

Activation of C(SP³)-H Bonds Promoted Oxidation of Sulfides by O₂ Under Catalyst-Free Conditions

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Summary: Oxidation of organic sulfides is a significant reaction due to its application in many fields. Herein, we have developed a novel catalyst-free oxidation of organic sulfides by O₂ under relatively mild conditions. The choice of the procedure was based on the well-acknowledged reactivity of the active C(sp³)-H bond of organic compounds to form the corresponding alkyl carbon free radicals (R·) in the presence of O₂. The results showed that hydrocarbons such as tetrahydronaphthalene (THN) and cumene possessing the active C(sp³)-H bonds due to their lower bond dissociation energy (BDE), as a solvent, markedly promoted this catalyst-free sulfoxidation. It has been proved that reactive oxygen species (ROS) in this reaction are alkyl-peroxide radicals that are produced from R·, which is derived from the homolytic cleavage of the active C(sp³)-H bond with the help of heating and dioxygen, and further its activation of molecular oxygen. On this basis, combined with the DFT calculation of the activation energy of two reaction pathways, a possible reaction mechanism is proposed. The work provided a green synthesis approach of sulfoxide and sulfone compounds, and a scientific basis for a green process of ultra-deep desulfurization of fuel oils.

Keywords: Organic sulfides; Catalyst-free; Molecular oxygen; C(sp³)-H bond; Alkyl-peroxide radicals.

Introduction

Oxidation of organic sulfides (OOS) is a very important organic reaction due to its widespread application in the synthesis of medicine [1-6], pesticide [7], functional materials [8-9], and precious metal extractant [10] as well as oxidative desulfurization of fuel oils [11-12]. At present, there are commonly two types of oxidants used in this reaction: active chemical oxidation systems including high valence transition metal oxides [13], halogen oxidation systems [14], nitric acid [15], etc., and green oxidation systems comprising hydrogen peroxide and molecular oxygen [16]. However, most of the former have the following drawbacks in different degrees: environmental pollution and high costs derived from low utilization [17] and poor selectivity originated from strong oxidation. As far as the latter is concerned, molecular oxygen is a cheaper, more easily available, safer, and more environmentally friendly green oxidant than hydrogen peroxide. Therefore, it is undoubtedly of great significance to study on the sulfoxidation using molecular oxygen as oxidant.

The key issue of the reaction is the activation of molecular oxygen. In recent years, the research on an economically effective and environmentally friendly molecular oxygen oxidation sulfide has attracted a large number of scholars' interest. Molecular oxygen activation has broad application potential in organic conversion, but it remains a challenge due to its relative inertness [18]. There are usually two ways to activate molecular oxygen: catalyst-free and catalytic activation. This conventional catalyst-free activation can be brought about by the conversion of the inactive triplet molecular oxygen to the active singlet molecular oxygen [19]. For example, The research results of E. Skolia [20] and Q. Fan[21] et al show that singlet oxygen plays an important role in the oxidation process of sulfide. Generally, this process is achieved under harsh reaction conditions such as high temperature and high pressure or high energy radiation [22]. As a result, this traditional catalyst-free OOS by O₂ requiring severe conditions limits its practical application in the green process [23]. The chief issue to make this reaction green is how to achieve the activation of

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molecular oxygen under relatively mild conditions. In general, molecular oxygen is difficult to activate directly under mild conditions [24]. In order to address this problem, a catalyst is usually needed. The catalyst commonly consists of two major categories: homogeneous and heterogeneous catalytic systems containing transition metals [25] or non-metal [26], respectively. However, both of them have some disadvantages to various extent: residual metal catalyst, complicated composition, high cost, and easy deactivation, etc. Accordingly, it is necessary to study the catalyst-free OOS by O₂ under relatively mild conditions.

