ORIGINAL ARTICLE

Activation of H_2O_2 by methyltrioxorhenium(VII) inside β-cyclodextrin

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Abstract The effect of β-cyclodextrin on the catalytic stability and reactivity of methylrhenium trioxide (MTO), CH_3ReO_3, which has been used for activation of hydrogen peroxide toward oxidation and epoxidation reactions, was studied using UV–Vis spectrophotometery. The stability and reactivity of the new catalytic system (MTO/β-CD) to activate H_2O_2 toward oxidation of indigo blue dye were investigated in basic media. Furthermore, effects of inclusion stoichiometry, temperature and concentrations of hydrogen peroxide on the stability and reactivity of the MTO/β-CD system were investigated. The formation of the inclusion complex between MTO and β-CD was confirmed experimentally using the changes in the UV–Vis absorption spectra. The results of this study demonstrate that the complexation process was better guaranteed when the amount of β-CD is higher than that of MTO, using a 1:2 molar ratio of MTO:β-CD enhances both the activity and stability of the catalyst. The results showed that the stability of the catalytic system was enhanced in presence of β-CD with maintaining good reactivity of the MTO even in the presence of high concentration of NaOH. The changes of thermodynamic activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) for the oxidation reaction of indigo with H_2O_2 catalyzed by MTO/β-CD system were determined on the basis of the experimental data.

Introduction

Many chemical reactions are of a great importance in our life, especially those involved in industrial applications. The epoxidation of olefins can be considered as one of the most important processes, since epoxides are useful intermediates for the preparation of a wide variety of products [1]. It was found that compounds of high valent metals of group IV–VI are excellent catalysts for epoxidation of olefins with organic peroxides [2]. Since the first report by Herrmann and co-workers with methylrhenium trioxide (CH_3ReO_3, commonly referred to as MTO, a rhenium(VII) derivative) [3], this area has been extensively studied and efficient catalytic olefination reactions with good stereoselectivity have been reported based on several transition metals complexes [3].

A convenient and efficient application of heterogeneous methylrhenium trioxide systems for the selective oxidation of lignin model compounds and lignins was reported by Crestini et al. [4]. In their study an environmental friendly and low cost H_2O_2 was used as the oxygen atom donor. MTO in combination with H_2O_2 has become in recent years an important catalyst for a variety of synthetic transformations, such as oxidation of olefins [5], alkynes [6], sulfur compounds [7], Bayer–Villiger rearrangement [8], oxidation of C–H bonds [9], and oxidation of aromatic derivatives [10]. Excellent conversions and good selectivities for the

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epoxidation reaction were observed using of catalytic MTO and urea hydrogen peroxide in room temperature ionic liquid by Soldaini et al. [11]. Oxidations of unsaturated steroidal compounds with H_2O_2 mediated by MTO have shown good region- and stereoselectivity [12]. Recently, an efficient catalytic olefination and polymerization of diazo compounds with good stereoselectivity have been reported based on rhenium and other transition metals complexes, demonstrating new possible applications [13].

Methylrhenium trioxide has the rare ability to stoichiometrically generate methanol at room temperature with an external oxidant (H_2O_2) under basic conditions. A computational mechanistic study by Gonzales et al. [14] using density functional theory has shown possible reaction pathways to form methanol from MTO/H_2O_2 system. Hermann et al. [15] observed that exposing MTO to hydrogen peroxide under neutral conditions leads to a series of μ-peroxo species and, under basic conditions, yields a perrhenate ion (ReO_4^-).

The homogeneous oxometal catalysts can be recovered from the reaction mixtures and reused, although catalytic activities tend to decrease with recycling runs. Catalysts losses are also a problem in purely homogeneous systems. There are two well known possible ways to facilitate catalyst/product separation these are heterogenization of the catalyst, and two-phase homogeneous catalysis. An alternative, yet largely unexplored, method for the modification of the catalytic properties of oxometal complexes is their encapsulation in cyclodextrins (CDs) [16, 17]. Metalloorganic complexes immobilized in CDs often exhibit markedly different physical and chemical characteristics compared to the bulk material [18]. In these oxometal compounds, the CDs act as second-sphere ligands noncovalently attached to the first-sphere ligands of the metal centre [19].

Methylrhenium trioxide has been considered as one of the best catalysts for H_2O_2 activation toward oxidation of organic and inorganic substrates, and for epoxidation of olefins [2]. MTO is a powerful Lewis acid which acts in semi aqueous or organic solvents, at low and moderate temperatures with high activity and catalytic turnovers [20, 21]. MTO activates H_2O_2 through the formation of two catalytically active intermediates (monoperoxide, **A**, and diperoxide, **B**) which exist in equilibrium with MTO and H_2O_2 in solution (Scheme 1) [2]. Both species are active oxidants,
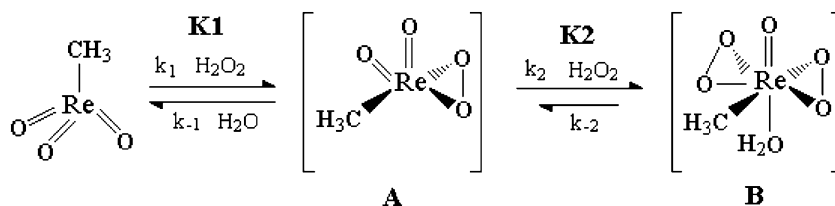
and they are 10^4–10^5 more reactive than H_2O_2 itself [2]. It is worth to mention that the stability of the catalytic system (MTO/H_2O_2) depends on the concentration of H_2O_2 and the pH of the solution [22]. It has been shown by Espenson and co-worker [2, 22] that the amount of **A** and **B** (Scheme 1) are determined by the concentration of H_2O_2 (in aqueous solutions: $K_1 \sim 10$, $K_2 \sim 100$) [2]. At relatively low concentrations of H_2O_2 (≤ 2.0 mM), **A** only exists. At higher concentrations, both **A** and **B** are present, and at extremely higher concentrations of H_2O_2 (≥ 0.1 M), **B** is the only rhenium species present. In each case the catalyst is theoretically recovered. In the case that **A** is the predominant species, then **MTO** is immediately recovered along with the epoxide. Similarly, if an oxygen atom is transferred from the diperoxide **B**, then **A** is generated [2].
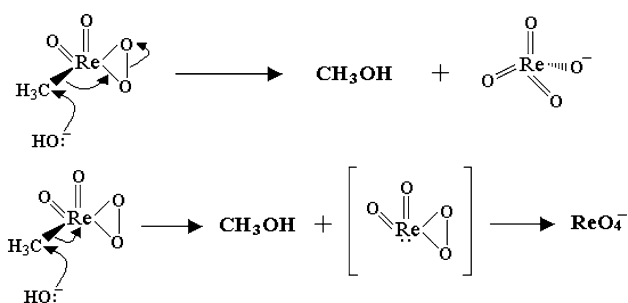
The instability of MTO in the presence of H_2O_2 can be explained by the irreversible decomposition of the MTO via the reaction of either **A** with hydroxide (OH$^-$) or MTO with HO_2^- ions, whereas the decomposition of **B** regenerates MTO upon expulsion of dioxygen, although it does decompose a corresponding amount of H_2O_2 [22].

