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Iron(II, III)-Catalyzed Oxidation of Limonene by Dioxygen

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Abstract Labile iron(II) and iron(III) complexes $\{[Fe^{II}(bpy)_2^{2+}]_{solv}$ and $[Fe^{III}(bpy)_2^{3+}]_{solv}\}$ in acetonitrile activate dioxygen for the oxidation of limonene to produce mainly carvone, carveol, limonene oxide, and perillaldehyde. Iron(III) complex is reduced by the substrate to iron(II) one, which activates dioxygen. Probably the catalyst interacts with substrate prior to the oxidation process. Perillaldehyde is likely formed directly from oxidation of methyl group (not via alcohol). However, the aldehyde is also reduced to perillyl alcohol by the reduced form of the catalyst.

Keywords Dioxygen activation · Limonene oxidation · Iron–bipyridine complexes

1 Introduction

Monoterpenes are widely used in flavor and fragrance industry. Among these compounds *R*-(+)-limonene (D-limonene) is the most abundant, low-priced, naturally occurring product, which is suitable feedstock for production of important compounds. Selective dehydrogenation of limonene is a convenient route to *p*-cymene production [1–3], which is then converted to terephthalic acid or *p*-cresol. Relatively much attention is paid to epoxidation of limonene because the products are valuable starting materials for the synthesis of fragrances and drugs [4]. The epoxidation reactions are performed using mainly heterogeneous catalysts and hydrogen peroxide as an oxidant [5–12]; however, the use of a homogeneous catalyst was also reported [13]. Dioxygen [14–17] and *tert*-butyl hydroperoxide [18–21] were used as oxidants in epoxidation of limonene as well. Recently, [22] epoxidation of limonene was performed using acetylperoxyborate (which decomposes to peracetic acid and hydrogen peroxide) catalyzed by metal-ion-substituted aluminophosphates. Usually the addition to the ring double bond dominates over the addition to the side chain double bond. Due to the large price difference, the most interesting process is the oxidation of D-limonene to menthol, carvone and perillyl alcohol. In the 50s two oxidation methods of limonene to carvone were reported. The first starts with the reaction of limonene with nitrosyl chloride. The resulting nitrosochloride is then dehydrochlorinated to carvone oxime, which is hydrolyzed to L-carvone [23, 24]. The other one involves the formation of the epoxide with peracetic acid, its hydrolysis to limonene glycol, which is oxidized by chromate [25, 26].

Two types of systems have been basically utilized for oxidation of limonene by dioxygen. The first is Wacker oxidation process using $PdCl_2/CuCl_2/O_2$ in glacial acetic acid [27–31]. Carveyl acetates, carveol, and carvone are among the major products. The system, however, is very sensitive towards catalyst composition. Recently, palladium supported on copper-magnesium-aluminum hydrotalcites was used for liquid phase oxidation of limonene by dioxygen [32]. The other approach uses cobalt(II) salts as catalysts [33, 34]. $Co(OAc)_2/Br^-/O_2$ in acetic acid gives similar products as Wacker system [33] whereas $CoCl_2/O_2$ system in acetonitrile [34] gives three main products: limonene oxide (in acetic acid: mixture of limonene glycol and its acetates), carvone and carveol. The use of pressurized air over the Mn(III)- and Co(III)-containing molecular sieves gives mainly epoxide (39–78%,

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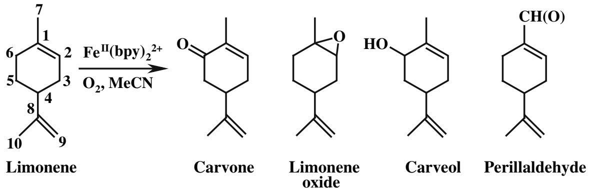


Scheme 1 Products of limonene oxidation

depending on the kind of the sieve) as well as carveol, carvone and *trans*-carveyl acetate among the other products [35]. The use of dioxygen as an oxidant gives a mixture of products, which is due to the similar electronic properties of the allylic methylene groups (carbons 3, 6) and allylic methyl groups (carbons 7, 10) [36, 37] (see Scheme 1). Oxidation of limonene with dioxygen promoted by heterogeneous sol-gel Co/SiO$_2$ catalysts gives both epoxidation and allylic oxidation products [38]. The similar profile of products was observed when limonene was oxidized using different catalyst/oxidant systems like: carbon anchored cobalt acetylacetonate/*tert*-butyl hydroperoxide [39], mesoporous silica anchored VO(Salten) {Salten = 3-[*N*,*N*-bis-3-(salicylidenamino)ethyltriamine}/urea hydroperoxide [40], Mn(Salen)Cl and Ni(Salen)/PhIO in supercritical carbon dioxide [41], and photoexcited porphyrin/dioxygen [42].

