

Co(II) catalysed oxidation of α -pinene by molecular oxygen

Part III

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Abstract

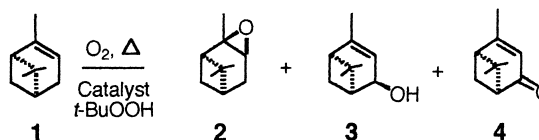
Herein are described the results of *t*-BuOOH aided air oxidations of (–)- α -pinene, catalysed by [Co(pyridine)₂Br₂] or [Co(4-methylpyridine)₂Br₂], and observations about the nature of the reactions. The use of a small amount of *t*-BuOOH showed a clear beneficial influence on air oxidation under mild temperatures. Raising the temperature did not increase yields markedly. An increase of the hydroperoxide concentration sped up air oxidation and brought up the amount of oxidised products, especially allylic ones. The oxygen atom in oxidised products was not derived from peroxide. Instead, the reaction needed the presence of molecular oxygen to proceed. The present air oxidation is a homogeneous catalytic reaction, and the formation of verbenone took place via *trans*-verbenol. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Air oxidation; Co(II) catalyst; α -Pinene; *t*-BuOOH

1. Introduction

For some time, we have been involved in studies of (–)- α -pinene (**1**) air oxidation catalysed by Co(II) pyridine complexes under solvent free conditions [1]. During our recent air oxidation studies, we noticed that an old peroxidated α -pinene started to oxidise more quickly than the fresh one [2]. This indicates that peroxides might work as an initiator of the radical chain reactions which are the liquid-phase olefin autoxidations [3]. A preliminary air oxidation experiment of (–)- α -pinene with dry *tert*-butyl hydroperoxide (*t*-BuOOH) in *i*-octanol catalysed by [Co(4-methylpyridine)₂Br₂], showed a marked

increase in the reaction rate. The rapid decomposition of alkyl hydroperoxides in hydrocarbon solution in the presence of trace amount of metal compounds is well known reaction. Surveillance of oxidation reactions containing *t*-BuOOH showed that *t*-BuOOH can act as an oxidant [4–9] itself, or together with molecular oxygen in the catalytic air oxidation [10–15] of alkenes. Therefore, we were interested in systematically studying the influence of *t*-BuOOH on the air oxidation of (–)- α -pinene (**1**) catalysed by Co(II) pyridine complexes, and comparing that influence to our former results.



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Herein, we present the results of *t*-BuOOH aided air oxidations of (–)- α -pinene (**1**) catalysed by [Co(pyridine)₂Br₂] ([Co(py)₂Br₂]), or [Co(4-methylpyridine)₂Br₂] ([Co(4-mepy)₂Br₂]), as well as observations about the nature of these reactions.

2. Experimental

2.1. Reagents

Cobalt(II) complexes were prepared as before [1]. (–)- α -Pinene (99%) was purchased from Fluka and used as such. *tert*-Butyl hydroperoxide (70%, the remainder water, Aldrich) was extracted by CH₂Cl₂ and the organic-phase was dried by refluxing with a Dean–Stark trap [16]. Anhydrous *t*-BuOOH was stored over molecular sieves (3 Å) in the refrigerator. Solvents were dried and distilled using standard methods.

2.2. A typical air oxidation experiment

(–)- α -Pinene (**1**) (3 ml, 25.2 mmol) air oxidation was carried out in a thermostated glass reactor (oil bath 60–100°C) equipped with a reflux condenser and a gas inlet in the bottom of the reactor. Co(II) catalyst (0.15 mol%) and anhydrous *t*-BuOOH (0.5 ml, 8–12 mol%) were added and molecular oxygen was passed through the reactor (5 ml/min) under atmospheric pressure. The reactor also contained glass beads (diameter 2 mm, 5 ml) which worked as oxygen dispensers.