The decomposition of **A** occurs by the direct nucleophilic attack of OH$^-$ at the methyl group via S_N2 mechanism in which it produces methanol and perrhenate ion (ReO_4^-) directly or through the formation of peroxorhenium(V) intermediate which yields the final products after internal electron shifts (Scheme 2) [22]. Consequently, a computational mechanistic study by Oxgaard and co-worker proposed that the reaction between MTO and H_2O_2/NaOH in THF proceeds through an insertion of the oxygen into the C–Re, forming methoxyrhenium trioxide [14].

According to what we have mentioned about this catalytic system (MTO/H_2O_2), it looks like it is a complicated one in which the catalyst decomposition depends on many factors such as the concentration of the catalyst, the concentration of hydrogen peroxide, the substrate, and the solvent. However, if we look back directly to the decomposition mechanisms, we find that it involves the attack of HO_2^- or OH$^-$ on the methyl group of MTO, **A**, or **B**. These two nucleophiles are deactivated in acidic medium, but they are not deactivated in other media. This problem can be overcome if the methyl group of MTO can be protected from the attack of HO_2^- and OH$^-$. At first sight, this idea seems to be difficult, but it may be possible to think about it after we introduce cyclodextrins.

Scheme 1 Equilibrium formation of peroxorhenium complexes

Scheme 2 Mechanistic scheme for the decomposition of monoperoxide (*the catalytically active intermediate*) in basic media

MTO can effectively catalyze oxidation reactions with hydrogen peroxide with a high reactivity and very good selectivity. However, MTO decomposes in the presences of H_2O_2 in neutral or basic media. In this study, an examination of the catalytic behavior of the resultant inclusion of MTO in β-cyclodextrin is reported in basic medium. β-cyclodextrin is used to stabilize MTO against decomposition and maintain its activity over a period of time rather than increasing the reaction rate or selectivity. Encapsulation of the methyl group of MTO by means of monomolecular inclusion complex formation offers a new way of protecting MTO from the nucleophilic attack of OH^- and HO_2^-.

Experimental

Materials and methods

Methylrhenium trioxide was obtained from Aldrich. β-cyclodextrin was obtained from Aldrich and Lancaster Synthesis (FW = 1,135 g/mol). The hydrogen peroxide (35 wt%) was obtained from Acros Organics. Indigo blue was obtained from Aldrich (dye content 94%, FW = 466.36 g/mol). Deionized water was obtained from Arabia Company-Jordan, and was used as received; also double distilled water has been used.

Spectral measurements and kinetic experiments were carried out by Shimadzu double-beam UV–Visible spectrophotometer (UV-2401 (PC) S, Shimadzu Corporation), using UV-quartz 2.0 mL cuvettes (8.0 mm path length). The data were analyzed by Kaleida-Graph program (Synergy Software). Stock solutions of H_2O_2 (0.1–1.0 M) were prepared by dilution of 35% H_2O_2 in deionized water. These solutions were standardized daily by iodometric titration. Stock solutions of indigo blue dye (1–5 mM) were prepared in water and standardized spectrophotometrically ($\varepsilon_{620} = 1.9 \times 10^4 \, M^{-1} \, cm^{-1}$). ^{1}H-NMR spectra were recorded on a Bruker 400 spectrometer at room temperature in D_2O.

All materials and solutions were kept under 0 °C temperature, and were protected from light. In kinetic experiments, the cell housing was controlled at temperature of interest using a temperature control device (TCC-controller) connected to the spectrophotometer, and covering temperatures from 15 to 70 °C with a precision of ±0.1 °C.

Sample preparations

MTO was freshly prepared for each experiment. A stock solution (20–40 mM) was prepared in a 2.0 mL volumetric tube by dissolving a small amount of crystalline MTO in a 2.0 mL deionized water. From this unknown concentrated stock solution, 50 µL was transferred to the cell and diluted in 1.8 mL of deionized water. Then, the absorbance at two wavelengths ($\lambda = 238$ and $\lambda = 270$ nm) was measured by scanning in the 200–400 nm region. The concentration of the diluted solution of MTO was calculated using Beer's Law (extinction coefficients: ε_{238} and ε_{270} are 1,900 and 1,200 $M^{-1} \, cm^{-1}$, respectively). Finally, the actual concentration of the stock solution is calculated by considering the dilution factor.

Kinetic determinations

The inclusion process was carried out in a total 10-mL solution. The desired amount of β-cyclodextrin was dissolved completely in water. Then the desired amount of MTO was injected into the β-cyclodextrin solution under stirring. The solution was then covered with a watch glass, and wrapped with aluminum foil to protect the solution from light. The stirrer was then adjusted at 350–400 rpm, and allowed to stir for 180–210 min.