Considering the generation of ROS in hydrocarbon auto-oxidation by air under ambient conditions [27], however, this reaction is a slow process. Utilizing this mechanism and meanwhile overcoming its deficiency, namely, accelerating the activation of molecular oxygen, we propose a novel catalyst-free OOS approach by O₂: i.e. alkyl carbon free radicals (R·) produced with the assist of heating and dioxygen mediate the activation of molecular oxygen to form reactive oxygen species (ROS) such as alkyl-peroxide radicals for this reaction.

Activation of the C (sp³)-H bond is critical in many chemical, industrial, and biological processes [28-30]. The critical problem to achieve this new approach is how to rapidly generate R· under relatively mild conditions. It is well-known that the active C(sp³)-H bond of organic compound has a lower bond dissociation energy (BDE) [31]. Therefore, the homolysis of active C(sp³)-H bond assisted by relatively mild heating and O₂ can probably faster produce R· as compared to a hydrocarbon with a higher C-H bond dissociation energy (BDE). We used molecular oxygen as oxidant in the oxidation of sulfide in organic solvents with different C(sp³)-H bond activity. In order to verify this new approach, this work is intended to perform the following research: 1) Comparative experiments were carried out using organic solvents with high C(sp³)-H bond dissociation energy (BDE) and organic solvents with low C(sp³)-H bond dissociation energy (BDE); 2) On the basis of the above experiments, using organic compounds containing C(sp³)-H bonds with a lower BDE as solvents, OOS with molecular oxygen as oxidant by a relatively mild conventional heating is to be explored; 3) The structure-activity relationship between the C(sp³)-H bonds properties and their reaction performance will be investigated; 4) The catalyst-free OOS by O₂ in short times under mild conditions, free-radicals quenching, and quantum chemical calculation of the activation energy of reaction pathways are further to be carried out. And according to the experimental results,

a possible reaction mechanism is to be proposed. The objective of this work is to develop a green synthesis methodology of sulfoxide and sulfone compounds, and to provide a scientific basis for the environment-friendly preparation process of these compounds and the green process of ultra-deep desulfurization of fuel oils.

Experimental

Reagents and Material

All chemicals and solvents used in this work were AR grade. Thioansole, Cumene, 1,2,3,4-Tetrahydronaphthalene(THN),azobisisobutyronitrile(AI BN),2,2,6,6-tetramethylpiperidine oxide (TEMPO), p-benzoquinone (PBQ) and p-cresol were provided by Shanghai Macklin Biochemical Co., Ltd. The high-purity molecular oxygen and nitrogen were supplied by RuiYuan Gas Company in China. Methanol, Acetonitrile, Toluene, Xylene, Ethylbenzene, N-octane, and Cyclohexane were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

Oxidation of organic sulfides and products analysis

Catalyst-free oxidation reactions were performed in a glass reactor. Sulfide (0.8 mmol) and 10 mL of an organic solvent were placed in a 25 mL three-necked round bottom flask equipped with a thermometer and a serpentine condenser tube. Dioxygen was introduced into the reactor from a glass tube with a rubber tube. The reaction was performed in an oil bath with a magnetic stirrer at 500 rpm for a certain time at a certain temperature. When using low-boiling reagents such as n-octane and n-hexane as solvents, the reaction was carried out in an autoclave reactor equipped with a magnetic stirrer, a thermometer, an automatic temperature controller and a pressure gauge. After the desired amount of reactants and solvent were added into the reactor, the autoclave was sealed. Dioxygen was charged to 1 MPa. The reaction was carried out for a certain period of time when the reactor was heated to the desired temperature within 20 min at a stirring rate of 500 rpm. After completion of the reaction, the reactor was cooled to the ambient temperature. The products were determined by Gas Chromatography (SHIMADZU GC-2010Pro) with a flame ionization detector (FID) equipped with a capillary column (Stabilwax, 30 m×0.32 mm×0.25 μm) using anisole as the internal standard.under the following analytical conditions: split ratio, 1/100; carrier gas, ultra-purity nitrogen with column flow of 30 mL·min⁻¹; reagent gases, air flow of 400 mL·min⁻¹, hydrogen flow of 40 mL·min⁻¹; the injection volume of sample was 1μl;

to detect reactant and product: injection port temperature, 250 °C; detector temperature, 250 °C; oven temperature, 100 °C old for 1 min, to 140 °C at 10 °C·min⁻¹, hold for 2 min, to 200 °C at 10 °C·min⁻¹.