2.2.1. Reduction of verbenone

(–)-Verbenone (**4**) (4.7 g, 31.3 mmol) was dissolved in methanol (70 ml) and cooled to 0°C in an ice bath. CeCl₃·7H₂O (11.7 g, 31.4 mmol) was added to the reaction mixture [17]. When the salt had dissolved, 1.6 g (42.0 mmol) of NaBH₄ was added in small portions, keeping the reaction temperature below 5°C. All the verbenone had reduced after 1 h. After the usual work-up the yield was 4.0 g. The crude product contained 43% of *cis*-verbenol, 11% of *trans*-verbenol (**3**) and 33% of methyl verbenyl ether. The components were identified by comparing their GC retention times and MS with authentic samples [2]. Separation of the components was performed by flash chromatog-

raphy (silica gel 60 (230–400 mesh), Merck, eluents *i*-octane/acetone 10:1 and hexane/ethyl acetate 15:1).

2.2.2. Air oxidation of verbenols

The mixture (1:1) of *cis*- and *trans*-verbenol (500 mg, 3.3 mmol) was oxidised by using 1.88 mg (0.15 mol%) of [Co(py)₂Br₂] as the catalyst at 80°C. The progress of the reaction was followed by GC for 24 h. Air oxidations of pure alcohols were performed in a similar manner: *trans*-verbenol (176 mg, 1.2 mmol) was oxidised by using 0.66 mg (0.15 mol%) of [Co(py)₂Br₂] as catalyst. *cis*-Verbenol (410 mg, 2.7 mmol) was oxidised with 1.53 mg (0.15 mol%) of [Co(py)₂Br₂] as the catalyst.

Oxygen flow in all air oxidations was 5 ml/min and it was controlled by Brooks Mass Flow Meter Model 5850TR. Progress of the reaction was monitored by TLC (on silica gel 60 F₂₅₄ plates from Merck) and GC (Perkin-Elmer AutoSystem XLTM, column OV-1701, length 25 m, i.d. 0.25 mm, phase layer 0.25 μm). The TLC chromatograms were visualised by UV-light and staining with an ethanolic anisaldehyde/glacial acetic acid/H₂SO₄ reagent. Reaction temperatures refer to bath temperatures.

Air oxidation products were identified by comparison with the authentic samples [2].

3. Results and discussion

3.1. Effect of *tert*-butyl hydroperoxide on air oxidation of (–)- α -pinene

We have reported that increasing the reaction temperature with the same catalyst accelerated the air oxidation of α -pinene [1]. We wanted to know, how *t*-BuOOH would effect α -pinene air oxidation carried out at different temperatures. The dry *t*-BuOOH [16] used in our reactions was in *i*-octanol or CH₂Cl₂, and its concentration varied from 2.5 to 5 M. A typical amount of peroxide in the reaction was 0.5 ml (8.6–11.5 mol%). No solvent effect was then detected. CH₂Cl₂ or acetonitrile as the reaction solvent (25 ml), together with *t*-BuOOH, considerably retarded air oxidation compared to the reaction in non-solvent conditions.

Air oxidation experiments with *t*-BuOOH were performed by adding a known amount of the peroxide (0.5 ml) to the air oxidation mixture (3 ml, 25.2 mmol