To confirm that inclusion of MTO with β-cyclodextrin has occurred, the resulting MTO/β-CD complex was directly placed in the UV-quartz cell, and the absorption spectra of solution was recorded in the range 200–400 nm. After that, a certain amount of indigo blue (0.08 mM) was added, and the initial absorbance at 600 nm (λ_{max} of indigo blue) was recorded. Finally, hydrogen peroxide, was added to the reaction mixture, and the absorbance change at 600 nm due to oxidation of indigo blue was followed with time. When needed, a second (and more) injection of indigo blue was added to the original solution after the first reaction was finished, i.e. the absorbance was almost zero, and after 1 min of completion.

Results and discussion

Binding of MTO with β-cyclodextrin

A wide variety of chemical reactions were found to be accelerated by cyclodextrins [23]. The ability of CDs to include a part of an organometallic complex in their

internal hydrophobic cavities has been demonstrated by numerous researchers [24]. As a result of inclusion into nonpolar cyclodextrin cavity, the guest molecules undergo some geometric and electronic changes that can be responsible for dramatic differences in their action [25, 26]. Furthermore, in some cases CDs have been used as catalysts to increase the reaction rate or to affect the selectivity of the reaction [27, 28]. Recently, an original example of catalysis in a multi-phase system, in presence of a noble metal catalyst with β-CD has been reported by Monflier and co-workers [29]. In their study, the catalytic investigations demonstrate that CDs act as efficient protective molecules against side reactions through the formation of inclusion compounds [29]. In this study the β-cyclodextrin is used to stabilize MTO against decomposition and maintain its activity over a period of time in basic media.

Figure 1 shows the UV–Vis absorption spectra of β-cyclodextrin, MTO, and the MTO-β-cyclodextrin complex in aqueous solution. The absorption spectrum of MTO-β-CD was recorded directly after stirring for 3 h, and the observed spectral changes have been used to confirm the inclusion of MTO into the cavity of β-CD. In the presence of β-CD (Fig. 1) the intensity of the absorption band ($\pi \rightarrow \pi^*$) increases and shifted to higher energy while the intensity of $n \rightarrow \pi^*$ decreases and shifted to lower energy, these spectral changes proposed the formation of a complex between MTO and β-CD. In each experiment the inclusion was examined by comparing the UV–Visible absorption spectra before and after the inclusion. Furthermore, it has been found that the intensity of these absorption bands depends on many factors such as,
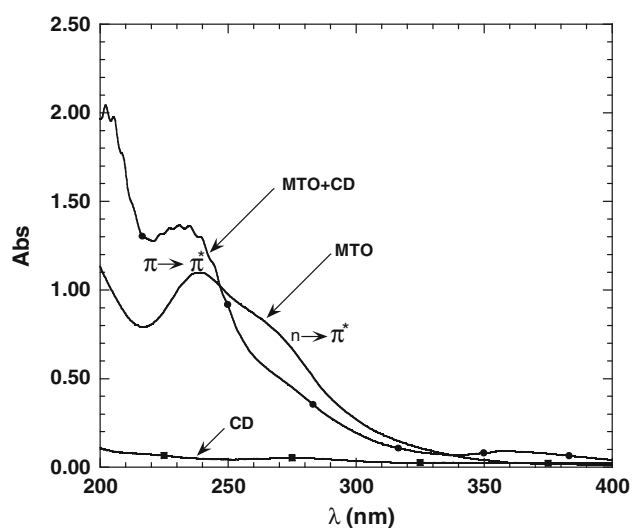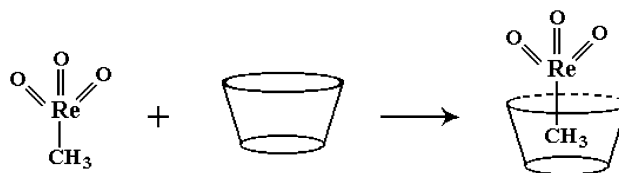
the stirring time, concentrations of MTO and β-CD, temperature, and the pH of the solution. The proton NMR signal corresponding to the methyl group of MTO in the MTO-β-Cyclodextrin complex appears at δ 2.89 which is slightly shifted downfield compared with the un-coordinated MTO δ 2.67. The results of UV–Vis and NMR studies give a clear indication that the methyl group of MTO is included in the cavity of β-CD. Furthermore, there is a possibility that the indigo blue may form inclusion complex with β-CD, but to exclude this assumption, in this study after it has been confirmed that inclusion of MTO with β-cyclodextrin has occurred, the resulting MTO/β-CD complex was directly placed in the UV-quartz cell, and the oxidation of small amount of indigo blue (0.08 mM) was followed with short period of time.

The idea of inclusion of MTO in β-CD was invented on the basis of the fact that MTO having two main parts, the nonpolar Re-CH$_3$ and the polar Re-(=O)$_3$. As a consequence of the relatively nonpolar character of the cavity of β-CD, metal complexes bearing hydrophobic ligands (such as CH$_3$) should be suitable guests. On the other hand, the nonbonding electron pairs of the glycosidic oxygen bridges in cyclodextrin are directed toward the inside of the cavity, producing a high electron density and lending it some Lewis base characteristics. It is well know that MTO is a powerful Lewis acid, so this supporting coincidence of Lewis acid–base combination is another beneficial factor that will promote the inclusion of MTO in the cavity of β-CD. MTO interaction as a Lewis acid will prefer to interact with β-CD cavity as a Lewis base from the Re-CH$_3$ side rather than the other Re-(=O)$_3$ side (Scheme 3). It is worth to mention that our experimental data demonstrate that the diameter of the cavity of CDs (cavity diameter of α-CDs, β-CDs, and γ-CDs are 5.2, 6.6, an 8.4 Å, respectively [30]) appeared as a crucial point to act as a host for MTO. The β-CDs that have intermediate cavity diameters among the other CDs was found the best host for MTO. The cavity diameter of α-CDs is too small to fit the methyl group of MTO, whereas the cavity diameter of γ-CDs is too big for MTO, since γ-CDs have a noncoplanar flexible structure with great permittivity that would allow the MTO to pass through the cavity without binding or bind weakly to methyl group of MTO [30].

