

Novel Schiff base complexes as catalysts in aerobic selective oxidation of β -isophorone

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Abstract

A series of novel metal–Schiff base complexes with the general formula ML_nX_m (where $M = \text{Cu, Ce, Nd, etc.}$, $L = \text{disalicylaldehyde–arginine (DSALA)}$ and the derivatives, $n = 1, 2$, $X = \text{Cl}$, $m = 1, 2, 3$) have been synthesized and applied in aerobic oxidation for the first time, especially, the oxidation of β -isophorone to keto-isophorone was explored. The ML_nX_m complexes were synthesized from arginine, salicylaldehyde with the derivatives and metal chloride. They were characterized by physicochemical methods such as elemental analysis, IR, $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra, etc. A new practical method was studied for β -isophorone oxidation with Cu–DSALA and the derivatives. Compared with the general ones, the catalysts described herein are much more efficient with the β -isophorone conversion up to nearly 100% and the keto-isophorone yield exceeding 95%. Moreover, the catalysts in use were much less than that of salen catalysts, while the reaction time was relatively shorter. Additionally, the mechanism of β -isophorone oxidation with influence factors such as temperature, catalyst, solvent, assistant solvent, etc. were also studied in detail.

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1. Introduction

Oxidation reaction is so important that it continues to be an area of attracting intense interests among academic and industrial chemists [1,2]. Nowadays, the environment trends have forced them to re-evaluate and improve traditional technologies and processes [3–6]. An ideal oxidation system would employ inexpensive, readily abundant terminal and environment-friendly oxidants like H_2O_2 , molecular oxygen (O_2 or air) and so on, instead of the noxious traditional oxidants such as KMnO_4 , K_2CrO_7 , MnO_2 , OsO_4 , etc. [7,8]. At present, molecular oxygen used as oxidant is studied more and more in organic, organometallic and inorganic chemistry because of no pollutant [9–13]. However, to our knowledge, it is not a kind of active oxidant which can reach the same oxidation potential as the traditional oxidants. Hence, various catalysts are commonly studied and applied into molecular oxidation systems and have become a key point [14–20]. As a result, the development of

metal-catalyzed methods for aerobic selective oxidation remains a tremendous challenge in both laboratories and industries [6,21–23]. The allylic oxidation of 3,5,5-trimethylcyclohex-3-en-1-one (β -isophorone, β -IP) to 3,5,5-trimethylcyclohex-2-ene-1,4-dione (keto-isophorone, KIP) (Fig. 1) is a typical chemoselective aerobic oxidation using molecular oxygen (O_2 or air), and many conventional oxidation routes have been described in literatures to prepare KIP [24–30]. KIP is a kind of useful chemical material used widely as flavoring and fragrance in foodstuffs or cosmetic formulations. Moreover, KIP is an important intermediate for preparing vitamins, carotenoids and so on [9,31–35]. Nowadays, the increasing demands of KIP materials and the much more rigorous environmental requirements make it more attractive to develop a cheap, efficient and environment-friendly technology from β -IP to KIP. Till now, many kinds of catalysts have been studied and applied in β -IP oxidation, among which bionic catalysts attract most of the attentions, due to bionic catalysts like metal–Schiff base complexes, metal–porphyrin complexes and metal–phthalocyanine complexes, etc. are more efficient and stereo-selective [9,36,37]. They are excellent catalysts while much of them have been synthesized and applied in both laboratories and industries. However, compared with bio-

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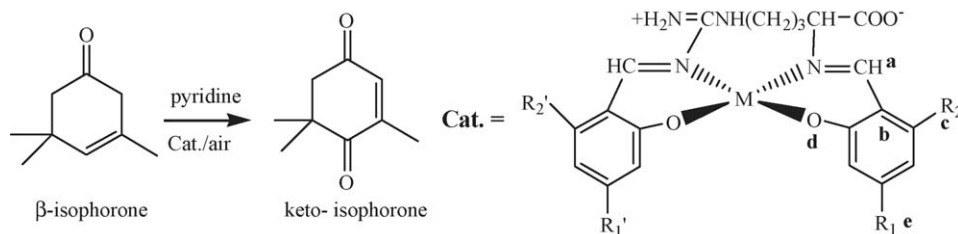


Fig. 1. The oxidation of β -isophorone to keto-isophorone using pyridine as the solvent, air as the oxidant. A series of catalysts with different metals and different substitute functional groups was used. Where $M = \text{Cu(II)}$, Nd(III) , Ce(IV) , etc., R_1 , R_2 , R_1' , $R_2' = \text{H}$, OH , OCH_3 , etc., a–e displays half of the main substitute places of the ligand.

logic catalyst like enzyme [38], which has high efficiency and perfect selectivity, there is still a long way to go. It is believed that bionic catalyst could be studied and improved extensively.