Our recent studies have indicated that labile iron complexes {$[\mathrm{Fe^{III}(bpy)_2^{3+}}]_{\mathrm{MeCN}}$, $[\mathrm{Fe^{II}(bpy)_2^{2+}}]_{\mathrm{MeCN}}$, $[\mathrm{Fe^{III}(H_2O)_6^{3+}}]_{\mathrm{MeCN}}$, and $[\mathrm{Fe^{II}(H_2O)_6^{2+}}]_{\mathrm{MeCN}}$} in base free acetonitrile activate dioxygen for oxidation of cyclohexene [43] to ketone and alcohol with relatively high yield. Moreover, the oxidized form of the catalyst is reduced by the substrate. Similar behavior was observed during oxidative dealkylation of *N*,*N*-alkyl anilines by dioxygen catalyzed by the same complexes [44]. Therefore, we have applied these catalysts to oxidize limonene with dioxygen in acetonitrile.

2 Experimental

2.1 Equipment

The reaction products were separated and identified with a Hewlett-Packard 4890A Series gas chromatograph equipped with an HP-1 capillary column (cross-linked methylsilicone-gum phase, 30 m × 0.53 mm i.d).

A three-electrode potentiostat (Princeton Applied Research Model 273A) was used to record the voltammograms. The experiments were conducted in a 15-mL electrochemical cell with provision to control the presence of dioxygen with an argon-purge system. The working electrode was a Bioanalytical Systems glassy-carbon (area, 0.09 cm^2) inlay, the auxiliary electrode—a platinum wire, and the reference electrode—an Ag/AgCl wire in an aqueous tetramethylammonium chloride solution that was adjusted to give a potential of 0.00 V vs. SCE The latter was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a Luggin capillary [45].

The UV-vis spectrophotometric measurements were made with a Hewlett-Packard Model HP-8453 diode array rapid scan spectrophotometer.

2.2 Chemicals and Regents

The reagents for the investigations and syntheses were the highest purity commercially available and were used without further purification. The solvent for all of the experiments was acetonitrile (99.93+%, HPLC grade) purchased from Aldrich. High-purity argon gas was used to deaerate the solutions. Tetraethylammonium perchlorate (TEAP, GFS Chemicals) was dried in vacuo over CaSO$_4$ for 24 h prior to use. Iron(II) and iron(III) perchlorates, $\mathrm{Fe(ClO_4)_2{\cdot}6H_2O}$ and $\mathrm{Fe(ClO_4)_3{\cdot}6H_2O}$ were obtained from GFS Chemicals. The organic substances included: (*R*)-(+)-limonene, 97 %; (–)-carveol, mixture of isomers, 97 ; (*R*)-(–)-carvone, 98%; (+)-limonene oxide, mixture of *cis* and *trans*, 97%; (*S*)-(–)-perillyl alcohol, 96%; (*S*)-(–)-perillaldehyde, 92%; (*S*)-(–)-perillic acid, 95%; 2,2'-bipyridine (bpy, 99+%); and biphenyl (PhPh, 99+%), were obtained from Aldrich.

2.3 Methods

The appropriate amounts of metal salt and ligand were combined in acetonitrile followed by the addition of substrate (1 M) (total volume = 5 mL) in the reaction cell (25 cm^3 vial with cut-out cap and Teflon-faced septum). The solution was saturated with dioxygen (O$_2$, 1 atm) or air (O$_2$, 0.2 atm) or high-purity argon gas (O$_2$, 0 atm). In case of dioxygen and air the appropriate gas saturated with acetonitryle was passed over the solution to maintain a constant solution concentration of dioxygen. The reactions were allowed to proceed for 24 h with constant stirring at room temperature (23 ± 1 °C). After the experiment samples of the reaction solution were injected into a capillary-column gas chromatograph for analysis. Authentic samples were always used to confirm product identifications and to produce standard curves for quantitative assays of the product species. Biphenyl (10 mM) was used as an internal standard. All experiments were done in triplicate. The presented values of concentration are the mean values of three independent experiments.