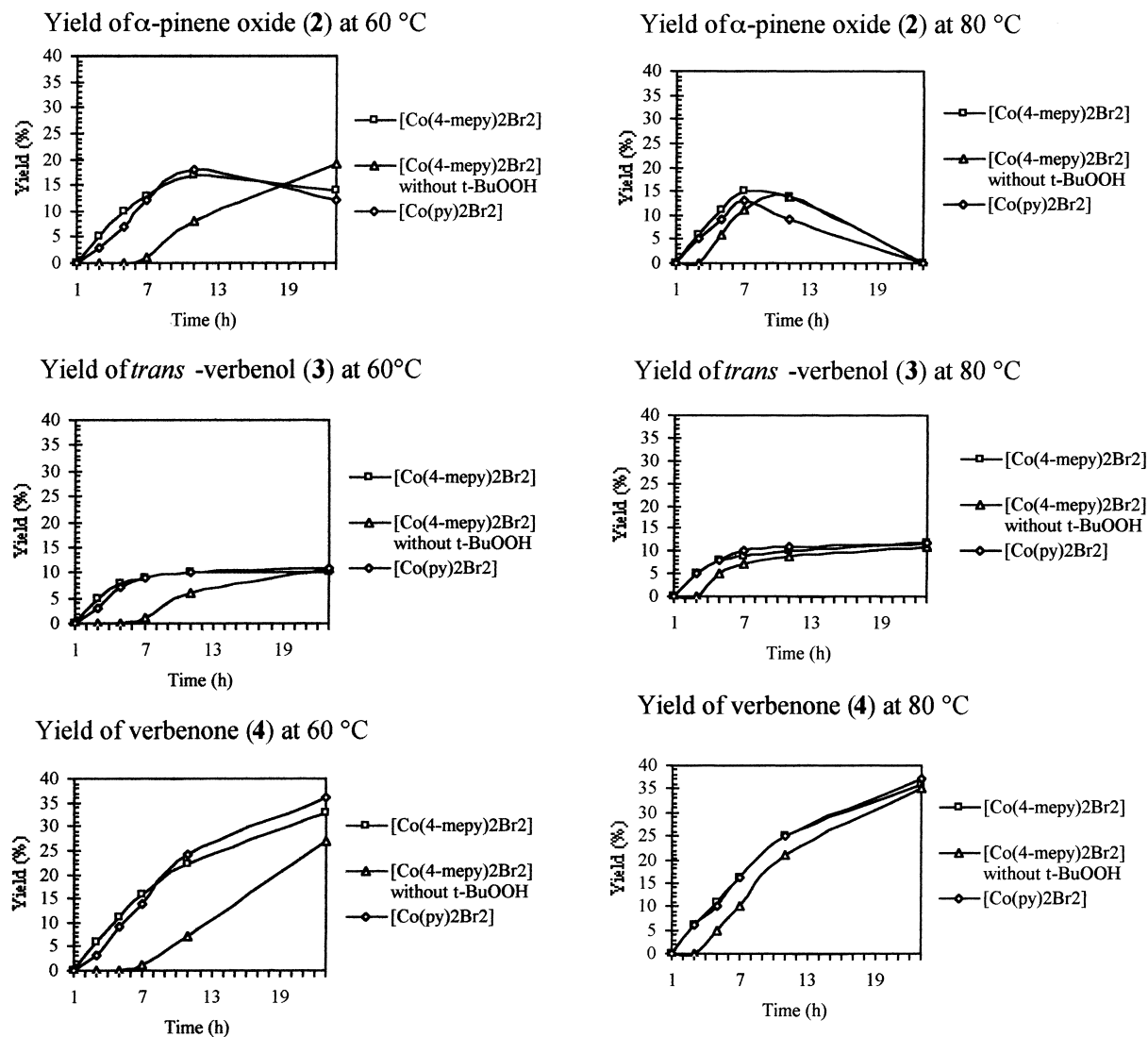


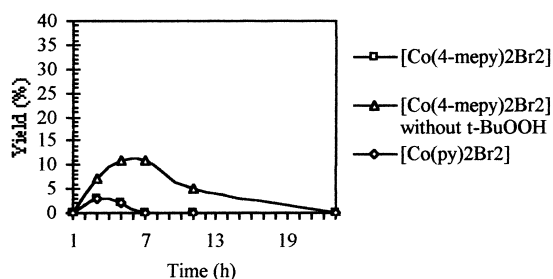
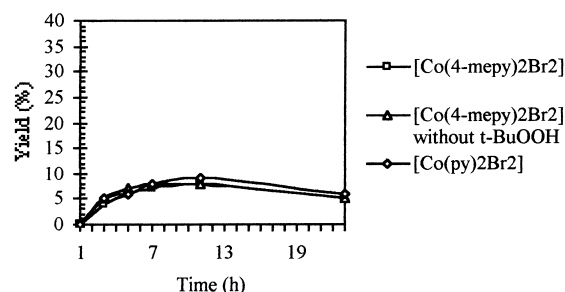
Fig. 1. *tert*-Butyl hydroperoxide aided air oxidation of (–)- α -pinene catalysed by Co(II) complexes at 60°C.

Fig. 2. *tert*-Butyl hydroperoxide aided air oxidation of (–)- α -pinene catalysed by Co(II) complexes at 80°C.

of (–)- α -pinene and 0.15 mol% of $[\text{Co}(4\text{-mepy})_2\text{Br}_2]$ or $[\text{Co}(\text{py})_2\text{Br}_2]$ and by bubbling molecular oxygen (5 ml/min) through it. The reaction mixture was then heated to 60, 80 or 100°C, and the progress of the reaction was monitored by GC. The bright blue $[\text{Co}(4\text{-mepy})_2\text{Br}_2]$ and $[\text{Co}(\text{py})_2\text{Br}_2]$ were not soluble in α -pinene, but the addition of the hydroperoxide, depending on its amount, quickly turned the reaction mixture cloudy (*t*-BuOOH is probably not soluble

in α -pinene) turquoise green. When the amount of *t*-BuOOH was 0.5 ml, then the change in colour was very slight. The influence of 0.5 ml (11.5 mol%) of *t*-BuOOH on air oxidations at 60, 80 or 100°C is presented in Figs. 1–3.

