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A Highly Selective Na_2WO_4-Catalyzed Oxidation of Terpenic Alcohols by Hydrogen Peroxide

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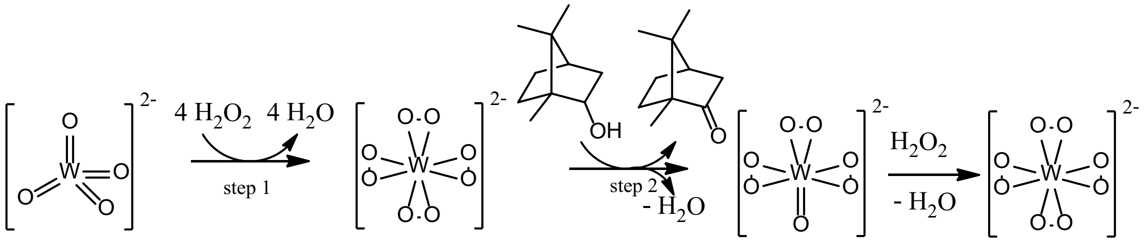
Abstract

Sodium tungstate was found to be an active and highly selective catalyst to oxidation of various primary or secondary origin renewable alcohols by hydrogen peroxide as green oxidant. Borneol, nerol, geraniol and β-citronellol were efficiently and selectively converted to respective carbonyl derivatives by hydrogen peroxide. ATR/FT-IR measurements confirmed that $Na_2W(O_2)_4$ was the specie active catalytically. The role of the main reaction variables, including temperature, reactants and catalyst concentration, solvent, and nature of substrate were also assessed. In addition to use a green oxidant, this simple and environmentally friendly catalyst system did not require additive to control pH, molecular sieves or phase transfer catalyst.

Graphical Abstract



Keywords Sodium tungstate · Catalytic oxidation · Terpenic alcohols · Hydrogen peroxide

1 Introduction

Monoterpenes are versatile and renewable feedstocks that may replace petroleum derivative raw materials [1]. Presently, to develop friendly environmentally processes to convert monoterpenes into fine chemicals have been a great challenge in the fragrance and pharmaceutical industries [2–4]. In special, monoterpenes containing carbonyl groups are key intermediates and building blocks for synthesis of flavors, pharmacies and agrochemicals [5–7].

Nonetheless, industrial processes to production oxygenates terpenic derivative still are based on toxic and corrosive stoichiometric oxidant. For instance, camphor is used for its scent, as a flavoring agent, an ingredient in cooking, as an embalming fluid, and for medicinal purposes, has been industrially produced through multistep process. In this case, camphene is converted to isobornyl acetate and then separated and converted by sodium hydroxide alcoholic solution to isoborneol, which is finally purified and oxidized by stoichiometric oxidants (i.e., Cr or Mn salts, nitric and sulfuric acids) providing the camphor [8]. However, these oxidants are toxic and unfriendly environmentally, generating residues that should be discarded.

Hydrogen peroxide is a green oxidant that has been used to oxidize origin natural alcohols. It is an attractive oxidant because it is an inexpensive and environmentally benign reactant, which produces water as the only by-product with an atom efficiency of *ca*. 47% [9–11]. However, it is always requires the presence of metal in order to activate hydrogen peroxide and or organic substrate, in

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addition to phase transfer agents and alkaline additives to control pH.

There are several metal-catalyzed processes frequently used in oxidation reactions with hydrogen peroxide; nonetheless, those based on tungsten catalysts have received a great deal of attentions to achieve high efficiency and selectivity mainly in alcohols oxidation [12–14]. For instance, deserves highlight the seminal work of Noyori et al. where they described the first use of sodium tungstate as homogeneous catalyst in oxidation reactions [15, 16]. Those authors developed a practical, efficient and environmentally acceptable oxidative process by using of hydrogen peroxide as stoichiometric oxidant [17]. Nonetheless, this system needs strong acidic conditions and requires expensive phase transfer catalysts.

Although heterogeneous oxidative processes have a great advantage of reusability of catalyst, they require longer reaction times and higher temperatures than homogenous ones [18–20]. Moreover, notwithstanding the significant advances obtained in this area, the catalyst efficiency and selectivity especially in the case of alcohol oxidations still remains a challenging to be overcome.

In this paper, after a careful solvent selection, we developed an efficient and selective Na_2WO_4-catalyzed process to oxidize natural origin alcohols (i.e., borneol, β-citronellol, nerol and geraniol) by hydrogen peroxide. This simple and environmentally friendly route, no acid or alkaline additive, molecular sieves or phase transfer catalyst (i.e., PTC) were required. High substrate conversions and selectivity toward carbonylic products were achieved. The role of the main reaction variables, including temperature, reactants concentration and catalyst, solvent and nature of substrate were assessed.