3 Results

Iron(II) and iron(III) complexes activate dioxygen for oxidation of limonene to produce carvone, carveol, limonene oxide, perillaldehyde, and perillyl alcohol (Scheme 1, Table 1). We have tried to find perillic acid and limonene glycol among the oxidation products. Analysis by GC and HPLC will not confirm the presence of the products. Maybe some traces are formed, however the results of analysis are ambiguous. The product profiles after 24-h reaction time indicate that the 1 mM $[Fe^{II}(bpy)_2^{2+}]_{solv}$/$O_2$(1 atm)/2 M substrate combination is the most reactive—156 products/catalyst turnovers. In the absence of the catalyst no products are formed. Under argon atmosphere the use of 50 mM of catalysts and 1 M substrate gives no products in the case of $[Fe^{II}(bpy)_2^{2+}]_{solv}$, whereas in the presence of $[Fe^{III}(bpy)_2^{3+}]_{solv}$ small amounts of oxidation products were observed. The results presented in Table 1 indicate that: (a) the use of bipyridine complexes of iron gives much better yields than aqua/solvent complexes, (b) there is no substantial difference in yields using Fe(II) or Fe(III) complexes, (c) the increase of the reaction yield is proportional to the increase of substrate concentration, (d) the products yield is proportional to the catalyst concentration in its low concentrations region, and (e) the use of air instead of dioxygen causes the decrease of the reaction yield approximately three times.

Figure 1 presents the dependence of products concentrations on time. The products profiles suggest that the products are formed independently. The almost linear increase of concentration of all products in time indicates that the catalyst is active during the time of reaction. The increase of indicated products concentrations took place also after 24 h, which indicates that the catalyst is stable over extended period of time. As a matter of fact we observed the destruction of catalyst only after 8 days. However, the amounts of by-products increased substantially (observed by number of small GC peaks) as well as the formation of polymeric products was observed. Similar behavior was also reported during oxidation of limonene in the liquid phase over V_2O_5/TiO_2 using *tert*-butyl hydroperoxide as an oxidant [46]. Therefore, we decided to analyze products after 24 h.

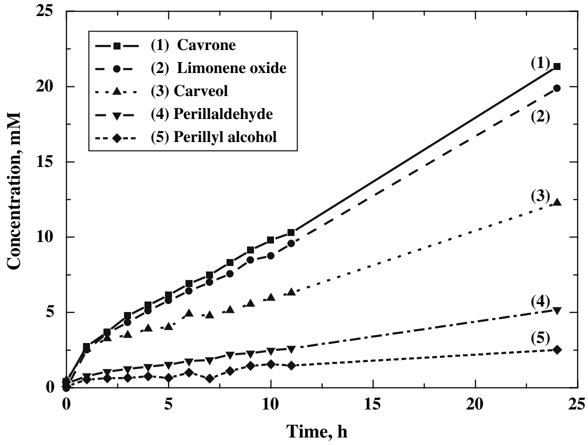


Fig. 1 Dependence of products concentration (1) carvone, (2) limonene oxide, (3) carveol, (4) perillaldehyde, and (5) perillyl alcohol on time for oxidation of 1 M limonene by dioxygen catalyzed by $[Fe^{II}(bpy)_2^{2+}]_{solv}$ in acetonitrile

It is worth to notice that the use of hydrogen peroxide as an oxidant gives much smaller yields than in the case of dioxygen. Thus, the combination of 1 mM $[Fe^{II}(bpy)_2^{2+}]_{solv}$, 1 M limonene and 100 mM hydrogen peroxide gives 6.0 mM carvone, 5.2 mM carveol, 4.6 mM limonene oxide, 2.4 mM perillaldehyde, and 1.1 mM perillyl alcohol after 24 h reaction time.