Upon addition of the hydroperoxide, air oxidation started directly at each temperature. The fast change in colour at the beginning of the reaction indicated the oxidation of Co(II) to Co(III) and spoke for

Yield of α -pinene oxide (2) at 100 °CYield of *trans*-verbenol (3) at 100 °C

Yield of verbenone (4) at 100 °C

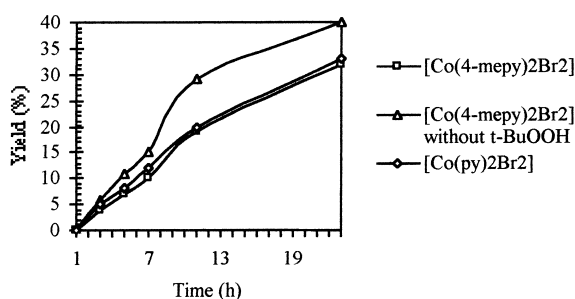


Fig. 3. *tert*-Butyl hydroperoxide aided air oxidation of (–)- α -pinene catalysed by Co(II) complexes at 100 °C.

the formation of the Co(III)-butyl peroxide complex [18]. Peroxide sped up air oxidation, especially at the mild temperature (60 °C). At 80 °C, air oxidations with and without peroxide were very similar, but at 100 °C the reaction containing peroxide became slower than the reaction without peroxide. The retardation can probably be attributed to thermal decomposition of *t*-BuOOH and subsequent termination by the self-reaction [3]. Decomposition is strongly de-

pendent on the temperature and the medium [19,20]. The use of *t*-BuOOH also retarded the further rearrangement of pinene oxide (2) at 60 °C, but at high temperature (100 °C) it led to the direct rearrangement of the epoxide (2). At the mild temperature, *t*-BuOO• was more stable than at the higher temperature. It, therefore, added the amount of epoxide and was observed to retard rearrangement. Co(II) complexes showed almost equal activity with *t*-BuOOH.

3.2. Uncatalysed air oxidation of (–)- α -pinene

Plain (–)- α -pinene (1) in uncatalysed air oxidation conditions showed interesting features. In a former paper [2], we reported that without a catalyst at 60 °C no reaction happened after 30 h and later the same result was detected at 80 °C. When air oxidation was carried out at 100 °C, (–)- α -pinene air oxidated without a catalyst by producing 14% of *trans*-verbenol (3) and 22% of verbenone (4) in 23 h. Anyhow, no products were detected after 10 h reaction time. The study also revealed that autoxidation produced both pinene oxide (2) and verbenone (4) as in cobalt catalysed air oxidations. The formation of pinene oxide was judged by the presence of rearrangement products. These results showed that air oxidations of α -pinene at temperatures higher than 80 °C contained some amount of products coming from autoxidation as well.

3.3. Effect of various amounts of *tert*-butyl hydroperoxide on air oxidation

Because the hydroperoxide had an improving effect on air oxidation at 60 °C, the reaction was further studied by using varying amounts of *t*-BuOOH at 60 °C. The increase of the hydroperoxide content sped up the oxidation of α -pinene and increased the amount of oxidised products, especially allylic ones. Two air oxidations, with 0.5 and 1.0 ml of *t*-BuOOH, gave nearly equal results (Fig. 4). When the amount of *t*-BuOOH was increased further, it mostly increased the yield of verbenone (4). This suggests that *t*-BuOOH or its cleavage product, *tert*-butoxy radical, acts as an initiator by abstracting an allylic hydrogen rather than by adding to the double bond [21,22]. The more *t*-BuOOH there was present, the more hydrogen abstraction happened, increasing the yield