Calculation of activation energy

The Kinetics and Statistical Thermodynamics Package (KiSTheLP) is a cross-platform free open source program for estimating molecular and reaction properties from electronic structural data, which enables us to change input data and simulation parameters directly through a graphical user interface, and visually explore how it affects results. Users can access the results in the form of graphs and tables. To date, three computational chemistry software formats are supported (Gaussian, GAMESS, and NWChem) [32]. In this work, all structures have been optimized with the Gaussian 16 A03 package with tight SCF convergence and ultrafine integration grids [33]. We adopted density functional theory (DFT) methods [34] with the basis set Def2-TZVP of Ahlrichs and coworkers added diffuse functions (ma-Def2-TZVP) [35]. The M062X exchange-correlation energy density functional was used throughout [36]. Truhlar and coworkers' SMD solvation model was employed to simulate the solvent effect of tetralin [37-38]. The frequency calculations were performed to ensure that the final structures of zymolytes don't have imaginary frequency and final structures of transition-state have only one negative frequency whose vibration mode corresponds to the bond formation and bond breaking process. In addition, an intrinsic reaction coordinate (IRC) run was performed to verify the relevance of transition-state structures [39]. Activation energy was calculated with the KiSTheLP package by the TST method.

Results and Discussion

Catalyst-free oxidation of thioanisole by O₂ in the organic solvents with different C(sp³)-H bond properties

The organic solvents containing different active C-H bonds (with different C(sp³)-H BDE) were applied in catalyst-free oxidation of thioanisole with molecular oxygen as oxidant (as listed in Table 1). The yield in catalyst and solvent-free oxidation of thioanisole was 0% (Entry 1). No product was detected in this reaction in such organic solvents as methyl-substituted aromatic hydrocarbon, acetonitrile, and some alkanes like n-octane, cyclohexane, and dodecane with relatively inactive C-H bond (with higher C(sp³)-H BDE) (Entry 2,3,4,8,9,10). However, other alkyl aromatics (i.e. non methyl-substituted aromatics) like the ethylbenzene, cumene, and tetrahydronaphthalene (THN) possessing relatively active C-H bonds (with lower C(sp³)-H BDE) as solvents evidently contributed to promote this catalyst-free oxidation (Entry 5,6,7). Especially, with THN or cumene as a solvent (with the lowest C(sp³)-H BDE in the solvent used, ca.360 KJ/mol), it gave the highest conversion of thioanisole. The results indicated that the oxidation conversion of thioanisole depends on the C(sp³)-H BDE of the solvents used, in other words, the low value of BDE was favorable for this reaction. This may be due to the alkyl aromatics with low C(sp³)-H BDE facilitating the homolytic dissociation of its C(sp³)-H bond under relatively mild heating and aerobic conditions, and further the formation of the active alkyl carbon free radicals (R·), which can rapidly activate molecular oxygen into ROS, i.e. alkyl peroxy radicals [40]. This finding may provide a novel approach for catalyst-free sulfoxidation by O₂.