Fig. 1 The UV–Vis absorption spectra of (*dashed line*) free MTO (1.0 mM), (*filled squares*) free β-cyclodextrin (2.0 mM), and (*filled circles*) MTO:β-CD complex (1.0:2.0 mM) at 25 °C
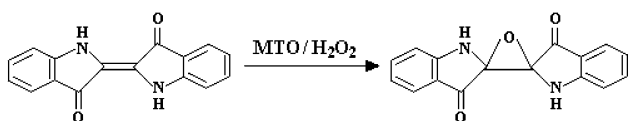

Scheme 3 Inclusion complexation of MTO/β-CD

Stability of MTO-H$_2$O$_2$ catalytic system

As mentioned earlier in introduction, a significant amount of MTO decomposes in the presence of H$_2$O$_2$ in aqueous neutral or basic medium. Therefore, the efficiency of MTO to oxidize alkenes is decreased as the decomposed amount of MTO is increased. Also, the rate of oxidation is affected by this decomposition. In this work, the capability of MTO to catalyze the oxidation of alkenes in the presence of H$_2$O$_2$ was investigated by using a certain type of indigo blue dyes (organic dyes) as a substrate.

Scheme 4 shows the oxidation of indigo dyes by MTO/H$_2$O$_2$ catalytic system. As a result of oxidation, the dark blue color is bleached to light yellow (epoxide) then finally to colorless solution, which indicates the formation of diols. Therefore, all experiments were followed by observing the change in absorption at $\lambda = 600$ nm (the molar absorptivity (ε) of indigo blue at 600 nm $= 1.9 \times 10^4$ M^{-1} cm^{-1}). In each experiment, a certain amount of indigo blue was oxidized quickly by H$_2$O$_2$ in the presence of MTO and NaOH (0.01 M). Under similar conditions, another amount of indigo dye was added to the same MTO/H$_2$O$_2$/NaOH solution which was used in the first oxidation, directly after 1 min finishing the first oxidation. The rate of oxidation was decreased, and when the third amount of indigo blue was injected to the system, the rate of oxidation was decreased significantly, and the catalytic system became almost inactive indicating that almost 95% of the catalyst was decomposed. Figure 2 shows the absorbance decay curves for three successive oxidations of indigo blue dye.

Inclusion of MTO with β-CD offers a new catalytic system, in which the new catalyst is the MTO/β-CD complex. Cyclodextrin does not only protect MTO from decomposition, which in turns improves the stability of the catalyst, but it also keeps the catalyst active for longer time toward oxidation reactions.

Figure 3 shows the improvement in the stability of the catalytic system upon inclusion of MTO into β-CD. MTO/H$_2$O$_2$ maintains good reactivity even after the third injection of indigo dye. Although in the absence of β-CD, the rate of oxidation for the first injection was very high in basic solution, the rates of the second and the third injections were better in the presence of β-CD, Table 1. In overall assessment, this complex (MTO/β-CD) has higher rates in all of the three successive oxidations of indigo blue
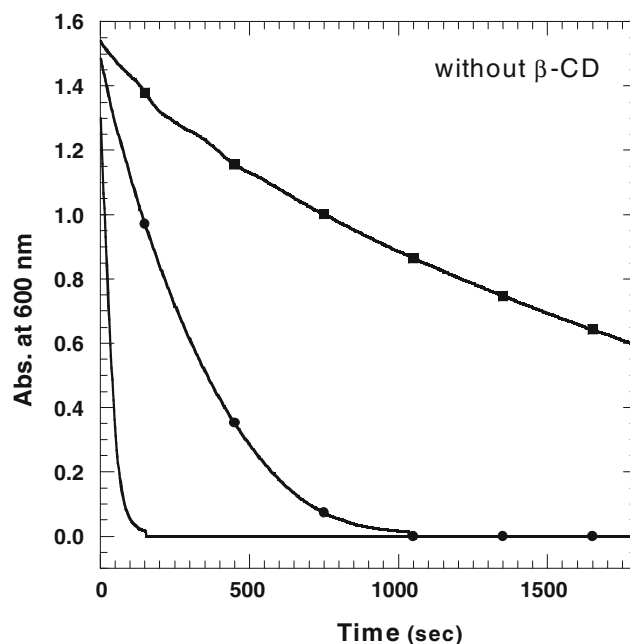

Fig. 2 Variation of absorbance with time for three successive oxidations of indigo blue dye (0.08 mM) with H$_2$O$_2$ (0.1 M) catalyzed by MTO (1.0 mM) at 25 °C, in the presence of NaOH (0.01 M) within 1 min interval between the first injection (*dashed line*), the second (*filled circles*), and the third (*filled squares*) at 600 nm

Fig. 3 Variation of absorbance with time for three successive oxidations of indigo blue dye (0.08 mM) with H$_2$O$_2$ (0.1 M) catalyzed by MTO:β-CD (1.0:2.0 mM) at 25 °C, in the presence of NaOH (0.01 M) within 1 min interval between the first injection (*dashed line*), the second (*filled circles*), and the third (*filled squares*) at 600 nm
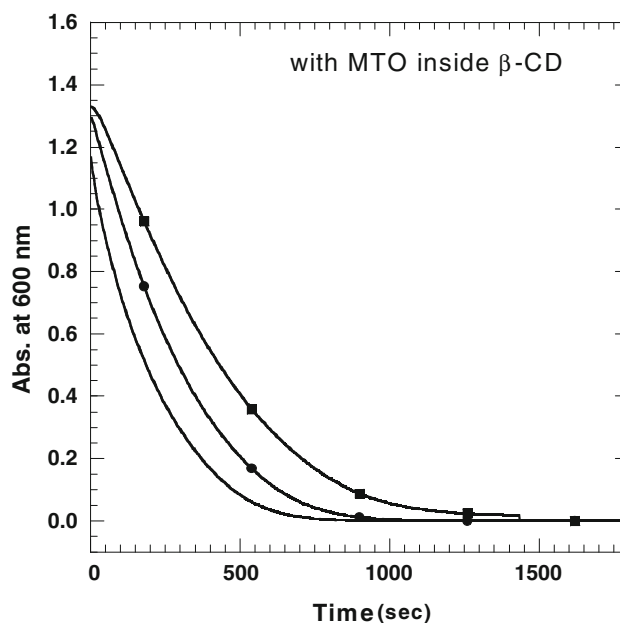