2 Experimental Procedures

2.1 Materials

All chemicals were purchased from commercial sources. Sodium tungstate was acquired from Sigma-Aldrich (99 wt%). Borneol (99 wt%, racemic mixture Sigma Aldrich), β-citronellol (racemic mixture 90–95 wt%, Sigma Aldrich), linalool (Sigma Aldrich, 99 wt%), nerol (Sigma Aldrich, 97 wt%) and geraniol (Sigma Aldrich, 98 wt%) were used as received. Toluene, dimethylacetamide (DMA), dimethylformamide (DMF), CH_3OH and CH_3CN, all were acquired from Sigma Aldrich (ca. 99 wt%) and used as received. The 34 wt% aqueous H_2O_2 (Sigma) was the oxidant in all reactions.

2.2 Catalytic Tests and Reaction Monitoring

Reactions were carried out in a glass reactor (50 mL) equipped with a magnetic stirrer, a sampling system and connected to reflux condenser. In a typical run, the Na_2WO_4 catalyst (0.06 mmol; 2.5 mol %), terpenic alcohol (2.40 mmol) were dissolved in DMA (10.0 mL) and magnetically stirred and heated to reaction temperature. Furthermore, after addition of hydrogen peroxide, the reaction was started and followed by GC analysis (Shimadzu 2010 instrument, FID) during 4 h.

The GC analyses conditions were as follows: 80 °C (3 min); rate of temperature increase: 10 °C/min; final temperature: 260 °C; injector temperature: 250 °C; and detector temperature: 280 °C. Conversion and selectivity were estimated from the corresponding GC peak areas of substrate and products in comparison with the corresponding calibrating curves. Naphthalene was used as an internal standard.

2.3 Products Chromatographic Analysis

Compounds were identified by GC/MS analyses (Shimadzu MS-QP 2014 mass spectrometer instrument operating at 70 eV electronic impact mode coupled with a Shimadzu 2014 GC). Additionally, the main products were also identified by co-injection with the authentic samples in GC as described in the Sect. 2.2.

3 Results and Discussion

3.1 General Aspects

The pH control has been vital for the success of the Na_2WO_4-catalyzed alcohols oxidation reactions by hydrogen peroxide. While assessed the oxidation of 2-octanol by H_2O_2, Hida and Nogusa verified that the addition of NaH_2PO_4 to the DMA solution containing oxidant and Na_2WO_4 catalyst dissolved resulted in an increase on pH of 5.4–6.5, which improved the yield of 2-octanone of 74–94% [21]. They concluded that under those pH conditions, strong donor solvents favor the reaction because they stabilize a tetraperoxotungstate intermediate, which was isolated by them and characterized. Those authors assumed that this intermediate was the active catalytically specie in those oxidation reactions. In the system $Na_2WO_4/H_2O_2/DMA/NaH_2PO_4$ some aliphatic saturated alcohols or aromatics containing electron donating or withdrawing groups were efficiently oxidized [21].

Herein, our intention was to extend the reaction scope to the natural origin unsaturated alcohols (i.e., terpenic alcohols), which are renewable raw material and useful for fine chemicals industries [22]. Nonetheless, the use of additives such as sodium phosphate looks for us an inconvenient and may trigger undesirable reactions that will compromise the oxidation selectivity, such as rearrangement of carbon skeletal, isomerization, nucleophilic addition or oligomerization.

So, after verify the effect of solvent under our reaction conditions (i.e., without control of pH or PTC), we performed the catalytic runs without any additive. Borneol was the terpenic alcohol selected as model-molecule and used on assessment of the effects of main reaction parameters. Further, the reaction scope was successfully extended to the other monoterpene alcohols.

3.2 Effects of Solvent on the Na_2WO_4-Catalyzed Oxidation Reaction of Borneol by H_2O_2

In Table 1 are the conversion results obtained from reactions carried out at reflux temperatures of the different solvents. GC and GC-MS analyses showed that camphor was the principal carbonylic product formed in all reactions.

Although the camphor has been selectively formed regardless the solvent used, only in the reactions in the presence of strong donor solvents (i.e., DMA and DMF), the Na_2WO_4-catalyzed reactions achieved high conversions.

It is important to note that whereas the data previously reported, no additive to control pH was used [21]. Moreover, whereas some reports on literature, no PTC was employed [16, 23, 24].

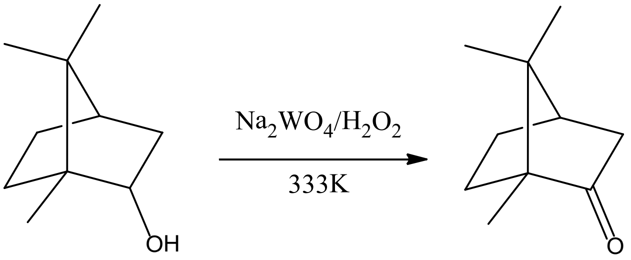
The efficiency of DMA and DMF was attributed to the effect stabilizing provoked by the interaction of these solvents with a tetraperoxotungstate intermediate [21]. On the other hand, the lower activity of catalyst in methyl alcohol or acetonitrile solutions was ascribed to low solubility of sodium tungstate in these solvents.