The cyclic-voltammetric measurements of iron(III) in the presence of limonene (Fig. 2A) show that after mixing the reagents the reduction peak of Fe(III)-complex is

Table 1 Oxidation of limonene by dioxygen catalyzed by iron complexes in acetonitrile (reaction time 24 h)

Catalyst	Substrate concentration, M	Catalyst concentration, mM	Oxidant	Carvone	Carveol	Limonene oxide	Perillyl aldehyde	Perillyl alcohol	TON
$Fe^{III}(bpy)_2^{3+}$	1	1	O_2	31.6	16.5	24.9	14.4	3.6	91
$Fe^{III}(bpy)_2^{3+}$	1	1	Air	7.7	7.5	8.1	2.3	1.0	27
$Fe^{II}(bpy)_2^{2+}$	1	1	O_2	21.7	13.0	20.4	6.8	3.0	65
$Fe^{II}(bpy)_2^{2+}$	1	1	Air	8.6	7.3	8.2	2.1	1.0	27
$Fe^{II}(H_2O)_6^{2+}$	1	1	O_2	4.1	2.8	2.1	2.1	0.6	12
$Fe^{II}(bpy)_2^{2+}$	1	0.25	O_2	8.3	4.9	7.7	1.8	1.1	95
$Fe^{II}(bpy)_2^{2+}$	1	0.5	O_2	14.6	8.1	13.9	3.4	1.7	83
$Fe^{II}(bpy)_2^{2+}$	1	5	O_2	45.0	22.8	42.1	22.7	3.1	27
$Fe^{II}(bpy)_2^{2+}$	0.5	1	O_2	6.6	4.0	8.0	2.2	1.2	22
$Fe^{II}(bpy)_2^{2+}$	2	1	O_2	54.0	29.9	45.6	20.1	5.9	156

TON, product molecules per catalyst molecule

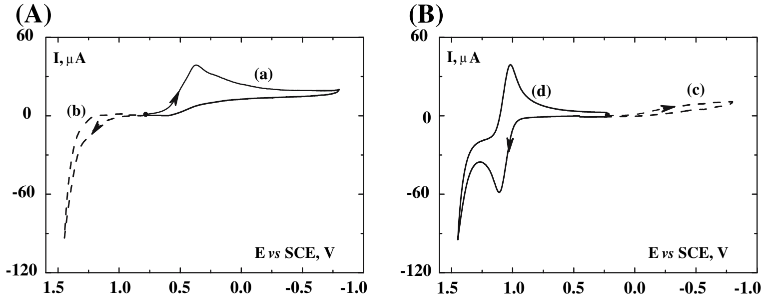


Fig. 2 Cyclic-voltammograms in acetonitrile [0.1 M $(Et_4N)ClO_4$] for (**A**) the mixture of 5 mM $[Fe^{III}(bpy)_2^{3+}]_{solv}$ and 1 M limonene immediately after mixing—(a) cathodic scan was recorded first—(b) anodic scan was recorded first; (**B**) the same as (**A**) after 24 h under Ar atmosphere—(d) anodic scan was recorded first—(c) anodic scan was recorded first. Scan rate, 0.1 V s^{-1}, GCE (0.09 cm^2); SCE vs. NHE, +0.242 V

observed in the first cathodic scan (a, solid line) and no peaks are present in the first anodic scan (b, dashed line). After 24 h under argon atmosphere (Fig. 2B) there are no peaks in the first cathodic scan (c, solid line) whereas reversible oxidation of Fe(II)-complex is visible in the first anodic scan (d, dashed line). This phenomena is also observed in the presence of dioxygen (not shown on cyclic-voltammograms). The results indicate that during the limonene oxidation process $[Fe^{III}(bpy)_2^{3+}]_{solv}$ is reduced by limonene to $[Fe^{II}(bpy)_2^{2+}]_{solv}$, which is a real catalyst.

The observation was confirmed by UV-vis measurements (Fig. 3). Fe(II)-complex shows the adsorption peak at 520 nm (see inset), whereas Fe(III)-complex does not. As it is shown in Fig. 3 the combination of 0.8 mM $[Fe^{III}(bpy)_2^{3+}]_{solv}$ and 0.8 M limonene in acetonitrile under Ar atmosphere causes the complete reduction of Fe(III) complex after approximately 5 h, and Fe(II) remains in this oxidation state. The similar behavior was observed when the solution was saturated with dioxygen. Analogous UV-vis experiments indicate that among limonene oxidation products carvone, carveol and perillyl alcohol reduce the Fe(III)-complex completely; whereas both limonene oxide and perillaldyehyde cause that the equilibrium between the Fe(III)- and Fe(II)-complexes is achieved regardless of the oxidation state of iron complex used as the starting material. Limonene, we used for the oxidation reaction, contained 0.4 mM carveol and 0.4 mM carvone. Therefore, the small concentration of carvone and carveol in limonene (pure reagent approx. 6.17 M) does not influence the reaction of Fe(III) reduction by limonene.