Table 1 Influence of solvents with different C-H bond BDE on oxidation of thioanisole by O₂

Entry	Solvent	Conv./% ^c	Sel./% ^c		C(sp ³)-H bond dissociation energy	
			sulfoxide	sulfone	C-H bond ^d properties	BDE ^f (KJ/mol)
1	- ^a	0	0	0	-	-
2	Methylbenzene ^a	0	0	0	Pri-C-H	380.3
3	Xylenes ^a	0	0	0	Pri-C-H	378.7
4	Acetonitrile ^b	0	0	0	Pri-C-H	408.8
5	Ethylbenzene ^a	54	93	7	Sec-C-H	366.2
6	Cumene ^a	98	61	39	Tert-C-H	359.8
7	Tetralin ^a	97	64	36	α -Sec-C-H	360.9
8	Octane ^b	0	0	0	Sec-C-H	409.9
9	Cyclohexane ^b	0	0	0	Sec-C-H	410.4
10	Dodecane ^a	0	0	0	Sec-C-H	409.6

Standard reaction condition: ^aTemp, 110 °C; Solvent, 10 mL; thioanisole, 0.8 mmol; Oxidation in a round bottom flask by O₂ under atmospheric pressure for 2 h. ^bTemp, 110 °C; Solvent, 20 mL; thioanisole, 1.6 mmol; Oxidation in an autoclave reactor by O₂ at 1 MPa. ^cDetermination of conversion of thioanisole by GC internal standard method (Internal standard: Anisole). ^dPri-Primary, Sec-secondary, Tert-tertiary. ^eCalculation of the BDE of C-H bond at 298 K by DFT based on the level of m062x/ma-def2-tzvp and SMD solvation model

Effects of its concentration on oxidation of thioanisole in THN

The catalyst-free oxidation of thioanisole at its concentration ranging from 0.08 to 0.8 M with THN as a solvent is shown in Fig.1. It is apparent that the conversion of thioanisole rapidly decreased to ca. 50 % with increasing its concentration to ca. 0.2 M, and then slowly lowered to ca. 20 % at its concentration of 0.64 M, whereas the corresponding selectivity of methyl phenyl sulfoxide increased to 85 % and gradually approached to 100 %. The results may be elucidated in two aspects: i) the rapidly reduced conversion may result from the formation of a definite amount of ROS under a certain condition of temperature and pressure despite the excess dioxygen; ii) the excellent selectivity was due to the oxidized capability of thioanisole stronger than that of its sulfoxide leading to the lesser further oxidation of its sulfoxide to its sulfone with the increasing the concentration of thioanisole.

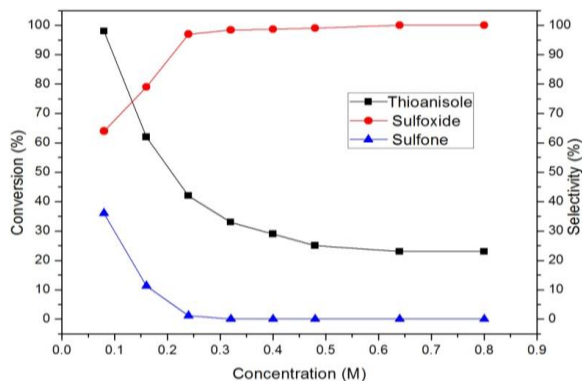


Fig.1: Effect of thioanisole concentration on its oxidation.

Condition: Temp, 110 °C; Solvent, 10 mL THN; Oxidation in a round bottom flask by O₂ under atmospheric pressure for 2 h.

Influence of temperature on catalyst-free oxidation of thioanisole

The influence of the reaction temperature on the catalyst-free oxidation of thioanisole by O₂ in THN is illustrated in Fig.2 (AIBN, a free radical initiator, added as a control). With increasing temperature from 80 °C to 120 °C, whether no initiator or initiator was added, the conversions of both increased gradually. However, the conversion of the control was approximately twice as high as that of no initiator. On the one hand, the result may be due to be that the active secondary C(sp³)-H bond of THN is more conducive to homolytic cleavage

producing its carbon free radical for the activation of molecular oxygen under the higher temperature, and thus boosts the oxidation of thioanisole. On the other hand, AIBN, a free radical initiator, can be heated generating free radicals with abstraction hydrogen effect [41-42], which can make the secondary C(sp³)-H bond in THN easier homolysis producing THN's secondary carbon free radical and promote the reaction. It was also indirectly demonstrated that ROS in the reaction were produced from THN's secondary carbon free radical activating molecular oxygen.