Schiff base catalyst is a kind of bionic catalyst used normally in β -IP oxidation. However, most of it cannot provide the satisfying efficiency, including reaction rate, conversion, selectivity and so on. It has been found that the structure of Schiff bases and the coordination of them to metals play important roles in the reactions. We described herein a series of novel metal–Schiff bases with the general formula ML_nX_m (where $M = \text{Cu}$, Ce , Nd , etc., $L = \text{disalicylaldehyde-arginine (DSALA)}$ and the derivatives, $n = 1, 2$, $X = \text{Cl}$, $m = 1, 2, 3$) (Fig. 1). They are synthesized on the basis of arginine, which has two kinds of asymmetric $-\text{NH}_2$ (Fig. 2). It is suggested that asymmetric Schiff bases usually have better selectivity for reactions, due to their special structures.

In this study, the novel Schiff base catalysts were used in β -IP oxidation. We adopted a new practical method using air as the oxidant, pyridine as the solvent and DMSO as the assis-

tant solvent instead of pure oxygen as the oxidant, and the mixture consists of methyl ethyl ketone (MEK), acetylacetone, triethylamine and water as the solvent [39]. Compared with previous processes, the novel catalysts (Cu-DSALA and the derivatives) were excellent providing the KIP yields exceeding 95% as expected. Besides, the amount of catalysts used here were much less than the others, while the reaction time was relatively shorter when it was done under very mild conditions. We also studied herein the oxidation mechanism on the basis of different conditions like temperature, catalyst, solvent, assistant solvent and substitute functional groups, etc. in detail.

2. Experimental section

2.1. Preparation of novel metal–Schiff base complexes

The asymmetric Schiff bases (DSALA and the derivatives) were obtained by condensation of arginine, salicylaldehyde and the relevant. And then the metal–Schiff base catalysts were

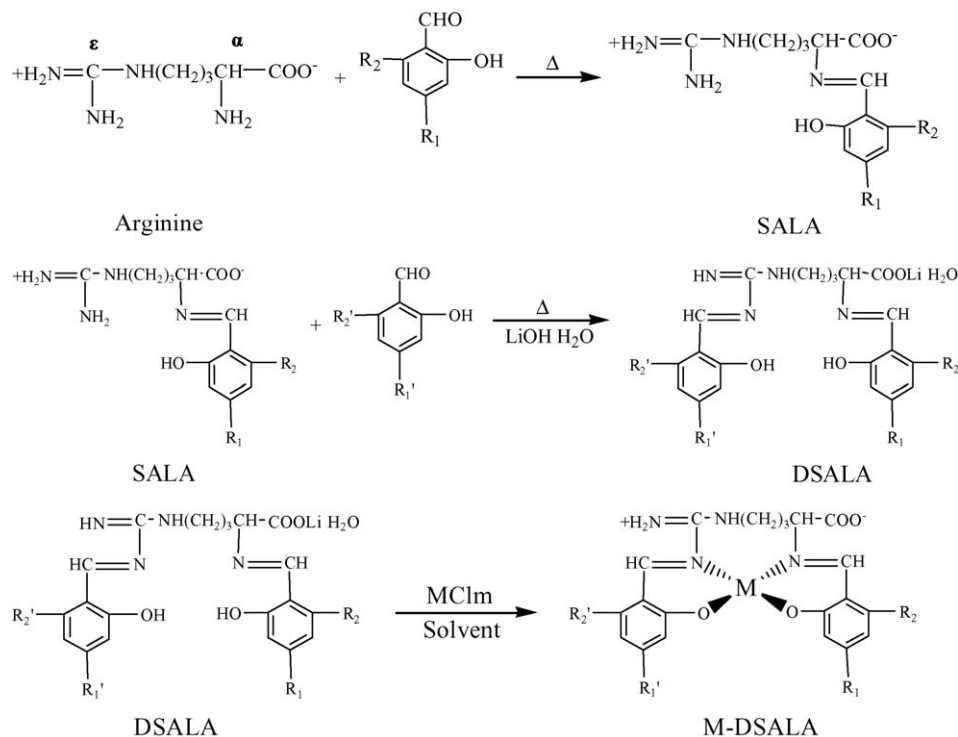


Fig. 2. Overall synthesis path for the preparation of M -DSALA and the derivatives. α - and ϵ - are two active places combined with $-\text{NH}_2$ of arginine, R_1 , R_1' , R_2 , $R_2' = \text{H}$, OH , OCH_3 , etc., $M = \text{Cu(II)}$, Ce(IV) , Nd(III) .

