5 summarizes the representative results for the charge and condensed Fukui function value of a typical carbon atom in the molecular structure of α -pinene. The negative charge is mainly concentrated on the carbon atom. From Table 5, it is clear that the condensed Fukui function value ($f^0(r)$) of the C₁ atom is the highest, which shows that its chemical reactivity is the highest and the stability of the formed hydroperoxide intermediate in the C₁ site is the highest. Likewise, the selectivity for the oxidation products

Fig. 2. Optimized geometry of α -pinene and the two hydroperoxide intermediates.

Table 5 Charge and condensed Fukui function value of typical carbon atoms in the molecular structure of α -pinene

α -Pinene	Atom	Charge			Condensed Fukui function			Selectivity for products
		0	+1	-1	$f^+(r)$	$f(r)$	$f^0(r)$
C ₁	-0.41320	-0.46502	-0.39380	0.01940	0.05182	0.03561	78
	C ₂	-0.21022	0.06029	-0.36520	-0.15498	-0.27051	-0.21275	—
	C ₃	-0.01251	0.22598	-0.11162	-0.09911	-0.23849	-0.16880	—
	C ₄	-0.59011	-0.63993	-0.57313	0.01698	0.04982	0.03340	18
	C ₅	-0.23446	-0.24905	-0.22778	0.00668	0.01459	0.01064	—

in the C₁ site is also the highest from the obtained experiment results. From these calculation results the selectivity for the products correlate well with the condensed Fukui function value of the carbon atom.

Additionally, the selectivity for products is also clear from the hydroperoxide intermediate's energy during the photosensitized oxidation of α -pinene. During the photosensitized oxidation of α -pinene, molecular oxygen may react with the allylic hydrogen of α -pinene to form three transition states (ts_1, ts_2, and ts_3, see Scheme 2). The energy of the reactant, product, and the three transition states is listed in Table 6.

From the calculated results given in Table 6, the energy of the hydroperoxide intermediate R₂ is shown to be higher than R₁ ($\Delta E = E(R_2) - E(R_1) = 12.090428$ KJ/mol), which demonstrates that the stability of intermediate R₁ is greater than that of R₂. Therefore, the selectivity for the formed

oxygenated products on the C₁ site is also higher than for the C₄ site from the experiment results.

Moreover, a possible formation pathway for the hydroperoxide intermediate from α -pinene and molecular oxygen along the different reaction routes was determined in this work, as shown in Scheme 2. Path I proposes that the transition state ts_1 is obtained by a three-membered ring formed by an oxygen atom, a C₁ atom, and a hydrogen atom in the C₁ site; Path II proposes that the transition state ts_2 is obtained from a six-membered ring formed by dioxygen, a hydrogen atom in C₁ and the C₂ site; Path III proposes that the transition state ts_3 is obtained from a four-membered ring formed by dioxygen, a C₁ atom, and a hydrogen atom in the C₁ site. It is clear that the energy of the three transition states decreases as follows: $E(\text{ts}_3) > E(\text{ts}_2) > E(\text{ts}_1)$, as shown in Table 6. Among these three transition states the energy of ts_1 is the lowest, which shows that ts_1 is the most stable transition state. Therefore, the reaction route along pathway I is most likely to occur.

3 Conclusions

In summary, an efficient conversion and catalytic modulation approach for the photosensitized oxidation of α -pinene with molecular oxygen has been developed. Photosensitized oxidation products without post-reaction treatment by a reductive reagent can be obtained directly. DMF can modulate the selectivity of the obtained products. Moreover, a clear acid-base synergetic catalysis effect was evident and a possible photosensitized catalytic oxidation reaction mechanism in DMF is proposed in this work. Also, the relationship between chemical reactivity and selectivity was determined by DFT calculations. Our findings are significant for the establishment of a new synthesis and catalytic modulation approach in organic photochemistry.

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Scheme 2. Possible formation pathway of the hydroperoxide intermediate from the transition state during the photooxidation of α -pinene with molecular oxygen.

Table 6 Calculated energies of the reactants, product, and transition states

Substrate	Energy (a.u.)
R ₁	-541.148000
R ₂	-541.143395
ts_1	-541.068564
ts_2	-541.0641351
ts_3	-541.0385158
R ₀	-541.0730979

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