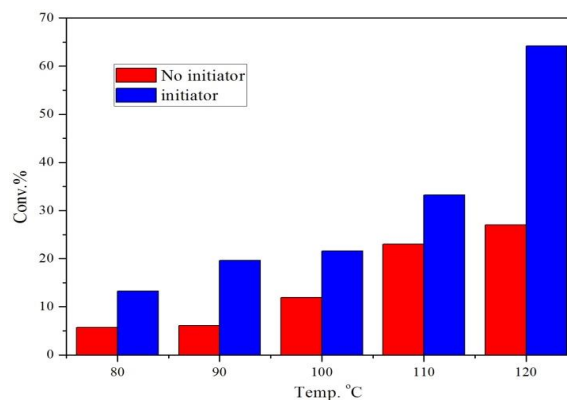


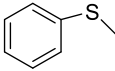
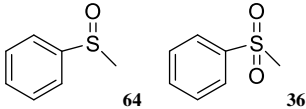
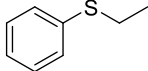
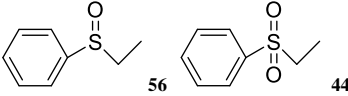
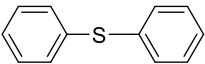
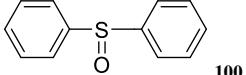
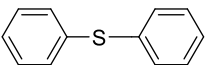
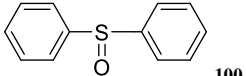


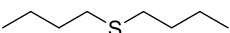
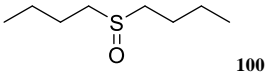

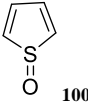
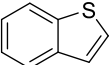
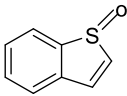
Fig. 2: Effect of temperature on thioanisole oxidation.

Condition: Temp, 110 °C; Solvent, 10 mL THN; thioanisole, 8 mmol; Oxidation in a round bottom flask by O₂ under atmospheric pressure for 2 h.

Catalyst-free oxidation of typical organic sulfides

The catalyst-free oxidation using typical organic sulfides as substrates by O₂ in THN is listed in Table 2. For all substrates examined, the catalyst-free OOS effectively occurred. Among substrates investigated, the oxidation of methyl phenyl sulfide and ethyl phenyl sulfide showed the highest conversion in an atmospheric condition (entry 1 and entry 2), while their oxidized products had a low selectivity. For alkyl- and aryl-sulfides, dimethyl sulfide and di-n-butyl sulfide exhibited the higher conversion than that of diphenyl sulfide, whereas diphenyl sulfide and di-n-butyl sulfide due to the steric effect displayed an excellent selectivity of sulfoxides (100 %) (entries 3, 4, 5 and 6). Like thiophenic sulfides such as thiophene and benzothiophene, the oxidation of them provided a lower conversion of ca. 16 % and 24 %, respectively, and yet an outstanding selectivity for sulfoxides (100%) (Entry 7 and entry 8). It is noteworthy that such a lower conversion of thiophenic sulfides is sufficient for ultra-deep oxidation desulfurization of fuel oil, because the content of thiophene derivative in fuel oil is as low as ppm level.

Table-2: Substrate scope.

Entry	Substrate	Conv./%	Sel./%
1 ^a		97	
2 ^a		96	
3 ^a		67	
4 ^b		90	
5 ^b		93	
6 ^b		94	
7 ^b		16	
8 ^b		24	

Condition: ^aTemp, 110 °C; Solvent, 10 mL THN; Substrate, 0.8 mmol; O₂, 1atm; Time, 2 h; ^bTemp, 110°C; Solvent, 20 mL; Sulfides, 1.6 mmol; O₂, 1 MPa; Time, 2 h.