obtained through DSALA and the derivatives coordinated to metal chloride. The overall synthesis path was shown in the following equation (Fig. 2).

As shown in Fig. 2, there are two kinds of active $-\text{NH}_2$ in arginine (α - and ε -). It is reacted in order when condensed to salicylaldehyde or the derivatives. It has been known that guanido was formed in ε -position and it was protected in neutral condition. Therefore, α -position was reacted to salicylaldehyde or the derivatives firstly. Then ε -position could be reacted while LiOH was added. After that, metal chloride was added to synthesize the complexes. The preparation and characterization of the catalysts were introduced in the following sections.

2.1.1. Preparation of salicylaldehyde–arginine Schiff base (SALA)

To prepare salicylaldehyde–arginine Schiff base (SALA), 10 mmol of arginine was dissolved into the heated methanol solvent. And equimolar quantities of salicylaldehyde were dropped to the solution slowly. Then the mixture was stirred and refluxed at about 65 °C, over the course of 30 min. A bright yellow solid was obtained after the distillation of most of the solvent. Finally, with the processes of filtration, washed by ethanol and dried in vacuo, SALA was prepared. Yields: 88%.

SALA ($\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_3$), elemental analysis: C%: 56.02 (56.05), H%: 6.54 (6.47), N%: 20.14 (20.12). In the bracket it is the theoretical value. IR absorption bands in 1482.1–1631.9 cm^{-1} region can be attributed to the C=O, C=N stretching vibrations. ^1H NMR (DMSO): δ 9.21 (s, 1H), 8.43 (s, 1H), 8.25–7.5 (m, 4H), 6.5–7.5 (m, 4H), 3.79 (t, 1H), 3.40 (s, 1H), 3.10 (t, 2H), 1.70–1.93 (m, 2H), 1.48 (t, 2H). ^{13}C NMR and DEPT135 (DMSO): δ 175.3 (C=O), 164.7 (C=N), 163.6 (C=N), 157.9 (C), 132.8–117.7 (5C, phenyl), 72.3 (CH), 26.3–40.8 (3 CH_2). The more detailed NMR analysis was described in supporting information.

2.1.2. Preparation of disalicylaldehyde–arginine Schiff base (DSALA)

For the preparation of disalicylaldehyde–arginine Schiff base (DSALA), 2 mmol of salicylaldehyde–arginine with the equimolar quantities of LiOH·H₂O were dissolved into the heated ethanol solvent (180 ml), and the indissolved deposits were filtrated. Then 2.4 mmol of salicylaldehyde was dropped slowly. The mixture was refluxed for 1 h. A yellow solid was isolated after the distillation of most of the ethanol solvent, freezing and adding some isopropyl alcohol. Finally with the processes of filtration, washed by isopropyl alcohol and dried in vacuo, DSALA was prepared. Yields: 34%.

DSALA ($\text{C}_{20}\text{H}_{21}\text{N}_4\text{O}_4\text{Li}\cdot\text{H}_2\text{O}$), element analysis: C%: 58.98 (59.11), H%: 5.94 (5.67), N%: 13.71 (13.79). In the bracket it is the theoretical value. IR absorption bands in 1461.5–1635.8 cm^{-1} region can be attributed to the C=O, C=N stretching vibrations. Compared with SALA, the absorption peaks are strengthened and shifted a little. ^1H NMR (DMSO): δ 9.90 (s, 1H), 9.16 (s, 1H), 8.43 (s, 1H), 7.50–7.79 (m, 4H), 6.45–7.40 (m, 8H), 3.80 (t, 1H), 3.10 (t, 2H), 1.70–1.93 (m, 2H), 1.48 (t, 2H). ^{13}C NMR and DEPT135 (DMSO): δ 175.3 (C=O), 164.7 (C=N), 163.6 (C=N), 157.9 (2C), 136.5 (C=N),

132.8–117.7 (10C, 2phenyl), 72.3 (CH), 26.3–40.8 (3 CH_2). The more detailed NMR analysis was described in supporting information.

