

Unexpected oxidation of β -isophorone with molecular oxygen promoted by TEMPO

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Lu Jia,^a Kexian Chen,^{ab} Congmin Wang,^a Jia Yao,^a Zhirong Chen^b and Haoran Li^{*ab}

A novel and efficient protocol for the oxidation of β -isophorone (β -IP) using molecular oxygen without any additives catalyzed by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has been established. The generally accepted catalytic mechanism of alcohols by the oxoammonium cation (TEMPO+) derived from TEMPO indeed fails to explain our experimental observations, because a favorable radical-based process is confirmed by electron spin resonance measurements. Our results show that a plateau of the time-dependence curve is observed in the oxidation of β -IP with TEMPO at low temperature, which is quite different from that of *N*-hydroxyphthalimide (NHPI). The proposed mechanism of this catalytic process is also compared with that of NHPI. The theoretically characterized reaction pathways show that unlike the phthalimide *N*-oxyl radical, TEMPO promotes the oxidation *via* its interaction with the active intermediate hydroperoxide (ROOH) rather than its initial interaction with β -IP, and byproduct water also assists the α -H atom transfer from ROOH to TEMPO. In addition to the intensive oxidation of alcohols catalyzed by TEMPO, the present study widens its specific applications in the active C–H bonds of hydrocarbons, and also provides new insights into its promoted metal-free oxidation.

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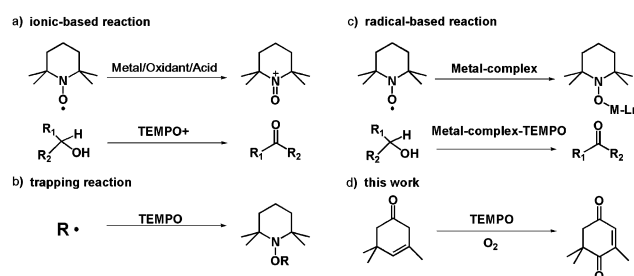
1 Introduction

The selective oxo-functionalization of hydrocarbons under mild conditions with molecular oxygen as the terminal oxidant has always been an attractive topic in academic and industrial chemistry. Usually, transition metal catalysts and harsh conditions are inevitable in conventional oxidation protocols.^{1–3} In this regard, environmentally benign catalytic systems are urgently required. The *N*-oxyl radicals are one kinds of the outstanding metal-free organocatalysts that attract great attention recently.^{4–7} Therein, the phthalimide *N*-oxyl radical (PINO) and its analogues, generated from the corresponding *N*-hydroxylamines, are prominent examples, as they have been successfully applied in the oxidation of hydrocarbons.^{8–12} In the past decades, great efforts have been made on the utilization of PINO,^{13–16} and theoretical investigations have been carried out to make further insight into their catalytic mechanisms.^{17–19} In addition to PINO, another charming *N*-oxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has been widely used in the oxidation of alcohols, sulfides, but seldom in the oxidation of hydrocarbons due to the low O–H bond dissociation enthalpy (BDE) of TEMPOH, which is thermally unfavorable for the oxidation of C–H bonds.^{20–22}

Since Golubev first reported the oxidation of alcohols by oxoammonium salts in 1965,²³ the oxoammonium cation

(TEMPO+) mechanism has been popularly recognized. Oxidants (NaOCl) or transition metals (Ru, Cu, Fe, and Co) are often demanded as co-catalysts to germinate a one-electron oxidation of TEMPO to TEMPO+ (Scheme 1a).^{24,25} Compared with the well-known ionic-based pathway, the radical-based route was less involved in the oxidation catalyzed by TEMPO, because it is generally considered as a trapper of the free radical process (Scheme 1b). Nevertheless, several successful examples have been reported that the metal-centered catalysts, such as Ru–TEMPO and Cu–TEMPO, could oxidize the alcohols *via* the radical-based channel (Scheme 1c),^{26–28} which is amazing to tune TEMPO from a radical inhibitor to a radical promoter. Although it is barely used in the oxidation of hydrocarbons like PINO due to its low enthalpy and polar effect,^{29,30} there is no doubt that the application of TEMPO in this route could be considered highly attractive with respect to the green chemistry.