Some insights into reaction mechanism may be done based on literature [21, 25–27] and experimental results. Firstly, in tungsten-catalyzed oxidation reactions, has been commonly accepted that H_2O_2 first binds to the metal center (step 1, Scheme 1), generating the active catalytically species such as bridging tungstoperoxo complexes.

Table 1 Effect of solvent on the Na_2WO_4-catalyzed borneol oxidation by H_2O_2

Run	Solvent	Temperature (K)	Conversion (%)	Camphor selectivity[a] (%)
1	DMF	343	80	91
2	DMA	343	83	94
3	CH_3CN	323	15	83
4	CH_3OH	323	14	82

Reaction conditions borneol (2.4 mmol); Na_2WO_4 (2.5 mol%); H_2O_2 (2.4 mmol), 4 h



Scheme 1 Na_2WO_4-catalyzed borneol oxidation reaction by H_2O_2

It is noteworthy that in tungsten-catalyzed oxidation reactions carried in DMA, until four peroxide groups may be coordinate to the metal cation generating $Na_2W(O_2)_4$ intermediate [21]. Herein, we confirmed this hypothesis through FT-IR analysis, recording spectra of Na_2WO_4 catalyst in the presence and absence of hydrogen peroxide (Fig. 1). The FT-IR spectra were also obtained in DMA. However, due to great amount of absorption bands of solvent, we will omit these data and discuss only the infrared spectra obtained without solvent. Nonetheless, we have found that no difference in relation to the results obtained with or without solvent was observed.

The ATR-FTIR spectrum of $Na_2WO_4{\cdot}2H_2O$ showed as main absorption bands the υ_{sym} and υ_{assym} stretching of W=O bond at wavenumbers 931.5 and 832.4 cm^{-1}, respectively. In addition, the spectrum displayed the absorption bands characteristic of water molecules, at 3270.7 and 1675.9 cm^{-1}, corresponding to the stretching of O–H bond and deformation of H–O–H, respectively (see spectrum (A), Fig. 1) [28].

The other typical absorption bands of the tungstate anions were observed at low frequencies (ca. 815–539 cm^{-1}). We have found absorption bands that may be assigned to the bridging and non-bridging oxygen atoms containing ions, which belong to the double or single bonded tetrahedron groups [29]. The bands placed between 800 and 950 cm^{-1} are associated to the υ_3 and υ_1 vibrations of the tetrahedral WO_4 [30]. All these data are agreed with literature [31].

After adding aqueous hydrogen peroxide in an enable amount to dissolve the sodium tungstate, we recorded the ATR/ FT-IR spectrum of solution, and verified that remarkable changes have occurred (see spectrum (B), Fig. 1).

It was verified that in addition to the absorption bands characteristics of deformation vibration of H_2O_2 and H_2O molecules (*ca*. 1633.4 and 1365.4 cm^{-1}, respectively), we have found stretching vibrations of O–O and W–O bonds (*ca*. 877.5 and 829.3 cm^{-1} respectively). Nonetheless, the main result was the disappearance of strong peak at 931.5 cm^{-1} wavenumber, which was present in the FT-IR