2.1.3. Preparation of metal–disalicylaldehyde–arginine Schiff base

Owing to the low yield of Li(I) salt of the ligand, synthesis of the complex has been improved using a direct method: The metal chloride (2 mmol) in ethanol was added dropwise to a solution of the above Schiff base (1 mmol) with continuous stirring for 20 min at room temperature, a precipitate was isolated gradually, filtered and washed by ethanol, dried in vacuo. The powder was finally obtained after recrystallization in anhydrous ethanol. Yields: 55%, air stability: stable in air. Solubility: soluble in H₂O, CH₃OH, C₂H₅OH, DMF, DMSO, etc. not soluble in pyridine.

The relative synthesis and characterizing methods for ML_nX_m (the derivatives) were described in relevant articles [40–42].

2.2. Characterization

The FT-IR spectra were recorded as KBr pellets using Bruker APEXIII equipment. ^1H NMR, ^{13}C NMR and DEPT135 spectra were detected by Bruker ARX 500 NMR spectrometer using methyl sulfoxide-D6 ($(\text{CD}_3)_2\text{SO}$ as the solvent), TMS as the internal standard. Elemental analysis of C, H and N content was detected by EA1110 equipment.

2.3. Catalyst evaluation

2.3.1. The new practical method for β -IP oxidation

The novel metal–Schiff bases complexes synthesized above were used as the catalysts for the oxidation of β -IP to KIP. In a typical reaction, 50 g β -IP, 20 ml pyridine and 0.1 g Cu–DSALA were added into the glass-reactor (250 ml), which was equipped with a mechanical stirrer and an air inlet tube. Then the reaction was carried out at 48 °C in water bath with highly stirring and air flowing at a constant flow rate. The result was monitored by the GC-1100 and detected by GC–MS. Besides, a series of comparative experiments with different catalysts and different conditions were carried out. The summary of reaction was shown in Table 1.

2.3.2. The experiments in different conditions

In order to explore the process and mechanism of β -IP oxidation, several comparative experiments were done in different conditions, including solvent (Table 1), temperature (48, 52, 56 and 60 °C) (Table 3), and catalyst concentration (0.5%, 1%, 2% and 4%) (Table 4).

3. Results and discussions

3.1. The catalytic behavior of β -IP oxidation

A series of Cu–DSALA and the relatives were synthesized and applied in β -IP oxidation. The comparative experiments

Table 1
The allylic oxidation of β -IP to KIP with different catalysts and different additives^a

Entry	Catalysts (%)	Pyridine/ β -IP (%)	Other additives	X (β -IP ^b) (%)	S (KIP ^b) (%)	S (α -IP ^b) (%)	S (HIP ^b) (%)	Time (h)
1	1 [#] Cu (1.47) ^c	19.66	–	99.3	85.10	4.13	7.54	56
2	2 [#] Ce (1.50) ^c	20.00	–	98	53.47	39.79	1.15	107
3	3 [#] Nd (1.95) ^c	19.96	–	77	61.82	32.45	3.92	120
4	4 [#] Cu (1.25) ^c	20.92	–	99.8	92.48	2.37	2.72	50
5	5 [#] Ce (2.05) ^c	19.76	–	98.5	45.99	44.21	2.45	120
6	6 [#] Cu (1.02) ^c	39.92	–	99.1	95.26	2.81	1.05	64
7	7 [#] Cu (1.02) ^c	39.76	10 ml DMF ^d	99.8	93.39	3.30	2.02	45
8	8 [#] Cu (1.03) ^c	39.66	4 ml DMSO ^d	98.3	92.78	2.23	1.56	34
9	9 [#] Cu (1.03) ^c	39.32	4 ml DMSO ^d	99.2	93.85	2.66	0.95	36
10	10 [#] Cu (0.99) ^c	40.07	4 ml DMSO ^d	96.3	95.02	2.47	1.42	30
11	11 [#] Cu (0.99) ^c	40.08	4 ml DMSO ^d /LiOH	92.5	54.3	26.49	2.88	29

^a Conversion of β -IP (X) and selectivity (S) to KIP/ α -IP/HIP as determined by GC and GC–MS analysis, temperature = 48 °C, pyridine as the solvent.