In this context, we are pleased to report an interesting and unexpected experimental observation in the selective oxidation

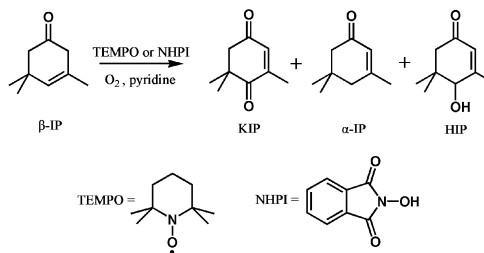


Scheme 1 Most common mechanisms with TEMPO.

^aDepartment of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou, 310027, P. R. China. E-mail: lihr@zju.edu.cn

^bState Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, P. R. China

of β -isophorone (β -IP) to ketoisophorone (KIP) with molecular oxygen promoted by the catalytic amount of TEMPO. Our results show that TEMPO plays a positive role in this oxidation, establishing the similar conversion and KIP selectivity to that of *N*-hydroxyphthalimide (NHPI). Relevant details of its mechanism are addressed herein by a combined experimental and theoretical study. The following points will be addressed in this study. (1) Which way will the oxidation of β -IP catalyzed by TEMPO take? an ionic-based or a radical-based route? (2) The role of TEMPO in this oxidation. (3) The mechanistic differences in the oxidation of β -IP catalyzed by TEMPO and PINO.



Scheme 2 The oxidation of β -IP with molecular oxygen catalyzed by TEMPO or NHPI.

2 Methodology

All the chemicals were analytically pure agents. The commercial-grade β -IP was provided by Zhejiang NHU Company. TEMPO and NHPI were purchased from commercial source and were all used as received unless otherwise stated. In a typical oxidation of the substrates, a mixture of β -IP (6.9 g, 50 mmol) and pyridine 20 mL was placed in a 50 mL three-neck, round bottom flask, which was fitted with a magnetic stirrer and O_2 inlet tube. The mixture was heated at 70 °C in an oil bath under vigorous stirring, then a stream of O_2 was conducted into the reaction solution. The catalysts were used as described in the manuscript. Samples of the reaction mixture were taken out regularly to monitor the reaction by GC with ethyl benzoate as the internal standard. The products were confirmed by comparison with standard chemicals and the reaction yields of products were also determined by GC equipped with a DB-17 column (30 m, 30 m \times 0.25 mm \times 0.25 μ m). All GC experiments were carried out and recorded using a Shimadzu GC-2010. Electron spin resonance (ESR) signals were recorded at room temperature (25 °C) with a Bruker ESR A300 spectrometer.

All calculations were performed within Gaussian 03 software.³¹ Unless stated otherwise, geometry optimizations and frequency calculations were carried out at the B3LYP/6-31G** level. All of the stationary points had no imaginary frequency, while the transition states had only one imaginary frequency. The intrinsic reaction coordinate was also performed to verify the minimal energetic pathways from transition states to their corresponding minima. All energies were obtained at the B3LYP/6-311++G**//B3LYP/6-31G** level throughout the paper.

3 Results and discussion

3.1 Oxidation of β -IP with molecular oxygen catalyzed by TEMPO

Though TEMPO is seldom used in the oxidation of hydrocarbons,³² Norton and co-workers have recently reported that the active hydrogen atom could be abstracted from a intermediate by TEMPO.³³ Inspired by this result, β -IP, with highly active allylic hydrogen atom,³⁴ is chosen as an example for the oxidation catalyzed by TEMPO (Scheme 2). To our delight, when TEMPO was employed in the oxidation, both the conversion of β -IP and selectivity of KIP went up as compared with that in the absence of any catalysts (Table 1), which indicated that TEMPO exhibited remarkable promoting effect on the selective

Table 1 The catalytic oxidation of β -IP with TEMPO^a

Entry	TEMPO (mol%)	Conversion (%)	Selectivity (%)		
			KIP	α -IP	HIP
1	0	9	45	53	1
2	1	15	77	19	2
3	2	23	81	17	2
4	4	49	85	11	1
5	8	76	83	13	2

^a Reaction conditions: β -IP (50 mmol), pyridine (20 mL), temperature: 70 °C, reaction time: 12 h.