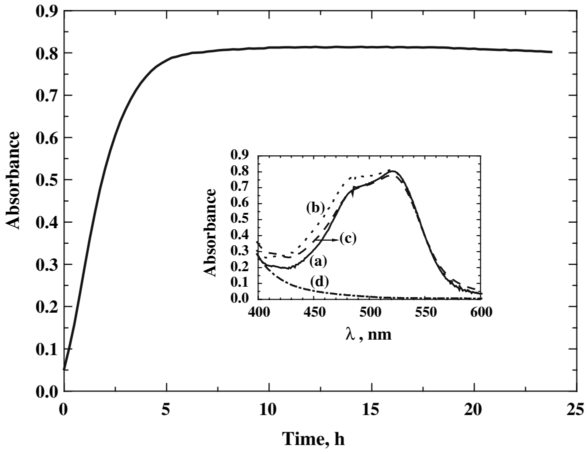


Fig. 3 The dependence of absorption at 520 nm on time for the combination of 0.8 mM $[Fe^{III}(bpy)_2^{3+}]_{solv}$ and 0.8 M limonene in argon atmosphere in acetonitrile. Inset: (**a**) UV-vis spectra of the described system after 24 h, (**b**) the same as (**a**) in dioxygen atmosphere, (**c**) [0.8 mM $Fe^{II}(bpy)_2^{2+}]_{solv}$, and (**d**) [0.8 mM $Fe^{III}(bpy)_2^{3+}]_{solv}$

The reaction products of the combination of 1 mM $Fe^{III}(bpy)_2^{2+}$ and 1 M limonene in argon atmosphere after 24 h are 1.2 mM limonene oxide, 3.3 mM of carveol, and 1.3 mM of carvone. The higher concentrations of products in comparison to 1 mM of oxidant are probably due to dioxygen leakage to the system.

As it is shown in Table 1 after 24 h small amounts of perillyl alcohol were detected. The combination of 1 M perillyl alcohol with 1 mM of $[Fe^{II}(bpy)_2^{2+}]_{solv}$ in the presence of dioxygen gives only about 14.0 mM of perillaldehyde after 24 h. Under argon atmosphere the combination of iron(II) catalyst and perillaldehyde forms small amounts of perillyl alcohol.

4 Discussion

The presented results indicate that labile iron-bipyridine complexes activate dioxygen for the oxidation of limonene. The discussed oxidation process is not selective, however the stability of the catalyst applied was observed during relatively long time. Four major products carvone, carveol, limonene oxide, and perillaldehyde are formed. Voltammetric and UV-vis measurements show that limonene, even in the presence of dioxygen, reduces Fe(III)-complex to Fe(II) one, which is active catalysts. The reduction process of iron(III)-catalyst by substrates seems to occur relatively often, since it was also observed during the oxidation of cyclohexene [43] and *N*-alkylanilines [44]. Therefore, the phenomena should be taken into account in the processes, which use iron catalysts.

The analysis of the results presented in Table 1 shows that the oxidation reaction exhibits the first orders with respect to substrate concentration and also with respect to the catalyst, for its small concentrations. It is interesting that the reaction order with respect to dioxygen is less then 1. This behavior can be explained by simple kinetic scheme, which includes the interaction between the catalyst (Catal) and substrate (S) to form an adduct (X), which is oxidized by dioxygen.

$$\text{Catal} + \text{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{X} \tag{1}$$

$$\text{X} + \text{O}_2 \xrightarrow{k_2} \text{P} \tag{2}$$

For this reaction scheme the kinetic equation describing the rate of products formation is:

$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_2[\text{Catal}][\text{S}][\text{O}_2]}{k_{-1} + k_2[\text{O}_2]} \tag{3}$$