^b The structures of β -IP/KIP/ α -IP/HIP were present in Fig. 3.

^c The structures of 1–11[#] catalysts were shown in Fig. 1, where 1[#] Cu: R₁, R₂, R₁', R₂' = H; 2[#] Ce: R₁, R₂, R₁', R₂' = H; 3[#] Nd: R₁, R₂, R₁', R₂' = H; 4[#] Cu: R₁, R₁' = OH, R₂, R₂' = H; 5[#] Ce: R₁, R₁' = OH, R₂, R₂' = H; 6[#] Cu: R₁, R₁' = OCH₃, R₂, R₂' = H; 7[#] Cu: R₁, R₂, R₁', R₂' = H; 8[#] Cu: R₁, R₁' = OH, R₂, R₂' = H; 9[#] Cu: R₁, R₂, R₁', R₂' = H; 10[#] Cu: R₁, R₁' = OCH₃, R₂, R₂' = H; 11[#] Cu: R₁, R₂, R₁', R₂' = H.

^d DMF/DMSO was used as the assistant solvent for the catalyst here. The reaction rate was obviously improved while no obvious effect was occurred for β -IP conversion and KIP selectivity in experiment. The ratio of DMF/pyridine = 1:2, DMSO/pyridine = 1:5, as the solubility of the catalysts in DMSO is better than in DMF.

with different conditions were carried out. A summary of more detailed studies on β -IP conversion (X) and KIP/ α -IP/HIP (Fig. 3) selectivity (S) with different catalysts and additives was shown in Table 1. The series of catalysts with different metals and different substitute functional groups were shown in Fig. 1.

As shown in Table 1, three kinds of metal ions were employed for the catalysts. It seems Cu(II) is notably superior to Ce(IV) and Nd(III), not only for the higher KIP selectivity (90% versus 60%), but also for the comparatively shorter reaction times (56 h versus 120 h) (Entry 1–5).

It has also been found that β -IP oxidation displayed a strong dependence on reaction conditions. In previous studies, β -IP was catalyzed by general metal–Schiff base catalysts with the

formula [LMn(III)(Cl)] at temperature in the range 10–27 °C and partial pressure 0.2–3 atm of high pure molecular oxygen. The solvent used in the oxidation consists of MEK and small amounts of acetylacetone, triethylamine and water.

Compared with previous processes, a new practical method was adopted. On one hand, pyridine was used as the solvent instead. It seems the amount of pyridine used can influence the selectivity notably. The selectivity of KIP was improved from 85.1% to 93.9% when the amount of pyridine increased from 20% to 40% (Entry 1, 7 and 9). It was observed from experiment that pyridine was an excellent solvent, which was better than the mixed solvent reported previously. Additionally, pyridine used as the single solvent is more convenient to separate than that of mixed solvent after β -IP oxidation.