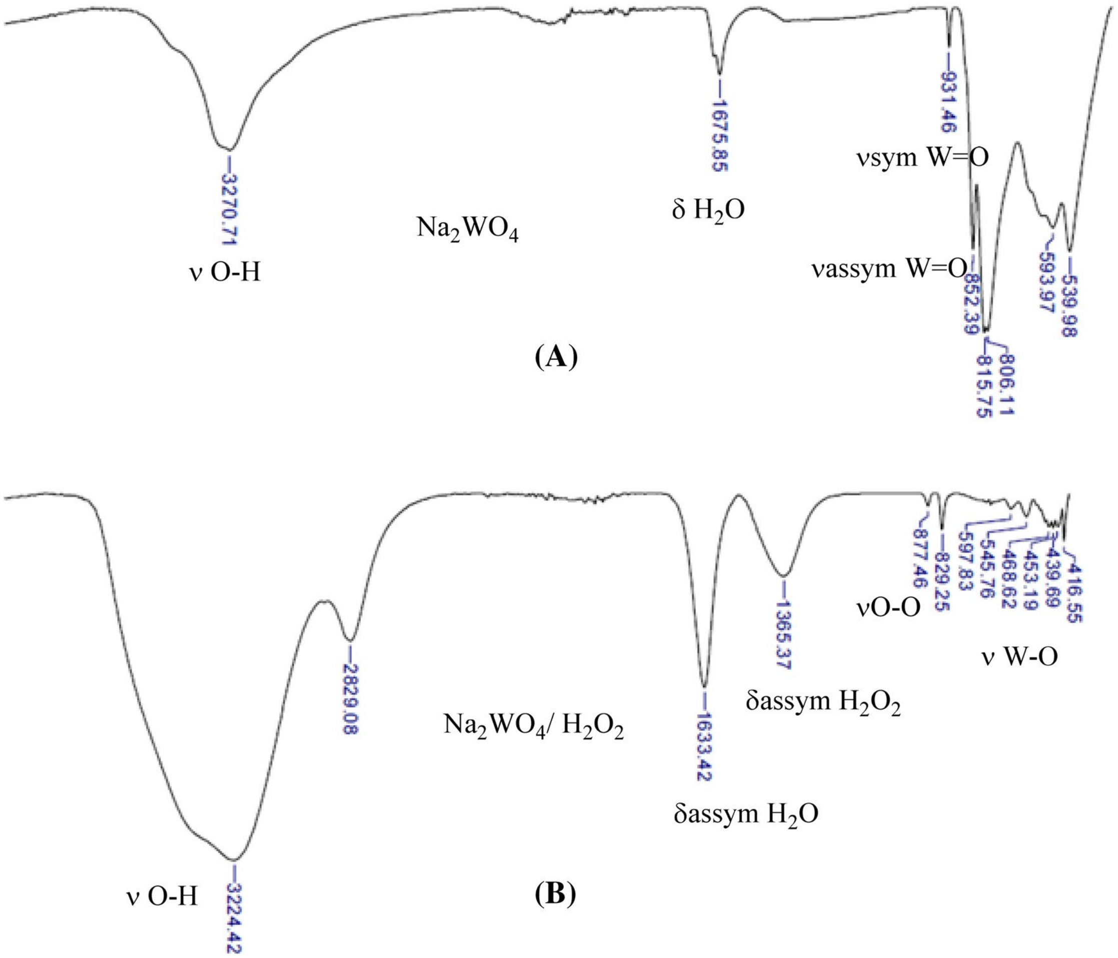
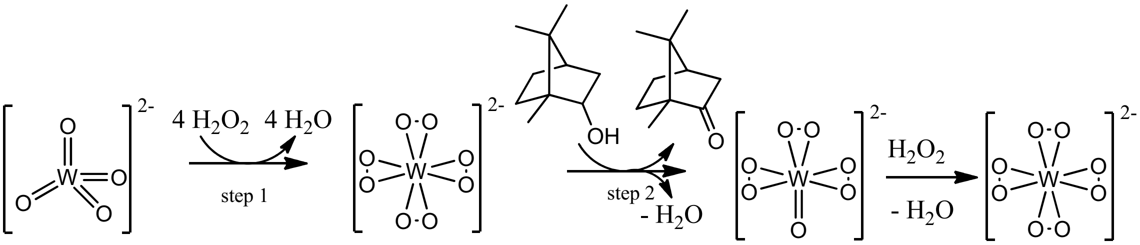


Fig. 1 FT-IR spectra of Na_2WO_4·dihydrate (**a**) and Na_2WO_4 dihydrate/$H_2O_{2(aq)}$ (**b**)

spectrum of Na_2WO_4 (see (A) spectrum, Fig. 1). It is an evidence that W=O double bonds that are typical of tungstate anion are absent [32]. On the other hand, we can note a notable change on absorption bands at frequencies lower than 597 cm^{-1}, that should corresponding tungsten–oxygen single bonds vibrations. These bands are close to those infrared data for peroxotungstate complexes [26, 32].

So, we can conclude that even without pH control, the tetraperoxotungstate complex is the catalytically active specie on this oxidation reaction, similarly to the described by Hida and Nogusa (Scheme 2) [21].

As can be seen in Scheme 2, the peroxided intermediate (**1**) has a highly electron-deficient metal center that may undergo nucleophilic attack of borneol hydroxyl group. This attack then results in an opening of highly unstable three-center ring, where a hydrogen atom will be transferred from borneol to the oxygen atom that is bonded to the tungsten, giving OOH group and bornyl-alkoxide. It is possible that



Scheme 2 Proposal for Na_2WO_4-catalyzed borneol oxidation reaction by H_2O_2 (adapted from Ref. [21])

in this step both groups remains coordinated to the metal. It is very common the formation of species like these (i.e., intermediates with peroxide and or alkoxide groups bonded to tungsten cation) in tungsten-catalyzed oxidations [21, 23–25]. Nonetheless, as we haven't any experimental evidence corroborating that this step has really occurred into tungsten coordination sphere, we do not included it in the Scheme 2.

In the last step, the simultaneous elimination of water and oxidized substrate generate the tungstate anion that after react with one mol of H_2O_2 is peroxided again and then can participate of more one catalytic cycle (Scheme 2).