Scheme 4 Oxidation of indigo blue dyes by MTO/H$_2$O$_2$ catalytic system

Table 1 Initial rate values of the different catalytic systems upon oxidation reactions with indigo blue dye

Catalytic system	Initial rate of oxidation of the first injection of indigo blue (M/s, 10^{-8})	Initial rate of oxidation of the second injection of indigo blue (M/s, 10^{-8})	Initial rate of oxidation of the third injection of indigo blue (M/s, 10^{-8})
MTO (1 mM) + H$_2$O$_2$ (0.1 M) in NaOH (15 mM)	150.0	18.0	3.1
MTO (1 mM) + β-CD (2 mM) + H$_2$O$_2$ (0.1 M) in NaOH (15 mM)	44.0	21.6	14.7

which means that MTO/β-CD is both more reactive and more stable than MTO in basic solution. The initial rate values of the two catalytic systems (MTO/H$_2$O$_2$/NaOH) and MTO/H$_2$O$_2$/β-CD/NaOH) upon successive oxidation of indigo blue dye are summarized in Table 1.

This study shows that the complexation process is better guaranteed when the amount of β-CD is higher than that of MTO, but it is limited to some extent above which increasing the concentration of β-CD will not enhance the stability of MTO. The best results were obtained with a 1:2 molar ratio of MTO:β-CD. At 1:2 (MTO:β-CD) molar ration, both the activity and stability of the catalyst were enhanced (Fig. 3). In addition, the results show that the reactivity and stability of MTO/H$_2$O$_2$ catalytic system was not directly proportional to the concentration of β-CD.

The stability of the catalytic system (MTO/β-CD) was investigated at different concentration of NaOH. For this purpose, the third injection of indigo blue to the catalytic system in the presence of different concentration of NaOH was selected, and the changes in the initial rate were determined to show the effect of NaOH on the stability and reactivity of the catalytic system (Fig. 4). The initial rate
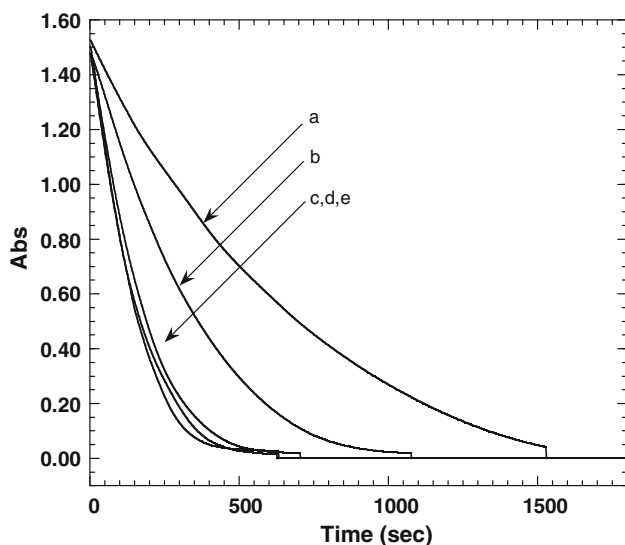
Table 2 Initial rate values of oxidation reactions of indigo blue dye catalyzed by MTO/β-CD (1:2 molar ratios) at different concentrations of NaOH

[NaOH] (mM)	Initial rate of oxidation of the first injection of indigo blue (M/s, 10^{-8})	Initial rate of oxidation of the third injection of indigo blue (M/s, 10^{-8})
0	88.5	42.4
1	66.7	41.4
5	60.7	36.7
10	48.8	18.6
50	39.4	9.88

values of indigo blue oxidation reactions in the presence of the catalytic system at different concentrations of NaOH were summarized in Table 2. As it is apparent from the values of initial rates in Table 2, the stability of the catalytic system is enhanced in presence of β-CD with maintaining good reactivity of the MTO even in the presence of NaOH up to 50 mM. Whereas in the absence of β-CD the reactivity of MTO remarkably decreased in the presence of NaOH (15 mM), Table 1.

Effect of hydrogen peroxide on reactivity of MTO/β-CD system

Hydrogen peroxide is a crucial component in the catalytic system as the oxidizing agent used, and so, its concentration has a great effect on the reactivity of MTO/β-CD. It was mentioned earlier in introduction that the concentration of H$_2$O$_2$ determines the relative amounts of the active forms of MTO (monoperoxide, **A**, and diperoxide, **B**) toward oxidation reactions. Espenson and co-worker showed that the catalytic epoxidation of most compounds by hydrogen peroxide using MTO as a catalyst, both **A** and **B** react, but **A** usually somewhat faster [2, 22].

In this study it has been found that H$_2$O$_2$ seems to have a different effect in the new MTO/β-CD catalytic system. The results of this study shows that at low concentrations of H$_2$O$_2$ (<10 mM), where only **A** is present in the solution [2, 31], the reactivity increases with increasing the concentration of H$_2$O$_2$. In contrast, at higher concentrations of H$_2$O$_2$ (>10 mM), where **B** is also present in the solution