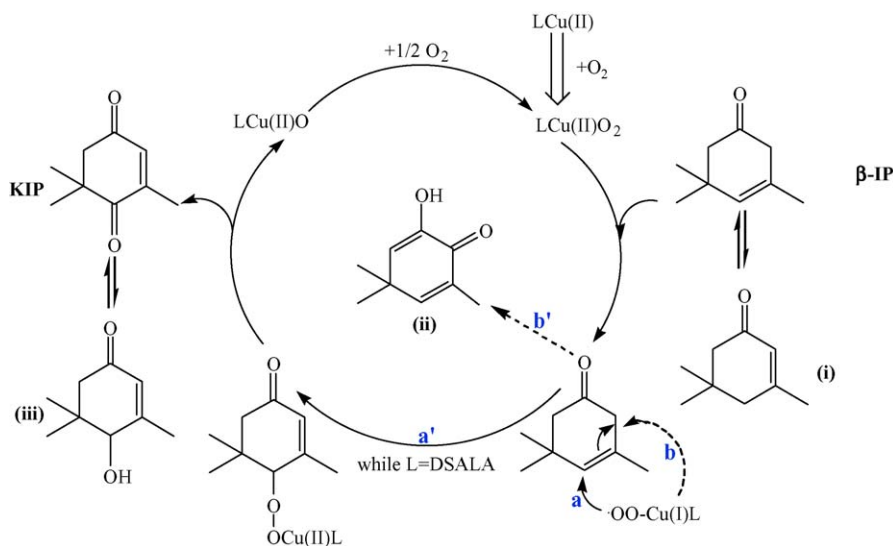


Fig. 3. The probable mechanism of β -IP oxidation. The reaction was started from the combination of LCu(II) to O₂. Then the active intermediate attacked to β -IP and KIP was obtained. The catalyst was recycled through gaining/losing [O] in the reaction. L = DSALA and the derivatives. Three kinds of by-products were: (i) 3,5,5-trimethyl-cyclohex-2-en-1-one β -IP; (ii) 4,4,6-trimethyl-2-hydroxy-cyclohex-2,5-dien-1-one EIP; (iii) 3,5,5-trimethyl-4-hydroxy-cyclohex-2-en-1-one HIP.

On the other hand, as Cu–DSALA catalysts were not totally soluble in β -IP and pyridine mixture, two kinds of assistant solvents were adopted, including DMF and DMSO. It seemed the solubility of Cu–DSALA in DMSO was well and the homogeneous mixture was formed. As a result, the reaction time was obviously decreased (36 h versus 64 h) in DMSO (Entry 6 and 9). Interestingly, the selectivity was not obviously improved in DMSO. According to the experiment, it was found that the Cu–DSALA catalysts could be dissolved in the product (KIP). The catalyst was dissolved into the mixture with the increasing of KIP while the homogeneous mixture was gradually formed. It appeared that KIP selectivity was not notably influenced in different assistant solvents, except for reaction time.

Additionally, LiOH, a kind of general co-catalyst in several oxidation reactions, was also used for β -IP oxidation. To our disappointment, we did not get the expected results while added LiOH. On the contrary, it was observed that the KIP selectivity decreased sharply while the yield of α -IP increased highly (Entry 11). As we know, the selectivity was expected to improve when adding the base. However, LiOH gave completely the opposite results. It is supposed that there is only one electronic shell around Li(I) nucleus. The smaller size and simpler structure make it different to the other alkali metals like Na(I) and K(I).

In order to study the effect of functional groups, three kinds of different substitute functional groups of Cu–DSALA complexes have been synthesized and applied for β -IP oxidation, including H, OH, OCH₃ at the place of R₁ and R'₁. It was observed from the experiment that there is no obvious difference among them (Entry 8–10). Due to R₁ and R'₁ were not the vital points to the catalyst. The structure of metal–Schiff base complex was not influenced notably. It is supposed that the places of “c” and “d” (Fig. 1) would make the crucial effect as it can influence the coordination of Schiff base to metal atom.

An extensive comparison between Cu–DSALA and the reported ones was carried out then. As shown in Table 2, three kinds of catalysts were generally used in β -IP oxidation, including metal–Schiff base complexes, metal–porphyrin or phthalocyanine complexes, metal–acetate complexes and the derivatives. Among the series investigated, the bionic catalysts were highly efficient. For example, the oxidation with manganese Schiff base and tetraporphyrin catalysts provide KIP in yields exceeding 90%. Manganese porphyrin complexes were

Table 2
Comparison between the novel catalysts and the others reported previously

Entry	Catalysts	S _{KIP} (%) ^a	Reference
1	M ^b –DSALA and the derivatives	Over 95	–
2	General Schiff base catalysts	60–70	[43]
3	Manganese Schiff bases	Over 90	[44]
4	Metal porphyrins	Nearly 93	[37]
5	Metal phthalocyanines	55–78	[45]
6	Cu(acac) ₂ and the series	84	[26]
7	Co, Mn, Pb acetates and V, Cr(III), Cu, Fe(III) (acac) complexes with pyridine	68–91	[28]

^a The selectivity of KIP, one of the most important criterions for β -IP the oxidation.

^b M was the metals used in our reaction. Cu was the most efficient one.

the most efficient catalysts providing the yield of KIP nearly 93% reported previously. In our study, Cu–DSALA with the derivatives applied in β -IP oxidation was excellent and could provide the yield of KIP exceeding 95%.

3.2. The mechanism and reaction conditions for β -IP oxidation

The oxidation of β -IP by Cu–DSALA and the derivatives gave KIP as the major products, along with small amounts of side products like α -IP (i), EIP (ii), HIP (iii), etc. The probable mechanism was shown in Fig. 3 according to the main process and the products detected by GC–MS.