oxidation of β -IP. The α -IP, FIP, and HIP were common byproducts in the oxidation of β -IP, but the amount of α -IP and HIP generated in this system was very small and no FIP was observed (Table 1, entries 2–5). The amount effect of TEMPO on the reaction was investigated. Increasing the amount of catalyst from 1 to 8 mol% had little influence on the selectivity of KIP (Table 1, entries 2–5). Alternately, it was decreased a little when the amount of TEMPO was increased up to 8 mol%. Only 4 mol % catalyst at 70 °C for 12 h gave KIP (85%) along with a small amount of byproducts (Table 1, entry 4). Therefore, the 4 mol% was considered as a preferable amount of TEMPO in this system. The present results showed that TEMPO largely promoted the oxidation of β -IP under mild conditions.

To elucidate how TEMPO promoted the oxidation of β -IP, relevant mechanistic studies were attempted. As the experiments were carried out in pyridine, lacking of super acid and base in the reaction system, this oxidation was unlikely to occur through an ionic pathway. Besides, there was little chance for TEMPO to be oxidized into TEMPO⁺ without any strong oxidants or metal co-catalysts.²⁴ Furthermore, the structure of β -IP was quite different from that of alcohols. As the O–H bond in alcohols could be oxidized into the carbonyl group *via* one-electronic redox of TEMPO⁺,³⁵ the C–H bond in β -IP might not be oxidized into the carbonyl group to form KIP *via* the same pathway because oxygen atom was required. Therefore, the traditional TEMPO⁺ mechanism for the oxidation of alcohols failed to explain our experimental observations. Moreover, the ESR signals of this system were detected by the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin trap technique. Due to the complex process of the oxidation, several kinds of radicals might exist simultaneously, which could lead to a mixed

spectrum of the ESR signals. As shown in Fig. 1, the split of the ESR spectrum became clear with the reaction going on. The signal of TEMPO with low consistency might be overlapped or TEMPO participated in the reaction and its signal might diminish. The spectrum observed at 15 min had the hyperfine coupling constants of nitrogen splitting (a_N) of 12.87 G and β -hydrogen splitting (a_H) of 10.31 G, which suggested these species might be the DMPO adducts of peroxy radicals.³⁶ Besides, another ESR signal with $a_N = 13.34$ G and $a_H = 7.43$ G was also observed, similar to the parameters of DMPO adducts of alkoxy radicals.³⁷ These ESR signals became weak after an hour and a new spectrum was observed at 90 min. The explanation might be that the DMPO adducts of peroxy or alkoxy radicals could disproportionate to yield a 2X-substituted DMPO (X = peroxy or alkoxy radical) and a 2X-DMPO hydroxylamine. The former might further react with peroxy or alkoxy radicals and the product 2,2-bis adduct of DMPO, which was lack of the β -hydrogen atom,³⁸ might account for this spectrum. The observed ESR spectrum of this system supports a radical-based process for this oxidation.

3.2 Comparison of β -IP oxidation catalyzed by TEMPO and NHPI

Another *N*-oxyl radical precursor NHPI was also tested in this reaction. It was noteworthy that the experimental observation in the oxidation of β -IP catalyzed by TEMPO and NHPI were quite similar (Table 2, entries 2 and 3). It seemed that both of them had the same effect on boosting the reaction, which was beyond the traditional sense that TEMPO was much less effective than PINO in the oxidation of hydrocarbons.³² According to the previous work,³⁴ the oxidation of β -IP catalyzed by PINO, *in situ* generated from its precursor NHPI, also occurred through the radical pathway, and its classical mechanism was delineated in Scheme 3. It is a general consensus that the hydrogen abstraction by PINO from substrates is a crucial step in the whole oxidation. TEMPO, unlike PINO, is involved in few cases as a good hydrogen abstractor. Therefore, it is interesting to clarify how TEMPO promotes the oxidation of β -IP. Time-dependence