Fig. 4 Variation of absorbance with time for 3rd oxidation step of indigo blue dye (0.08 mM) with H$_2$O$_2$ (0.1 M) catalyzed by MTO:β-CD (1.0:2.0 mM) at 25 °C, in the presence of different concentration of NaOH, at 600 nm. [NaOH]/mM: (*a*) 50, (*b*) 10, (*c*) 5, (*d*) 1, (*e*) 0
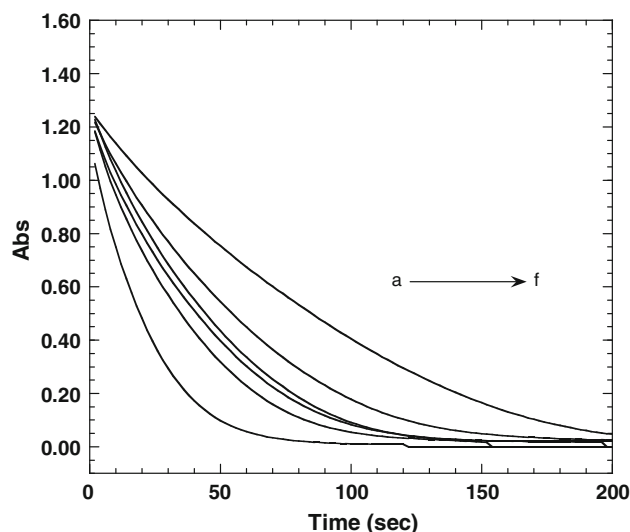
Fig. 5 Variation of absorbance with time for 1st oxidation step of indigo blue dye (0.08 mM) catalyzed by MTO:β-CD (1.0:2.0 mM) in the presence of NaOH (0.01 M), at 25 °C, in the presence of different concentration of H_2O_2, at 600 nm. [H_2O_2]/mM: (*a*) 10, (*b*) 20, (*c*) 30, (*d*) 40, (*e*) 50, (*f*) 100
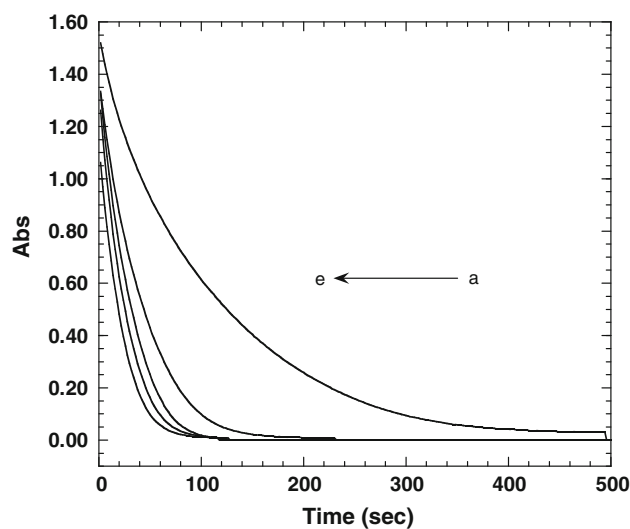

Fig. 6 Variation of absorbance with time for 1st oxidation step of indigo blue dye (0.08 mM) catalyzed by MTO:β-CD (1.0:2.0 mM) in the presence of NaOH (0.01 M), at 25 °C, in the presence of different concentration of H_2O_2, at 600 nm. [H_2O_2]/mM: (*a*) 1.0, (*b*) 2.0, (*c*) 4.0, (*d*) 7.0, (*e*) 10.0

Table 3 Initial rate values of oxidation reactions of indigo blue dye catalyzed by MTO/β-CD (1:2 molar ratios) at different concentrations of H_2O_2

[H_2O_2] (mM)	Initial rate of oxidation of the first injection of indigo blue (M/s, 10^{-8})
1.0	55
2.0	148
4.0	197
7.0	253
10.0	303
20.0	175
30.0	135
40.0	130
50.0	102
100.0	64

[NaOH] = 0.01 M

comparable activity. However, one of the most important discoveries in this study is that they differ in their reactivity in the presence of β-cyclodextrin. When the reaction was studied under a condition that involves only the active intermediate **A** (at low concentration of [H_2O_2], ≤10 mM), the values of rate constants k_1, k_{-1}, k_2, and the equilibrium constant K_1 for the reaction (Scheme 5) were calculated using the corresponding initial rate values in Table 3. These values were calculated using the following derived rate law for this catalytic system:
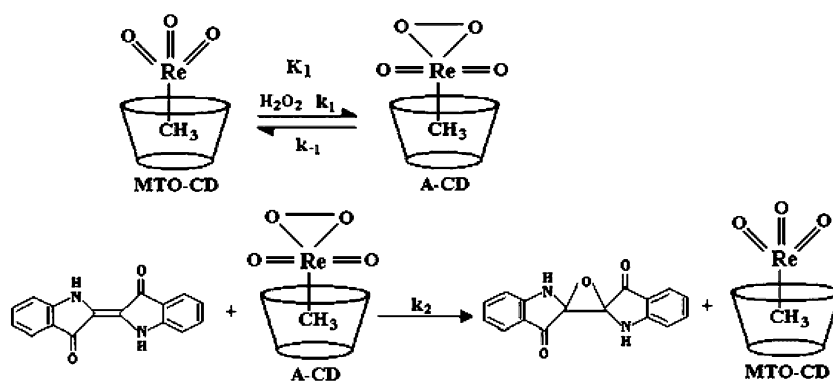
$$\text{Initial rate} = k_1 k_2 \,[H_2O_2]\, [\text{MTO}/\beta - \text{CD}]_T\, [\text{IB}]/(k_{-1} + k_1\, [H_2O_2] + k_2\, [\text{IB}]) \tag{1}$$

where [MTO/β-CD]$_T$ is the total concentration of the complex, [IB] is the concentration of indigo blue dye. It is worth to mention that Eq. 1 was derived using steady-state approximation method.

By fitting the experimental data of initial rates at different concentrations of H_2O_2 using Eq. 1, the following values for rate constants (in unit M/s) and equilibrium constant were obtained: $k_1 = 10.0 \pm 2.0$ M^{-1} s^{-1}, $k_{-1} = 0.032 \pm 0.007$ M^{-1} s^{-1}, $k_2 = 70 \pm 2.0$ M^{-1} s^{-1}, and $K_1 = 312.5$.

It was found that the monoperoxide, **A**, is more reactive than diperoxide, **B**, in the MTO/β-CD system. Looking at the data summarized in Table 3, we can conclude that the highest rate is obtained at 10 mM of H_2O_2, which represents the concentration at which the maximum amount of the monoperoxide, **A**, exists. At higher concentrations, the percent of the diperoxide, **B**, is increased and the rate of reaction is decreased. Indeed, we have demonstrated that in oxidations of Indigo blue, monoperoxide, **A**, somewhat faster than the diperoxide, **B**, same as obtained by Espenson and co-workers [31] in the epoxidation of olefins.

[2, 31], it was observed that increasing the concentration of H_2O_2 decreases the reaction rate. The best reaction rate was obtained at 10 mM H_2O_2 as an optimum concentration (Figs. 5, 6). The initial rate values of indigo blue oxidation reaction catalyzed by MTO/β-CD catalytic system at different concentrations of H_2O_2 were summarized in Table 3.