3.3 Effects of H_2O_2: Borneol Molar Ratio on the Na_2WO_4-Catalyzed Borneol Oxidation

The effect of variation on proportion borneol to hydrogen peroxide was initially assessed on the reactions in the absence of catalyst (Fig. 2).

Figure 2 shows that a maximum conversion of 27% was achieved in the reactions without Na_2WO_4 at molar ratio of 1:4 substrate:oxidant. Nevertheless, a remarkable result of these reactions is that although the borneol has been consumed, the amount of camphor formed was not compatible with substrate consumed, suggesting the formation of not detectable products. It was confirmed by the mass balance of reaction. It is possible that borneol has been converted into alkyl peroxides that probably undergone thermal decomposition on injector of the gas chromatograph and thus were not detectable [33].

To prove this hypothesis, we performed a test proposed by Shulpin et al. [33, 34]. This method comprises comparing the intensities of GC peaks of the alcohol in samples with and without the addition of triphenylphosphine. If alkyl peroxides are present, the intensity of substrate GC peak in the sample that was added PPh_3 will be increased, due to reduction of alkyl peroxide to alcohol.

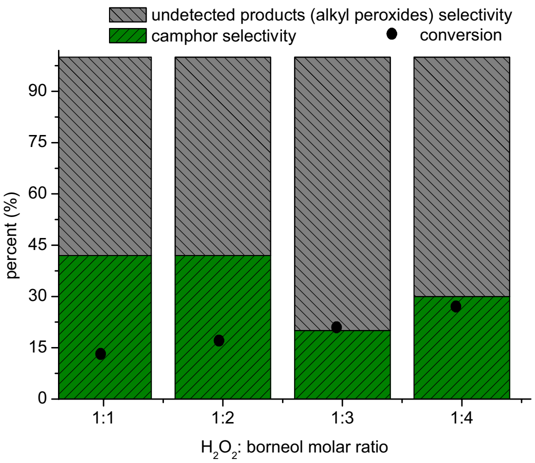


Fig. 2 Effect of reactants stoichiometry on the conversion and selectivity of the catalyst free borneol oxidation by H_2O_2. Reaction conditions: borneol (2.4 mmol); DMA (10 mL); 2 h; 343 K

Therefore, we analyzed two aliquots that were simultaneously collected from the catalytic run carried out with a proportion of 1:4 borneol:H_2O_2 after 2 h reaction. Before analysis, PPh_3 was added only to one of them. The GC analyses showed that expectedly, as described in Fig. 2, the camphor was minority in both aliquots. Nonetheless, the PPh_3-free sample presented the GC peak of borneol with an area lower than aliquot containing phosphine.

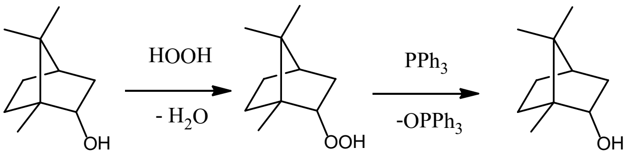
Indeed, only in this late aliquot the mass balance of reaction was achieved (i.e. borneol GC peak area remaining in the reaction + camphor GC peak area = borneol GC peak initial area) (Scheme 3).

These evidences suggest that in the presence of PPh_3 the alkyl peroxide species (i.e. ROOH, undetectable by GC analysis) formed during the reaction were reduced by the PPh_3 to borneol, regenerating the initial area of substrate peak. GC-MS analysis confirmed the presence of triphenylphosphine oxide resulting of this reaction. The preferential decomposition of ROOH species to alcohol is in agreement with literature [33, 34]. So, we can conclude that in the absence of catalyst, hydrogen peroxide convert borneol to alkyl peroxides in solution, but only a little amount is converted to camphor, remaining the larger part as alkyl peroxides.

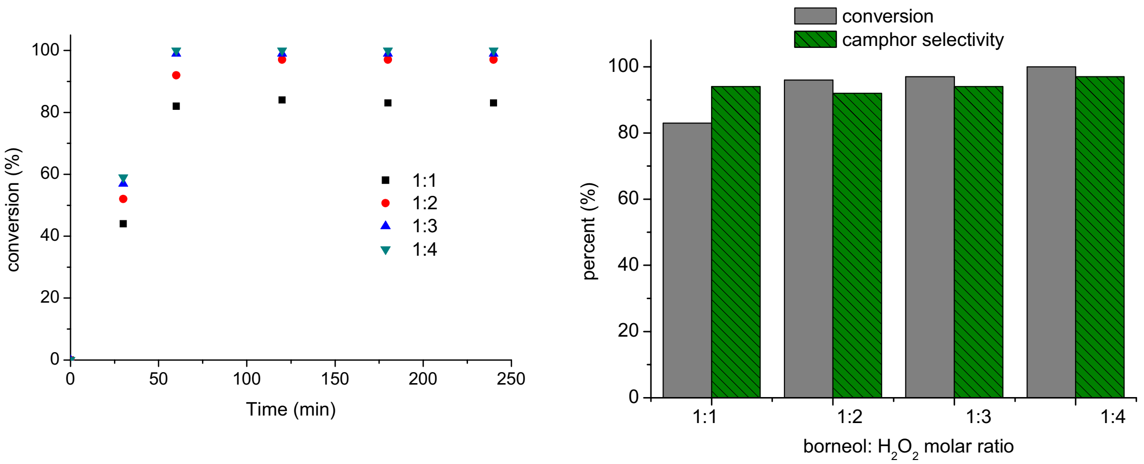
Conversely, when the reactions were performed in the presence of Na_2WO_4 catalyst, the borneol was preferentially converted to camphor, reaching constantly selectivity higher than 90% (Fig. 3b).