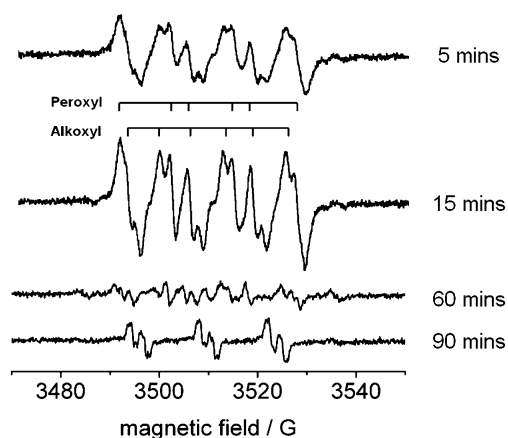
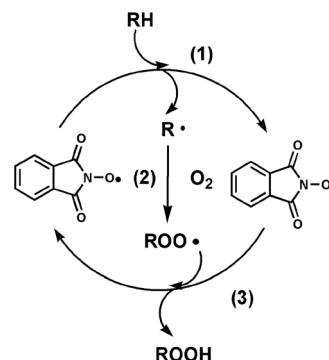


Fig. 1 X-band ESR spectrum obtained from the mixture of β -IP, TEMPO and DMPO at different time.

Table 2 The catalytic oxidation of β -IP with TEMPO and NHPI^a

Entry	Catalyst (mol%)	Conversion (%)	Selectivity (%)		
			KIP	α -IP	HIP
1	0	9	45	53	1
2	TEMPO/4	49	85	11	1
3	NHPI/4	57	90	8	2

^a Reaction conditions: β -IP (50 mmol), pyridine (20 mL), temperature: 70 °C, reaction time: 12 h.



Scheme 3 Recycle in the oxidation of hydrocarbons catalyzed by PINO.

curves, powerful tools for investigating the reaction process,^{39–41} were made to gain further insight into the oxidation of β -IP catalyzed by TEMPO, NHPI and no catalyst, respectively.

Firstly, three time-dependence curves were obtained at 70 °C. Compared with the autoxidation (Fig. 2), the conversion of β -IP was increased in the presence of catalysts. Higher conversions were obtained for both TEMPO and NHPI, which were in accordance with the results in Section 1. In Fig. 2, it was clear that the curve of autoxidation went up smoothly, while these with catalysts went up rapidly at the beginning of the oxidation. The slope of curve for NHPI was remarkable than that of TEMPO. The explanation is that PINO is easily produced from NHPI at high temperature and acts as a good hydrogen abstractor to promote the reaction. Meanwhile, TEMPO could also promote the oxidation at the beginning stage when compared with the autoxidation, but it was not as obviously as that with PINO (Fig. 2). Although the rate of hydrogen abstraction between TEMPO and the substrate could be accelerated by high temperature,⁴² the autoxidation of β -IP could not be overlooked when the temperature went up. Thus, it was still vague whether TEMPO promoted the oxidation independently like PINO or needing the assistance of the autoxidation intermediate, which was much more active than the β -IP. To eliminate the effect of the autoxidation, the evolutions of the β -IP conversion were obtained at lower temperature.

As the trends of these curves at 55 °C (Fig. 3A) were not as distinct as expected when compared with these at 70 °C, other experiments were performed. The temperature of reaction mixture kept at 55 °C for 4 h with stirring under an oxygen

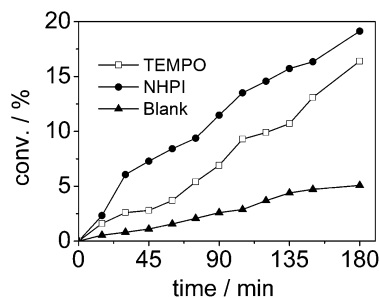


Fig. 2 Time-dependence curves for the conversion of β -IP in 3 hours at 70 °C catalyzed by TEMPO (\square), NHPI (\bullet), and no catalyst (\blacktriangle), respectively.

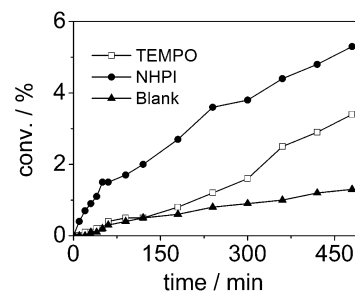


Fig. 4 Time-dependence curves for the conversion of β -IP in 8 hours at 40 °C catalyzed by TEMPO (\square), NHPI (\bullet), and no catalyst (\blacktriangle), respectively.