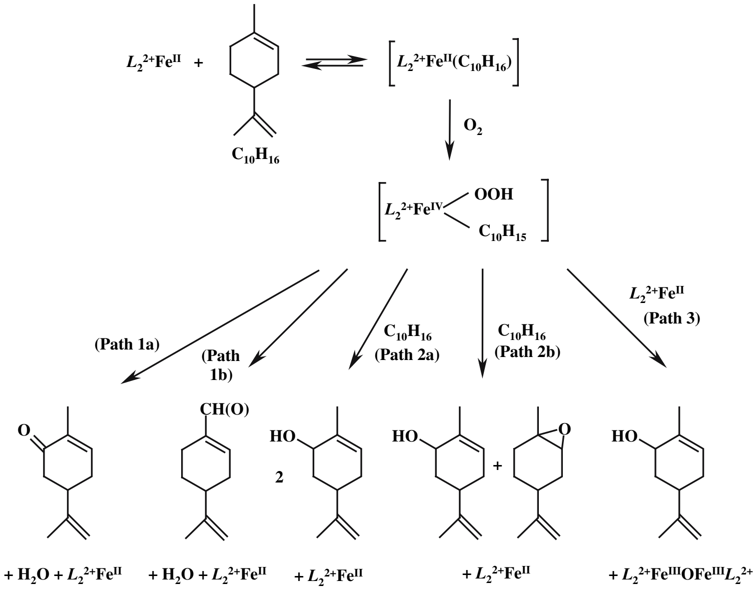
and no other combination of catalyst, substrate, and oxidant gives a kinetic equation that fulfills the observed product dependences.

As it is seen in Table 1 the TON increases for higher limonene concentration, which is in accordance with the presented assumption. However, the TON decreases slowly with the increase of catalyst concentration. This may be caused by the increase of the catalyst decomposition rate, according to Path 3 in Scheme 2.

It is characteristic that perillaldehyde is formed in the oxidation process. However, perillaldehyde can be reduced to corresponding alcohol by the reduced form of the catalyst, and therefore its steady-state can be reached. The formation of perillaldehyde was only reported during autooxidation of limonene by dioxygen, catalyzed by $Co(OAc)_2$/bromide system [33], but the amount of the product was not quantified. The low yield of the aldehyde formation during the oxidation of perillyl alcohol, in the same experimental conditions as limonene oxidation, indicates that perillaldehyde is formed directly from the limonene and not via alcohol. This makes the system analogues to that, which causes the *N*-dealkylation of *N*-substituted anilines, in which *N*-methylformanilide is formed directly from *N*,*N*-dimethylaniline [44].

The formation of carvone and carveol is somewhat similar to our previously published results [43, 47] on oxidation of unsaturated hydrocarbons, when the double bond was preserved and a ketene and an alcohol were the main products and only traces of an epoxide were formed. The present system, however, differs from the previous ones because of the formation of limonene oxide in large amount, which is comparable with the amount of ketone. The formation of higher concentrations of the epoxide can be explained assuming that terpenes form more stable oxides than alkenes. In our previous paper on oxidations of alkenes by dioxygen catalyzed by $[\text{Fe}^{\text{II}}(\text{bpy})_2^{2+}]_{\text{solv}}$ [43] we postulated that the reactive species is an iron-hydroperoxo adduct. It is known that porphyrin iron-oxo adduct is responsible for alkene epoxidation [48, 49]. It has been also shown [50–52] that iron-hydroperoxo adduct can be rearranged to iron-oxo species by the electronic and steric properties of ligand environment. In the discussed system

Scheme 2 Proposed, plausible mechanism for iron(II)-activation of dioxygen for oxygenation of limonene



the presence of several products (some of them are stereoisomers) and the presence of metal catalyst showing different oxidation states can enable such rearrangement and therefore an iron-hydroperoxo adduct can be considered as a reactive species. Based on these considerations the plausible mechanism is presented in Scheme 2. However, the large number of products would support also the hypothesis that autoxidation reaction takes place.

The presented results indicate, that the oxidation of limonene under continuous flow of dioxygen catalyzed by iron-bipyridine complexes can afford relatively large amount of valuable products. The reaction is not selective but the catalyst is stable over extended period of time. Therefore, separation of products from the reaction mixture has to be done to evaluate practical usability of the process.

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