In these runs, mass balance of reactions was always achieved. It reinforces the importance of tungsten catalyst, whose presence significantly improved either the reactions conversion as well as camphor selectivity.

The GC-MS analyses showed that a mixture of minority products (i.e. borneol isomer alcohols, camphor-derivatives) was formed; however, the selectivity was lower than 10%. An increase on oxidant load of 1:1 to 1:2 improved the initial rate as well as the conversion (Fig. 3a) and selectivity of the reactions (Fig. 3b). The values were close to 100% indicating the high efficiency of catalyst.



Scheme 3 Oxidation of borneol to alkyl peroxide followed by reduction with PPh_3 [33, 34]



(a)

(b)

Fig. 3 Effect of reactants stoichiometry on the kinetic curves (**a**), conversion and selectivity (**b**) of Na_2WO_4-catalyzed borneol oxidation by H_2O_2. Reaction conditions: borneol (2.4 mmol); Na_2WO_4 (2.5 mol %); DMA (10 mL); 343 K

3.4 Effects of Catalyst Concentration in Na_2WO_4-Catalyzed Borneol Oxidation by H_2O_2

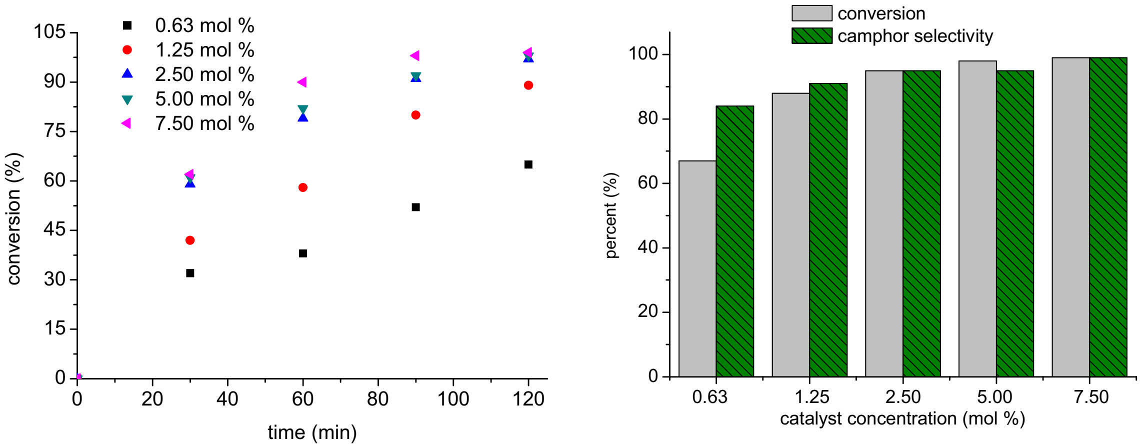
To determine what the lowest concentration provides the highest conversion and selectivity within time studied, we carried out reactions with different concentrations of catalyst.

The kinetic curves shown in Fig. 4 reveal that an increase on catalyst concentration had a beneficial effect on conversion and initial rate of reaction. In general, with concentrations higher than 0.63 mol% a virtually complete conversion of borneol was achieved (i.e., values close or higher than 90%). Moreover, regardless the catalyst concentration, the camphor selectivity was always higher than 90%.

3.5 Effects of Temperature in Na_2WO_4-Catalyzed Borneol Oxidation by H_2O_2

The reaction temperature can play an important role on oxidations with hydrogen peroxide. In special, the possible peroxided intermediates may be formed but remains intact on the solution reaction. This fact was observed in the borneol oxidation reaction by H_2O_2 performed at room temperature in the absence of catalyst (Fig. 5).

In addition to lowest conversion, the reaction carried out at room temperature displayed also the lowest borneol selectivity. In all the catalyst-free reactions the alkyl peroxide products were preferentially formed (Fig. 5).