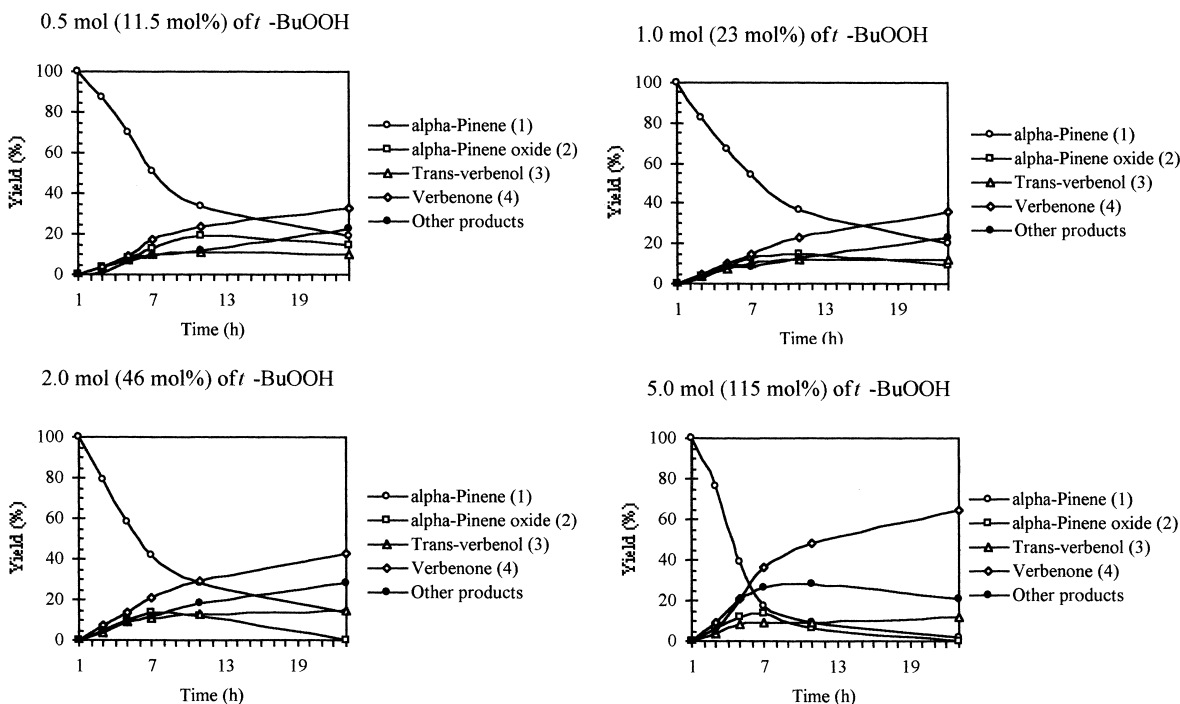


Fig. 4. The effect of the amount of *tert*-butyl hydroperoxide on air oxidation of (–)- α -pinene catalysed by $[\text{Co}(\text{4-methylpyridine})_2\text{Br}_2]$ at 60°C .

of verbenone. Concurrent rearrangement of pinene oxide (2) sped up, too. This indicates that reaction may follow some other pathway simultaneously. The results are presented in Fig. 4. Some experiments at the higher reaction temperature (80°C), using 0.5 or 2.0 ml of *t*-BuOOH, verified the observation that peroxide did not have any specific promoting effect at that temperature, regardless of its amount. The lower peroxide content (0.5 ml, 11.5 mol%) yielded a somewhat higher amount of verbenone than the same reaction at 60°C . The higher amount of peroxide (2.0 ml, 46.0 mol%) promoted the start of air oxidation, but soon led to its retardation. The higher reaction temperature with the both amounts of hydroperoxide resulted in an increased yield of the epoxide rearrangement.