As shown in Fig. 3, the reaction was started from LCu(II) catalyst combined to molecule oxygen and LCu(II)O₂ was formed. LCu(II)O₂ was inconstant as one of the electrons in it could transfer from O to Cu, and LCu(I)OO• was formed. Since there is an active C=C double bond in β -IP, it would be easily attacked by LCu(I)OO•. There are two paths for β -IP allylic oxidation. As shown in Fig. 3, oxidation through path “a” was the dominant one. Most of β -IP would be oxidized to KIP in appropriate conditions. Path “b” was the other way commonly occurred in β -IP allylic oxidation. However, it was inhibited and only a little of EIP was produced. In both paths, the catalyst combined to molecule oxygen and provided [O] to β -IP. It played an important role in transferring [O]. The catalyst itself can also be recycled through gaining/losing [O].

During β -IP oxidation, two other side reactions are unavoidable. The one is β -IP to α -IP. As mentioned previously, the conversion of β -IP to α -IP is reversible in thermodynamic equilibrium. Partial of β -IP will convert to α -IP along with β -IP oxidation. Similarly, HIP is also occurred in the reaction. It has been observed in experiment that the yield of α -IP and HIP is dependent on the reaction conditions. Therefore, it is important to choose appropriate conditions like temperature, solvent, catalyst, etc.

3.2.1. The effect of solvent

In order to improve KIP selectivity, it is necessary to inhibit side products like α -IP, EIP and HIP. Solvent is one of the important factors for β -IP oxidation. As mentioned above, β -IP is easily converted to α -IP. And the tendency of β -IP to α -IP was more easily than that of α -IP to β -IP, especially when protons were occurred. Constantini et al. [9] have also proposed that only a protic solvent are suitable, since in protic solvents β -IP will isomerize back to α -IP, which is unreactive under these conditions. And the selectivity of KIP would be obviously decreased in protonic solvent. It was similarly occurred to the conversion of KIP to HIP. As shown in Fig. 3, some of KIP would convert to HIP when protons occurred. Therefore, a kind of appropriate solvent was needed for β -IP oxidation.

In our research, pyridine was added as a solvent. As we know, pyridine is a heterocyclic aromatic tertiary amine. It was used as a kind of organic base and aprotic solvent here. The protons produced in the reaction would be captured. Therefore, most of the side reactions were expected to restrain. It was indeed proven in experiment that the conversion of β -IP to α -IP was

Table 3
Oxidation of β -IP to KIP at different temperatures

Entry	Temperature T ($^{\circ}\text{C}$)	X (β -IP) (%)	S (KIP) (%)	S (α -IP) (%)	S (HIP) (%)	S (EIP) (%)	Time t (h)
1	48	99.15	94.67	2.30	1.88	0.14	42
2	52	98.83	92.07	3.66	1.61	1.58	32.3
3	56	98.88	91.40	3.97	1.51	1.66	24
4	60	98.94	81.32	7.78	2.63	6.48	15.3

Conversion of β -IP (X) and selectivity (S) to KIP/ α -IP/HIP as determined by GC and GC–MS analysis. Pyridine used as the solvent. DMSO used as the assistant solvent. The structures of β -IP/KIP/ α -IP/HIP were presented in Fig. 3.

Table 4
Oxidation of β -IP to KIP with different catalyst concentration

Entry	Catalyst (%)	X (β -IP) (%)	S (KIP) (%)	S (α -IP) (%)	S (HIP) (%)	Time t (h)
1	0.5	98.99	89.06	6.69	2.25	47
2	1	99.15	94.67	2.30	1.88	42
3	2	99.05	95.55	1.59	1.63	35.3
4	4	98.19	94.64	0.91	1.49	36.5

Conversion of β -IP (X) and selectivity (S) to KIP/ α -IP/HIP as determined by GC and GC–MS analysis, temperature = 48 $^{\circ}\text{C}$, pyridine used as the solvent, DMSO used as the assistant solvent. The structures of β -IP/KIP/ α -IP/HIP were presented in Fig. 3.

hindered evidently in pyridine solvent. Besides, only a little of HIP was produced in the reaction. Hence, pyridine is proven to be an appropriate solvent in β -IP oxidation.

3.2.2. The effect of temperature

The effect of temperature on the oxidation of β -IP was studied in range of 38–60 $^{\circ}\text{C}$, keeping other conditions like catalyst, substrate, solvent concentration and air pressure in the same. A summary of the reactions in different temperatures was shown in Table 3.