(a)

(b)

Fig. 4 Effect of catalyst concentration on the kinetic curves (**a**), conversion and camphor selectivity (**b**) of Na_2WO_4-catalyzed borneol oxidation reaction by H_2O_2. Reaction conditions: borneol (2.4 mmol); H_2O_2 (4.8 mmol); DMA (10 mL); 343 K

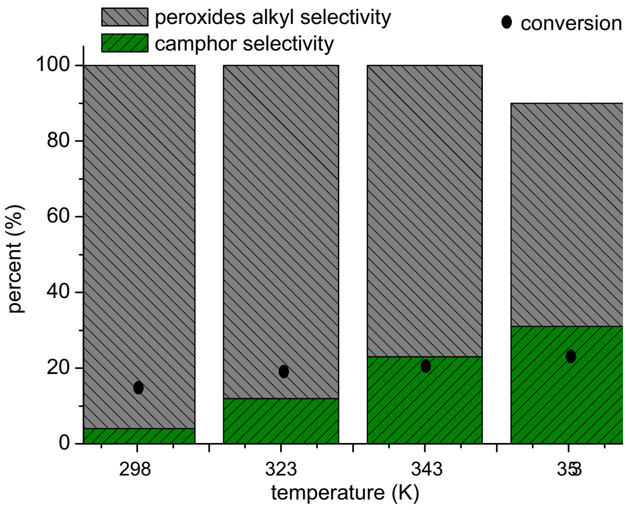


Fig. 5 Effect of reaction temperature on the conversion and selectivity of the catalyst-free borneol oxidation by H_2O_2. Reaction conditions: borneol (2.40 mmol); H_2O_2 (4.80 mmol); DMA (10 mL); 2 h; Na_2WO_4 (2.5 mol %)

On the other hand, in the presence of catalyst, the conversion of borneol into camphor was notably favored (Fig. 6). An increase of temperature resulted in a consequent increase in the conversion as well as the initial rate of reaction (Fig. 6a).

On catalytic runs, when the reactions were carried out at temperatures equal or higher than 323 K, the alkyl peroxide intermediates were decomposed by the catalyst, resulting in the selective formation of camphor.

3.6 Na_2WO_4-Catalyzed Terpenic Alcohols Oxidation Reaction by H_2O_2

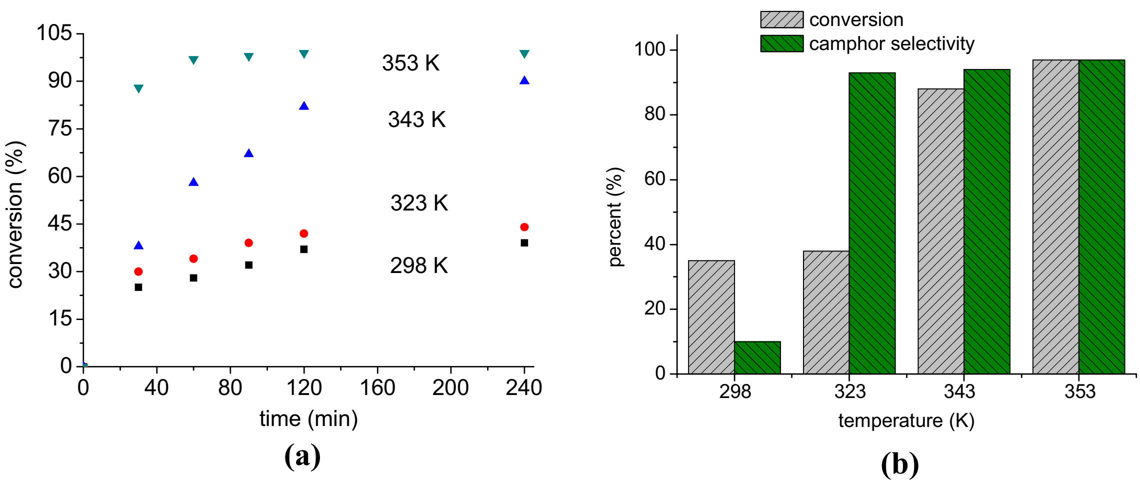
The presence of double bonds into structure of the terpenic alcohols, besides possibility of skeletal rearrangement reactions may complicate the selectivity of oxidation reactions. It becomes more difficult to be controlled when the oxidation proceeds through homolytic pathway, where radical intermediates are formed due to presence of peroxide oxidant [35].

As borneol is a saturated alcohol, we selected unsaturated terpenic alcohols to test the efficiency of catalyst system. To do it, we carried out the reactions with the optima conditions established for borneol. The structural of acyclic terpenic alcohols, the kinetic curves of reactions and selectivity results for carbonylic products are presented in the Fig. 7a–c, respectively.

In general, the reactivity of primary alcohols is higher than secondary one, while tertiary alcohols are not reactive. However, in addition to the hydroxyl groups, the acyclic terpenic alcohols studied have also double bonds that may also be oxidized (Fig. 7a). For this reason, the linalol that is a tertiary alcohol was included in this study. Nonetheless, as displayed in Fig. 7b, only it was the least reactive and only a poor conversion (ca. < 7%).