3.4. Mechanistic studies

Some other experiments concerning the effect of *t*-BuOOH were also performed. α -Pinene air oxidation

with *t*-BuOOH (10 mol%), but without a catalyst, at 60°C , affected a slow oxidation. The yield of verbenone (4) was 10% in 24 h showing that peroxide itself had a minor effect on oxidation. Therefore, the accelerating effect of *t*-BuOOH in air oxidation must be a consequence from its reaction with cobalt ion. The metal ion can act as an initiator via one-electron transfer with hydroperoxide, producing an alkoxy radical [20], which abstracts hydrogen from α -pinene. Abstraction of the allylic hydrogen produces the allylic radical capable of reacting with oxygen and yielding oxidised products like verbenol and verbenone. $\text{Co}(\text{III})$'s reaction with hydroperoxide, regenerates $\text{Co}(\text{II})$ and generates alkyl peroxy radical, which leads to formation of pinene oxide. The net transformation constitutes a catalytic decomposition of the hydroperoxide into alkoxy and alkyl peroxy radicals [22]:



Table 1

The effect of *tert*-butyl hydroperoxide on (–)- α -pinene oxidation in argon atmosphere catalysed by [Co(4-methylpyridine)₂Br₂] at 60°C

Time (h)	Reaction mixtures ^a								
	(–)- α -Pinene, [Co(4-mepy) ₂ Br ₂], <i>t</i> -BuOOH			(–)- α -Pinene, [Co(4-mepy) ₂ Br ₂]			(–)- α -Pinene, <i>t</i> -BuOOH		
	2 ^b	3 ^b	4 ^b	2	3	4	2	3	4
2.5	0.4	–	0.6	–	–	–	–	–	–
4.5	0.6	0.3	0.8	–	–	–	0.3	–	0.4
10.0	0.7	0.4	1.0	0.2	0.2	0.3	0.4	0.3	0.6
21.5	1.1	0.7	1.3	0.5	0.6	0.5	0.7	0.3	0.7

^a Mixture of 3 ml (25.5 mmol) (–)- α -pinene, 16 mg (0.15 mol%) [Co(4-mepy)₂Br₂], 0.5 ml (11.5 mol%) *t*-BuOOH/CH₂Cl₂.^b Reaction products: α -pinene oxide (2)/*trans*-verbenol (3)/verbenone (4), are in percentage.

The other possibility is that *t*-BuOOH forms the complex with cobalt catalyst complex, and thermal decomposition of this complex initiates air oxidation [23]. To study the later choice, a series of “air oxidations” were performed in an argon atmosphere. (–)- α -Pinene was warmed at 60°C with 0.5 ml of *t*-BuOOH/CH₂Cl₂ and 0.15 mol% of [Co(4-mepy)₂Br₂]. For comparison, one additional flask contained only (–)- α -pinene with the catalyst, and another contained (–)- α -pinene with 0.5 ml of *t*-BuOOH/CH₂Cl₂. Oxygen was removed from the reaction flasks by repeated evacuation and filling with argon. When the portions of *t*-BuOOH were added to the reactors, the colour of the reaction mixture, which contained the catalyst, turned light green. The change of the colour showed that Co(II) oxidised to Co(III). The reactions were followed by GC. Oxidation under oxygen-free conditions was very slight. The low yields in Table 1 clearly show that this air oxidation needs the presence of molecular oxygen to proceed, and that the oxidising influence of *tert*-butyl hydroperoxide alone with Co(II) complex is insignificant at this temperature (Table 1). Previous observations indicated that [Co(4-mepy)₂Br₂] formed an alkyl hydroperoxo complex with *t*-BuOOH. Decomposition of Co(III) butyl peroxy complex, [pyridine–Co(III)–OO–butyl], can generate either butoxy or butylperoxy radical. Of the two radicals, *t*-BuO• has more radical strength [24], and decomposition of *t*-BuOO• also generates *t*-BuO• by liberating 0.5 mol oxygen [25,26]. Butoxy and butylperoxy radicals in an oxygen atmosphere reacted with α -pinene producing *trans*-verbenol (3), verbenone (4) and pinene oxide (2), respectively.