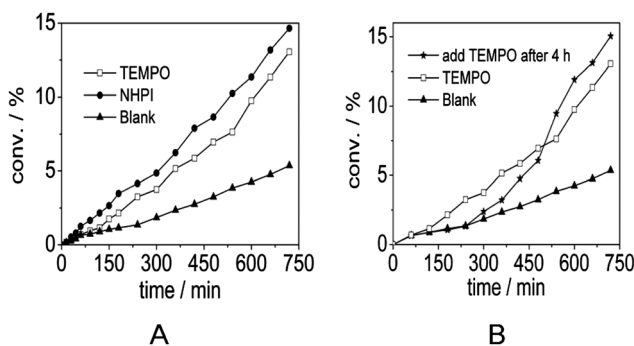


Fig. 3 Time-dependence curves for the conversion of β -IP in 12 hours at 55 °C. (A) Oxidation catalyzed by TEMPO (\square), NHPI (\bullet), and no catalyst (\blacktriangle), respectively. (B) Autoxidation of β -IP (\blacktriangle), adding TEMPO initially (\square) and after 4 h to the reaction (\star), respectively.

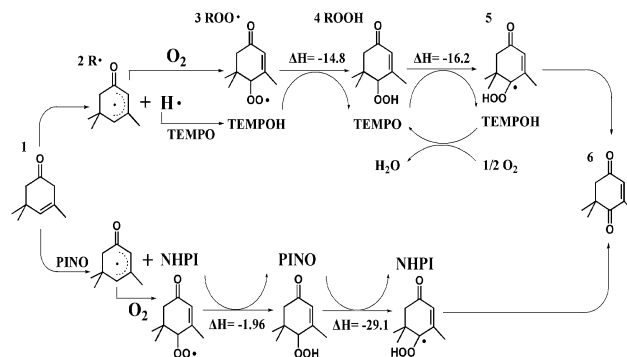
atmosphere without any catalyst, and then TEMPO (23 mg, 4%) was added to the flask for another 8 h. It was worth mentioning that the trends of the curves (Fig. 3B) for TEMPO and autoxidation were somewhat similar at the primary stage but a remarkable increase of the conversion appeared when TEMPO was added to the reaction mixture. With time going on, the distinction between them became larger and larger. It indicated that the dramatic change might be attributed to the peroxide intermediate, which yielded *via* the autoxidation of substrate.^{43,44} Herein, we speculated that the sum of the intermediate was accumulated after several hours, and then they associated with TEMPO to speed up the whole reaction.

More remarkable difference was found in time-dependence curves at 40 °C (Fig. 4), suggesting the different pathways for the oxidation catalyzed by TEMPO and PINO. The oxidation of β -IP catalyzed by NHPI was fast at the beginning stage when compared with that catalyzed by TEMPO and autoxidation. It was apparent that PINO was a much more active radical for abstracting hydrogen to rapidly trigger the chain reaction, which was different from TEMPO. Apparent platforms of time-dependence curves emerged in both TEMPO and the autoxidation system at the primary stage, implying that there was an induction period in the oxidation.⁴⁰ From this point of view, we proposed that the platform was caused by the process for the accumulation of the active intermediate, which was essential in

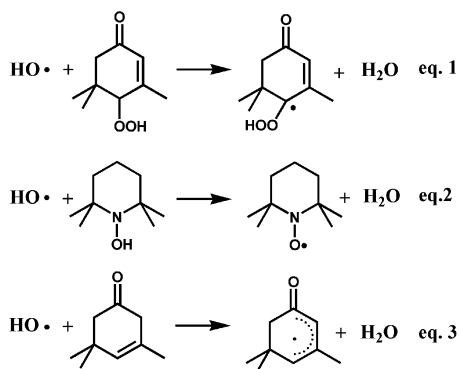
the oxidation catalyzed by TEMPO. Encouraged by these observations, theoretical calculations were performed to support this mechanism.