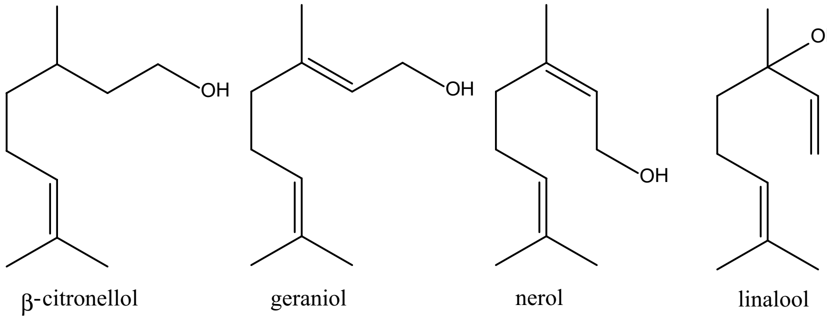
In terms of conversion, the behavior of alcohols was as follow; geraniol ad nerol that are allylic primary alcohols were more reactive than borneol, a saturated secondary alcohol. This result is in agreement with literature [36].

Conversely, although borneol is a secondary alcohol, it was more reactive than β-citronellol, a primary alcohol, even when this late was oxidized to higher temperature (363 K). It is possible that high rigidity of bornyl skeletal of borneol favor the formation of alkoxy–tungsten intermediate, formed

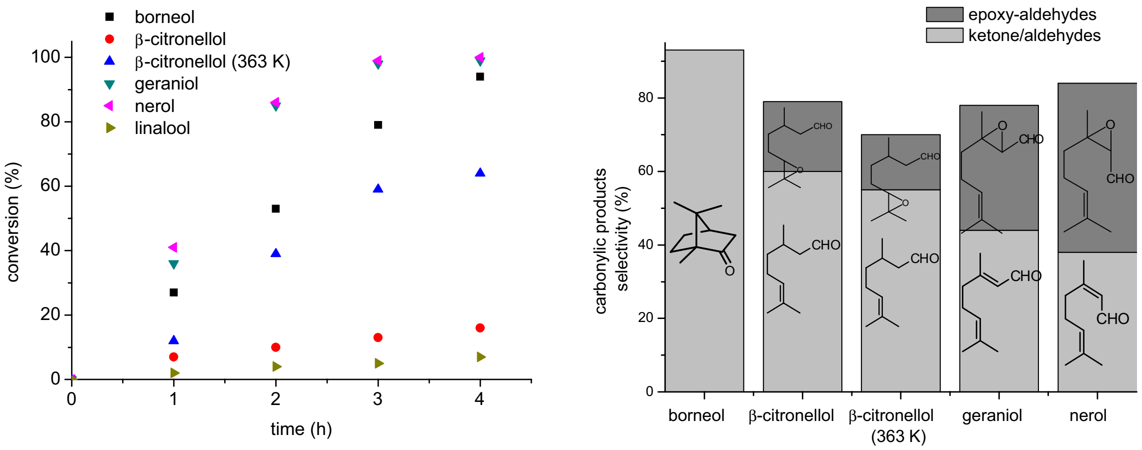

(a)

(b)

Fig. 6 Effects of temperature on the Na_2WO_4-catalyzed borneol oxidation by H_2O_2. Reaction conditions: borneol (2.40 mmol); Na_2WO_4 (1.25 mol %); H_2O_2 (4.80 mmol)



(a) acyclic terpenic alcohols



(b) kinetic curves

(c) products selectivity

Fig. 7 Kinetic curves (**a**) and products selectivity (**b**) of Na_2WO_4-catalyzed oxidation reactions of terpenic alcohols Reaction conditions: borneol (2.40 mmol); Na_2WO_4 (1.25 mol %); H_2O_2 (4.80 mmol)

during the step of hydrogen atom removal from hydroxyl group.

Expectedly, the double bonds into terpenic alcohols structure were another active site to oxidation. In almost of case the unsaturated aldehydes formed undergone further epoxidation. However, a high combined selectivity for carbonylic products (aldehydes and epoxy-aldehydes) close to *ca.* 90% was achieved in the oxidation reactions of β-citronellol, geraniol, nerol (Fig. 7c).

4 Conclusions

In summary, we have developed a catalyst system based on Na_2WO_4 for oxidation of terpenic alcohols in DMA with hydrogen peroxide to corresponding carbonyl compounds in high conversion under additives- and PTC-free conditions. FT-IR measurements confirmed that $Na_2W(O_2)_4$ is the active catalytically specie. The catalytic reactions were quite selective with high conversion for oxidations of acyclic and cyclic alcohols with primary or secondary hydroxyl groups. The Na_2WO_4 catalyst exhibits high activities in all runs under environmentally friendly oxidative conditions.

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