3.5. Homogeneous versus heterogeneous nature of air oxidation

The Co(II) catalysts used were not visibly soluble in α -pinene: the reaction mixture stayed clear until air oxidation started, and the mixture turned light green. As we mentioned before, when the reaction was carried out with a small amount of *t*-BuOOH, the reaction mixture turned cloudy and stayed nearly colourless. The homogenous versus heterogeneous nature of this air oxidation was studied by putting 3 ml of (–)- α -pinene together with 16 mg of [Co(4-mepy)₂Br₂] into two test tubes, and adding 0.5 ml of *t*-BuOOH/CH₂Cl₂ to one of the reaction mixtures. The tubes were kept in an oil bath (80°C) for 30 min. Warming turned the contents of the tubes bright blue for experiment 1 and light green and cloudy for experiment 2 (the sample with *t*-BuOOH), showing that the catalyst had partially dissolved. The catalysts were filtered off and both, now colourless reaction mixtures, were moved into the reactors, which were connected to the oxygen stream (5 ml/min) and kept at 80°C. The reactions were monitored by GC, and the results are shown in Table 2. The peroxide in experiment 2 seemed to react immediately with the catalyst (a change in colour) and formed a soluble compound, which catalysed air oxidation. In experiment 1, [Co(4-mepy)₂Br₂] as the catalyst was sparingly soluble and air oxidation started slowly. Although the catalyst was filtered off, these air oxidations produced the usual yield of products in 23.5 h. It was concluded, that this air oxidation was a homogenous reaction.

Table 2

The study of a homogenous versus heterogeneous nature of (–)- α -pinene air oxidation at 80°C

Experiment	Colour		Reaction time (h) and yields of pinene oxide (2)/ <i>trans</i> -verbenol (3)/verbenone (4) (%)											
	Before filtration	After filtration	2.5			6.5			11			23.5		
			2	3	4	2	3	4	2	3	4	2	3	4
1	Blue	Colourless	–	–	–	<1	<1	<1	4	3	3	7	16	20
2	Light green, cloudy	Colourless	7	5	7	12	8	11	12	11	17	–	14	30

3.6. Formation of verbenone

In general, of the three main oxidation products, pinene oxide (**2**) rearranged further to several other products during the run of air oxidation [2]. The yield of *trans*-verbenol (**3**) mostly barely exceeded 10% and when the reaction was nearly at the end, its amount decreased. Verbenone (**4**) could be formed either directly or via *cis*- or *trans*-verbenol (**3**). To study its formation, we reduced verbenone with NaBH₄ in the presence of CeCl₃·7H₂O to a mixture of *cis*- and *trans*-verbenol [17]. The alcohols were separated by flash chromatography. Pure *cis*- and *trans*-verbenol and their 1:1 mixture were oxidated by molecular oxygen with [Co(py)₂Br₂] as catalyst at 80°C. The reactions were followed by GC. First, we performed the air oxidation for the mixture of *cis*- and *trans*-verbenol. The product mixture contained only a small amount of verbenone and the remaining part consisted of a mixture of monocyclic rearranged compounds. Verbenone was not produced from *cis*-verbenol either, rather the same monocyclic products as in the *cis*–*trans* mixture were generated. Air oxidation of pure *trans*-verbenol (**3**), in contrast, produced verbenone (**4**) and only a minor amount of the monocyclic rearranged products. Consequently, α -pinene oxidises to pinene oxide (**2**) and *trans*-verbenol (**3**), which further oxidises to verbenone. This detection does not exclude the possibility that verbenone also is formed directly and simultaneously from α -pinene.

4. Conclusions

tert-Butyl hydroperoxide had a clear beneficial effect on α -pinene air oxidation catalysed by [Co(py)₂Br₂] or [Co(4-mepy)₂Br₂] under mild tem-

perature (60°C). Both complexes showed equal catalytic activity with *t*-BuOOH. The high temperature in connection with *t*-BuOOH did not promote air oxidation further. With low concentrations of *t*-BuOOH, the oxygen atom in oxidated products did not originate from the hydroperoxide. Instead, the reaction needed the presence of molecular oxygen to proceed. *t*-BuOOH without a catalyst did not effect oxidation of α -pinene. The fast start of air oxidation and the change in colour in the presence of *t*-BuOOH indicated the oxidation of Co(II) to Co(III). It is likely that air oxidation in the presence of *t*-BuOOH took place via the Co(II)-complex-induced formation of butoxy and butyl peroxy radicals. Butoxy radical effected the abstraction of the allylic hydrogen from α -pinene and subsequent reaction with molecular oxygen yielded *trans*-verbenol and verbenone. Butyl peroxy radical added to the double bond of α -pinene and the subsequent decomposition of the alkyl peroxy alkyl radical afforded pinene oxide. In addition, autoxidation of α -pinene occurred at high temperature (100°C). The present air oxidation was a homogeneous catalytic reaction and the formation of verbenone took place via *trans*-verbenol.

Acknowledgements

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