Reaction Mechanism

In order to demonstrate the reaction mechanism involved in the proposed new and green catalyst-free OOS approach: we designed and conducted the following experiments.

Catalyst-free oxidation by O₂ in short time under mild temperature

To clarify ROS produced from this reaction system, catalyst-free oxidation of thioanisole in short time at 30 °C was carried out (Table 3) after pretreating THN at high temperature (110 °C) for 30 min in a dioxygen and then quickly cooling from 110 °C to 30 °C. The results showed that high temperature pretreatment gave ROS with the similar oxidation ability at room temperature to the one at high temperature (seen the results from the aforementioned synchronous high temperature treatment and oxidation). It is generally believed that the autoxidation of hydrocarbon with active sp³ C-H bond can generate alkyl peroxy radicals and alkyl hydroperoxide [43]. Such ROS as alkyl peroxy

radicals have the rapid oxidation capacity without additional catalyst[43] [30]. Furthermore, there was no product in this control that thioanisole was oxidized by cumene hydroperoxide for different shorter time in THN at 30 °C in N₂. In general, the catalyst-free oxidation by organic peroxides is very slow at room temperature [44]. Therefore, we can draw a conclusion that a relatively stable ROS generated from high temperature aerobic pretreatment is likely to be THN-based-peroxy radicals.

Table3: Oxidation of thioanisole in different time at 30 °C after pretreatment of tetralin in O₂ at high temperature

Entry	Time/min	Conv./%	a	b
1	0.5	22	0	0
2	3	25	0	0
3	10	29	0	0
4	15	30	0	0

Condition: ^aAfter tetralin (10 mL) being pretreated at 110 °C for 30 min in O₂, then rapidly cooled to 30 °C and thioanisole (0.8 mmol) was added and oxidized for different times. ^bThioanisole (0.8 mmol) was oxidized by cumene hydroperoxide (1.6 mmol) for different time in tetralin (10 mL) at 30 °C in N₂; Conversion were determined based on GC Internal standard method (Internal standard: Anisole).

Quenching experiments of ROS

Alkylperoxy radicals [THN-based-peroxy radicals ($\text{ROO}\cdot$)], hydroxyl radicals ($\text{OH}\cdot$) and superoxide free radicals ($\text{O}_2\cdot^-$) are generally recognized as ROS in the aerobic oxidation [45]. The quenching experiments for these ROS were conducted by adding 0.8 mmol TEMPO (a quencher of $\text{ROO}\cdot$, $\text{OH}\cdot$ and $\text{O}_2\cdot^-$) [46-47], PBQ (p-benzoquinone, a quencher of $\text{O}_2\cdot^-$) [45], p-cresol (a quencher of $\text{OH}\cdot$) [48-53], respectively. The influence of the quencher on the oxidation of thioanisole by O_2 was illustrated in Fig.3. Catalyst-free oxidation of thioanisole was apparently quenched in the presence of TEMPO, whereas decelerated inapparently in the presence of PBQ or p-cresol. Quenching experiments suggested that $\text{ROO}\cdot$ were the main ROS for the catalyst-free oxidation.