3.3 Theoretical elucidation of the mechanism

Base on the above results, the oxidation pathway of β -IP catalyzed by TEMPO was postulated (Scheme 4). Firstly, alky radicals were generated *via* the homolytic dissociation of the β -IP (1) to trigger the whole oxidation. A resonance occurred in the radicals to form the conjugation structures (2). Adding oxygen to these species produced peroxy radicals (ROO^\bullet , 3), which could abstract hydrogen atom from the TEMPOH, thereby affording TEMPO and the intermediate hydroperoxide (ROOH , 4). On one hand, the ROOH could dissociate into the alkoxy radicals (RO^\bullet) and hydroxyl radical (HO^\bullet).^{34,45} On the other hand, it could react with TEMPO, leading to the formation of the TEMPOH and the $\text{R}_{(\alpha\text{-H})}\text{OOH}$ radical (5). Then, TEMPOH was oxidized to TEMPO with the assistance of oxygen²⁷ and the $\text{R}_{(\alpha\text{-H})}\text{OOH}$ radical was directly decomposed to KIP (6) and HO^\bullet . All of these might account for a high selectivity of KIP. It was worth to note that the reactive HO^\bullet radical played a positive role in the reaction. As shown in Scheme 5, it could enter the reaction quickly and react with ROOH to yield the $\text{R}_{(\alpha\text{-H})}\text{OOH}$ radical (eqn (1)). Besides, it could also react with TEMPOH to generate TEMPO (eqn (2)), which was of great helpful in the recycle of the catalyst.



Scheme 4 Proposed reaction pathways in the oxidation of β -IP catalyzed by TEMPO and PINO. ΔH (kcal mol^{-1}) refers to the enthalpy change of the reactions.



Scheme 5 The possible pathways involved with hydroxyl radical.

Moreover, it could abstract the hydrogen atom from the β -IP, producing the IP radicals (eqn (3)). The strong exothermic effects of all these processes are beneficial for the whole oxidation.³⁴

To further verify this mechanism, theoretical calculations were carried out. Besides the homolytic cleavage of C–H bond caused by heat or the trace impurities, the RO \cdot , ROO \cdot and HO \cdot radicals also trigger the reaction *via* the H-abstraction from substrate.³⁸ Our results showed that this process was somewhat different for TEMPO and PINO (Scheme 4). The H-abstraction barrier of β -IP by PINO was much lower than that of ROO \cdot (Fig. 5), leading to its high catalytic efficiency, but the reactivity of TEMPO was lower than that of PINO. Although the weak hydrogen atom transfer from the active N–H and metal–H bond to TEMPO were reported in recent studies,^{46–48} the higher barrier of the direct allylic H-abstraction by TEMPO (Fig. 5) made it little favorable in promoting the whole oxidation. However, after the induction period of the radical reaction, TEMPO obviously played a positive role in subsequent steps. On one hand, the weaker O–H bond of TEMPOH was more feasible in reacting with ROO \cdot , causing a much stronger exothermic effect than that of NHPI (Scheme 4). Although, the ROO \cdot could

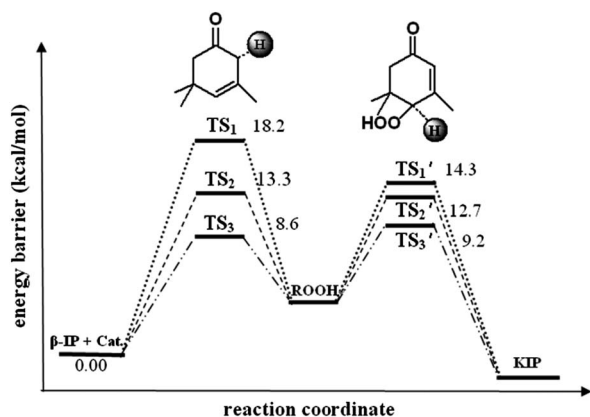


Fig. 5 Reaction energy profile for the transformation of β -IP to KIP at the B3LYP/6-311++G**//B3LYP/6-31G** level. TS₁ and TS₁', TS₂ and TS₂', TS₃ and TS₃' refer to the H-abstraction transition states catalyzed by TEMPO, ROO \cdot , and PINO, respectively.

also react with the β -IP (1) which was considered as a vital important step in the autoxidation of the hydrocarbons,³⁹ the exothermic effect of its reacting with TEMPOH was much more beneficial. On the other hand, the active α -H atom transfer from ROOH to TEMPO was much easier than TEMPO directly abstracted the allylic hydrogen from β -IP (Fig. 5), and its thermal effect of this process was about -16.2 kcal mol $^{-1}$, enabling a smooth oxidation.