Hydrogen peroxide is activated by MTO through the monoperoxide (**A**) and the diperoxide (**B**) active intermediates. In aqueous solution, both active intermediates have

Scheme 5 Oxidation of indigo blue dyes by MTO/β-CD catalytic system

Effect of temperature on reactivity and stability of MTO/β-CD

Most chemical reactions proceed at a higher rate with a larger conversion when those reactions are carried out at higher temperatures. In our system, there are many reaction that are accelerated by temperature, such as the reaction of H_2O_2 with MTO/β-CD, the reaction of the peroxo complexes with indigo blue, and the reaction of H_2O_2 with indigo blue, which are all desired reactions. In the other hand, there are some other undesired reactions which are also accelerated by temperature, such as the decomposition reaction of MTO. Therefore, the reactivity and stability of MTO/β-CD was examined at different temperatures ranging from 15 to 70 °C. When the temperature was increased until reached 50 °C, an obvious improvement in the reactivity was observed at the beginning and at the end of the reaction (Fig. 7). At temperatures above 50 °C (60 and 70 °C, not shown in Fig. 7), the reaction was fast at the

beginning, but then a sudden decrease in the reaction rate was observed later, indicating a loss of a large amount of the active catalyst.

Figure 8 shows the variation of ln(k/T) versus 1/T, which has been used to determine the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for the oxidation reaction of indigo with H_2O_2 catalyzed by MTO/β-CD system using Eyring equation [32]:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\neq}}{R} - \left(\frac{\Delta H^{\neq}}{R}\right)\left(\frac{1}{T}\right) \qquad (2)$$

where k is the rate constant, k_B and h are Boltzmann and Planck's constants, respectively.

From Fig. 8 and Eq. 2 the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined and found to be equal 68.0 ± 4.4 kJ/mol and −132.8 ± 14.1 J/mol K, respectively. The positive $\Delta H^{\neq}$ means that energy is needed for the reactants to reach the activated complex. The negative $\Delta S^{\neq}$ means that the activated complex is less disordered and the entropy is
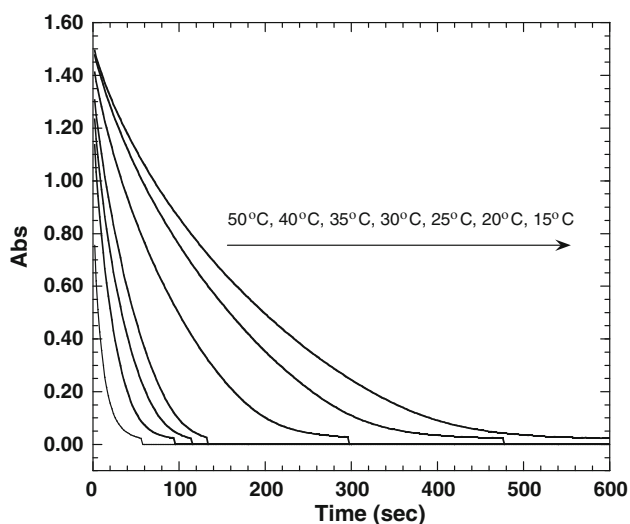

Fig. 7 Variation of absorbance with time for 1st oxidation step of indigo blue dye (0.08 mM) with H_2O_2 (0.1 M) catalyzed by MTO:β-CD (1.0:2.0 mM), in the presence of NaOH (0.01 M), at 600 nm, at different temperatures (15–50 °C)
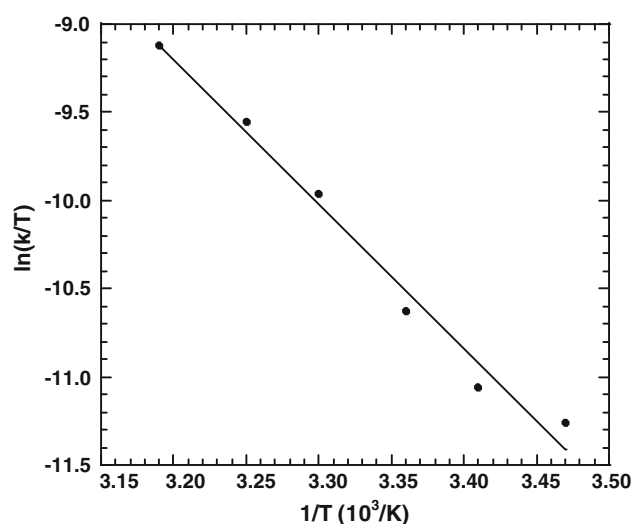

Fig. 8 The dependence of ln(k/T) versus 1/T for oxidation of indigo blue dye (0.08 mM) with H_2O_2 (0.1 M) catalyzed by MTO:β-CD (1.0:2.0 mM), in the presence of NaOH (0.01 M), at 600 nm

decreased reaching the activated complex. Also, a negative value of $\Delta S^{\neq}$ may indicates that the reaction go through the transition state by a bimolecular reaction between the two main reactants molecules ($\mathbf{A}$ and indigo blue). The same has been obtained by Espenson and co-worker [33], a positive $\Delta H^{\neq}$ and a negative $\Delta S^{\neq}$, for other type of catalyzed reaction of hydrogen peroxide. Also, a positive $\Delta H^{\neq}$ and a negative $\Delta S^{\neq}$ values have been obtained for the oxidative degradation of indigo carmine dye with hydrogen peroxide catalyzed with metal complexes [34].

The temperature has great effect on the inclusion process, and the inclusion of MTO in β-cyclodextrin is very sensitive to small changes in the temperature. Generally, the stability of an inclusion complex decreases with increasing temperature. It is expected that the effect of temperature on the stability of the MTO/β-CD complex will be high. This is may be due to an increase of motion of MTO inside the cavity of cyclodextrin by increasing temperature, which will cause the reverse process, exclusion of MTO outside the cavity into the solution. Furthermore, increasing the temperature accelerates the decomposition of MTO/H_2O_2 system.