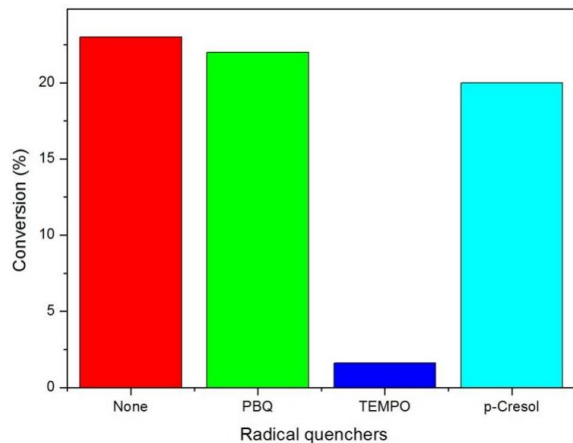
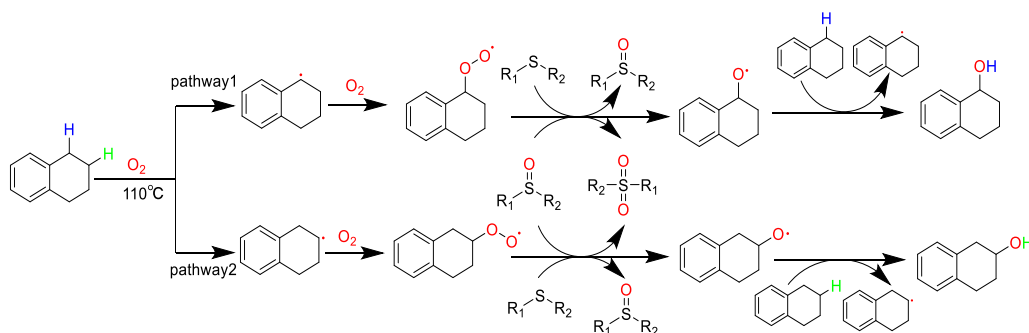


Fig. 3: The effect of quenchers on the oxidation of thioanisole.

Reaction condition: Thioanisole, 0.8 mmol; O_2 under atmospheric pressure; THN, 10 mL; Quencher, mmol; Reaction time, 2h.

The reaction mechanism of catalyst-free OOS by O_2

According to the results in the work and the relative literature [54], the above results are well explained according to the following reaction pathway 1 and pathway 2 (Scheme 1. THN as a case). We believe that the active $\text{C}(\text{sp}^3)\text{-H}$ bond of THN facilitating its homolysis can form the two THN based alkyl carbon free radicals ($\text{R}\cdot$) in the presence of O_2 under relatively mild heating conditions, then activate O_2 generating two peroxy radicals ($\text{ROO}\cdot$). Next, the two ROS directly oxidize sulfide to sulfoxide and sulfone with the concomitant production of alkoxy radicals ($\text{RO}\cdot$). Subsequently, the latter ($\text{RO}\cdot$) can abstract hydrogen from the secondary $\text{C}(\text{sp}^3)\text{-H}$ bond of THN forming $\text{R}\cdot$ to achieve the reaction cycle. Recently, Wu et.al. proposed a radical oxidation pathway in metal-free aerobic epoxidation of olefins [30]. Meanwhile, we further verify the proposed mechanism through DFT calculations. Calculation results showed that the activation energy required via radical pathway was ca. 105 kJ/mol, whereas organic hydroperoxide pathway demanded ca. 138 kJ/mol. Moreover, it has been observed that there was no product in the oxidation of thioanisole by organic cumene hydroperoxide at 30 °C (Table 3). Obviously, the radical pathway presents a lower activation energy. Therefore, we can conclude that the proposed mechanism based on the $\text{ROO}\cdot$ radical pathway is reasonable.



Scheme-1: Mechanism diagram of THN (THN as a case).

Conclusion

In summary, the active C(sp³)-H bonds significantly promoted the catalyst-free OOS by O₂ under relatively mild heating conditions. A possible mechanism has been confirmed: the active reactivity of the secondary or tertiary C(sp³)-H bond in THN or cumene facilitates their homolysis with the aid of heating and dioxygen and the production of alkyl carbon free radicals (R·), and further the activation of molecular oxygen generating the alkyl-peroxide radicals (ROO·) as ROS for the catalyst-free oxidation. Then, the concomitant alkyloxy free radicals (RO·) can abstract a H atom from the C(sp³)-H bond forming R· to achieve this reaction cycle. This work can provide a green synthetic method for sulfoxide and sulfone compounds and a scientific basis for the green process of ultra-deep desulfurization of fuel oils.

Acknowledgments

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