Clearly, as shown in Table 3, the reaction time was decreased when raising the temperature. However, on the other side, the KIP selectivity was decreased. Especially when the temperature was up to 60 $^{\circ}\text{C}$, the KIP yield was only 81%, much lower than 95%, along with the increasing of by-products like α -IP/HIP/EIP. It was in consistent with the mechanism aforementioned. To our knowledge, the oxidation of β -IP was easy to occur, and even could be oxidized without catalyst. Therefore, it would be oxidized to several kinds of products more quickly without the selectivity when raising the temperature.

As the catalysts with particular structures could accelerate only one reaction pathway, they were added to improve the selectivity. However, there seems no obvious effect to the side reactions. For example, the yield of EIP (one of the by-products) was in small amount (lower than 0.14%) when the temperature was lower than 48 $^{\circ}\text{C}$, compared with 6.48% at 60 $^{\circ}\text{C}$. It has increased by 50 times more. It was suggested that the side reaction would be restrained and the oxidation catalysts would have better selectivity at lower operating temperature. Therefore, as the selectivity was comparatively more important than the reaction rate, it is appropriate in the temperature range 48–56 $^{\circ}\text{C}$ according to the factors of reaction time and selectivity.

3.2.3. The effect of catalyst concentration

In order to make clear comparison from the catalyst, different amount of the novel catalysts varies from 0.5% to 4% was

added, while temperature, substrate, solvent and air pressure, etc. were kept constant. The summary of catalytic performance was shown in Table 4.

As mentioned above, the new synthesized Cu–DSALA complex was a kind of high efficient bionic catalyst for β -IP oxidation. The amount of catalyst used here was lower than 5%, while the reaction could be completed in comparatively shorter time, along with higher selectivity. Generally, it could be concluded that the reaction time was decreased when the amount of catalysts increased. For example, it can be found that the reaction time is longer and the selectivity was notably lower than the others (Entry 1 versus 2 and 3) when the catalyst concentration is only 0.5%. It seemed the amount of catalyst was not adequate for providing the high reaction rate and selectivity. However, it was not just the case that the more catalyst used, the less reaction time spent and the higher KIP yield got. Contrary, it could be found that the reaction time was longer than that of 2% (36.5 h versus 35.3 h), when the concentration reaches 4%, along with the reducing of KIP yield (Entry 2–4).

The main cause of the unusual result was that the reactant reacted with the molecular oxygen by the intermediary agent (catalyst). As the content of the molecular oxygen in the mixture was quantitative, it was inadequate compared to 4% of the catalysts. The excessive catalysts would not affect oxidation. Consequently, it seemed 1–2% was suitable for the oxidation in our study.

4. Conclusions

A series of novel metal–Schiff base complexes have been synthesized from arginine, salicylaldehyde with the derivatives and metal chloride in our study. The obtained catalysts were applied in aerobic oxidation of β -IP to KIP. Compared with the general metal–Schiff base complexes, the catalysts described here in particular Cu–DSALA and the derivatives were much more efficient. Additionally, several advantages were displayed

as follows:

- (1) The amount of Cu–DSALA used in experiment (0.5–4%), corresponding to the reactant, is much less than that of the reported ones (5% to 5%). However, the reaction could be completed in the same reaction time, even shorter.
- (2) The catalyst is high selective providing KIP in yields exceeding 95%. It is much higher than that of general Schiff base catalysts (60–70%), even higher than the porphyrin catalysts reported previously (93%).
- (3) The catalysts activate dioxygen under very mild conditions. Instead of pure oxygen under highly pressure condition reported previously, air is used as oxidant under normal pressure condition. The oxidation by air is more gently and could be controlled more easily. Additionally, it is much cheaper and safer in the view of economics and industries.
- (4) As mentioned previously, pyridine was used as solvent here instead of complicated mixed solvent reported previously. Pyridine is a good solvent as it can also provide the reaction in an alkaline solution (OH^-) and inhibit the side reactions. Besides, it is more convenient to separate than that of mixed solvent here.

In short, the novel synthesized Schiff base catalyst (Cu–DSALA) examined herein appeared to be suitable for β -isophorone oxidation, due to their high catalytic activity and remarkable selectivity under mild conditions. We believe that such special metal–Schiff base complexes may also be suitable for the other aerobic oxidation. Our researches on synthesizing more novel complexes with different metals or different substitute functional groups and the application of these catalysts in other oxidation reaction are in progress.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.05.051.

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