Apart from the above-mentioned plausible mechanism, TEMPO has several superiors over PINO. Compared with the non-persistent radical PINO, the persistent radical TEMPO makes the decomposition of it a less pronounced limitation, which is beneficial for catalysis.⁴⁹ Although it is difficult to activate the inertia hydrocarbons, the oxidation of the active C–H bond in β -IP using TEMPO can be achieved. Furthermore, the reverse process of TEMPOH to TEMPO is highly efficient in the presence of oxygen, while it is not contributed to the recycle of PINO.²⁷ In addition, the TEMPOH could bridge the transfer of hydrogen atom.⁵⁰ Unfortunately, this transition state have not located yet, which would be further studied in our future work. Although TEMPO is regarded as a radical trapper, the combination of it and alkyl radical could lower the energy barrier of radical initiation and the reversible trapping of radicals could protect the active species from undesirable byproduct to increase the selectivity of the oxidation.^{51,52}

Moreover, the common byproduct of oxidation water could be favorable for the α -H atom transfer from ROOH to TEMPO. As shown in Fig. 6, the C–H bond of the ROOH involved in the α -H atom transfer is elongated to 1.391 Å and 1.442 Å respectively in the transition state with and without water. This indicates that water might induce shorter distance in the α -H atom transfer, which could decrease the activation energy.⁵³ Besides, the difference of spin densities located on the oxygen and nitrogen atom of TEMPO in the transition state is enlarged in the presence of water (Fig. 6B), which might stabilize the transition state. Based on the above discussion, TEMPO was not as capable as PINO to trigger the radical reaction but it could play a positive role in the subsequent oxidation steps especially with the help of water and oxygen, which was not the same as PINO.

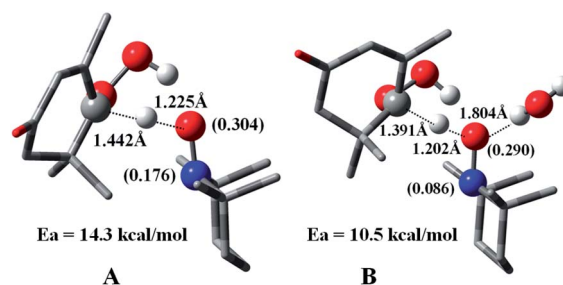


Fig. 6 Computed transition states for (A) the α -H atom transfer from ROOH to TEMPO and (B) the same process assisted by water. The values in the parentheses denote the spin density located on the atom. Ea refers to the activation energy at the B3LYP/6-311++G**//B3LYP/6-31G** level (partial hydrogen atoms are omitted for clarity).

4 Conclusions

In summary, TEMPO is found to be an effective catalyst in the selective oxidation of β -IP to KIP with molecular oxygen. Unlike the traditional TEMPO+ mechanism for the oxidation of alcohols, a radical-based process is suggested for our system. The different catalytic processes between TEMPO and PINO are interpreted by their time-dependence oxidative curves. Unlike PINO which could directly abstract the hydrogen atom from β -IP, the efficiency of TEMPO displays in the following oxidation step rather than at the primary stage. The initial autoxidation of the substrate triggered by heat or the ROO \cdot is essential for the oxidation promoted by TEMPO. The intervening water could lower the activation energy of active α -H atom transfer from ROOH to TEMPO, and the recycle of TEMPO could be easily completed in the presence of molecular oxygen. All of these make TEMPO an efficient catalyst to facilitate the oxidation of β -IP in the absence of any other additives. This protocol sheds new light on the oxidation of C–H bonds promoted by TEMPO under mild mediator-free conditions, and adds valuable information to its catalytic mechanism. The selective oxidation of other active hydrocarbons with TEMPO is quite appealing, which will be addressed in our oncoming work.

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