Conclusions

The stability and reactivity of MTO were studied in the absence and in the presence of β-cyclodextrin in basic solution. The initial rate values for the reaction of indigo dyes with H_2O_2 catalyzed by MTO/β-CD were estimated, and they were used to follow the behavior of the catalyst at the different conditions. The decomposition of MTO in the presence of H_2O_2 is attributed to the nucleophilic attack of OH^- and HO_2^- on the methyl group of MTO. Since the methyl group was a suitable guest, it was successfully included in the β-cyclodextrin cavity, and as a result, it was protected from the attack of the nucleophiles and the decomposition was greatly minimized, and the catalyst became more stable with a very reasonable reactivity in basic media. One of the most important conclusion of this study was that the two active intermediates of MTO (monoperoxide, $\mathbf{A}$ and diperoxide, $\mathbf{B}$) differ in their reactivity in the presence of β-cyclodextrin. It was found that $\mathbf{A}$ is more reactive than $\mathbf{B}$ in the MTO/β-CD system. An obvious improvement in the reactivity of the catalytic system was observed by increasing the temperature up to 50 °C. Effect of temperature on initial rate of the oxidation reaction of indigo blue with H_2O_2 catalyzed by MTO/β-CD system were used to determine the changes of thermodynamic activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$).

References

1. Laszlo, P., Levart, M., Bouhlel, E., Montaufier, M., Singh, G.P., Oyama, S.T., Hightower, J.W. (eds.): Catalytic Selective Oxidation, Chapter 4. American Chemical Society, Washington, DC (1993)
2. Al-Ajlouni, A.M., Espenson, J.H.: Kinetics and mechanism of the epoxidation of alkyl-substituted alkenes by hydrogen peorxide, catalyzed by methylrhenium trioxid. J. Org. Chem. **61**, 3969–3976 (1996)
3. Herrmann, W.A.: Olefins from Aldehydes in Applied Homogeneous Catalysis with Organometallic Compounds, 2nd edn, vol. 3, pp. 1078–1086. Wiley VCH, Weinheim, Germany (2002)
4. Crestini, C., Caponi, M.C., Argyropoulos, D.S., Saladino, R.: Immoblized methyltrioxorhenium (MTO)/H_2O_2 systems for the oxidation of lignin and lignin model compounds. Bioorg. Med. Chem. **14**, 5292–5302 (2006)
5. Saladino, R., Neri, V., Pelliccia, A.R., Mincione, E.: Selective epoxidation of monoterpenes with H_2O_2 and polymer-supported methylrheniumtrioxide systems. Tetrahedron **59**, 7403–7408 (2003)
6. Zhu, Z., Espenson, J.H.: Oxidation of alkynes by hydrogen peroxide catalyzed by methylrhenium trioxide. J. Org. Chem. **60**, 7728–7732 (1995)
7. Adam, W., Herrmann, W.A., Saha-Moller, C.R., Shimizu, M.: Oxidation of methoxybenzenes to p-benzoquinones catalyzed by methyltrioxorhenium(VII). J. Mol. Catal. A Chem. **97**, 15–20 (1995)
8. Bernini, R., Mincione, E., Cortese, M., Aliotta, G., Saladino, R.: A new and efficient Baeyer-Villiger rearrangement of flavanone derivatives by the methyltrioxorhenium/H_2O_2 catalytic system. Tetrahedron Lett. **42**, 5401–5404 (2001)
9. Schuchardt, U., Mandelli, D., Shul'pin, G.B.: Methyltrioxorhenium catalyzed oxidation of saturated and aromatic hydrocarbons by H_2O_2 in air. Tetrahedron Lett. **37**, 6487–6490 (1996)
10. Adam, W., Herrmann, W.A., Lin, J., Saha-Moller, C.R.: Catalytic oxidation of phenols to p-quinones with the hydrogen peroxide and methyltrioxorhenium(VII) system. J. Org. Chem. **59**, 8281–8283 (1994)
11. Soldaini, G., Cardona, F., Goti, A.: Methyltrioxorhenium catalyzed domino epoxidation-nucleophilic ring opening of glycals. Tetrahedron Lett. **44**, 5589–5592 (2003)
12. Ballistreri, F., Chillemi, R., Sciuto, S., Tomaselli, G.A., Toscano, R.M.: Regio and stereoselective oxidations of unsaturated steroidal compounds with H_2O_2 mediated by CH_3ReO_3. Steroids **71**, 565–577 (2006)
13. Zhang, Z., Wang, J.: Recent studies on the reactions of α-diazocarbonyl compounds. Tetrahedron **64**, 6577–6605 (2008)
14. Gonzales, J.M., Distasio Jr, R., Periana, R.A., Goddard III, W.A., Oxgaard, J.: Methylrhenium trioxide revisited: mechanisms for nonredox oxygen insertion in an M-CH_3 bond. J. Am. Chem. Soc. **129**, 15794–15804 (2007)
15. Herrmann, W.A., Fischer, R.W., Marz, D.W.: Methyltrioxorhenium as catalyst for olefin oxidation. Angew. Chem. Int. Ed. Engl. **30**, 1638–1641 (1991)
16. Petrovski, Z., Braga, S.S., Santos, A.M., Rodrigues, S.S., Goncalves, I.S., Pillinger, M., Kuhn, F.E., Romao, C.C.: Synthesis and characterization of the inclusion compound of a ferrocenyl-diimine dioxomolybdenum complex with heptakis-2,3,6-tri-O-methyl-β-cyclodextrin. Inorg. Chim. Acta **358**, 981–988 (2005)
17. Braga, S.S., Gago, S., Seixas, J.D., Valente, A.A., Pillinger, M., Santos, T.M., Goncalves, I.S., Romao, C.C.: β-Cyclodextrin and permethylated β-cyclodextrin inclusion compounds of a cylopentadienyl molybdenum tricarbonyl complex and their use as

cyclooctene epoxidation catalyst precursors. Inorg. Chim. Acta **359**, 4757–4764 (2006)

18. Caron, L., Bricout, H., Tilloy, S., Ponchel, A., Landy, D., Fourmentin, S., Monflier, E.: Molecular recognition between a water-soluble organometallic complex and a β-cyclodextrin: first example of second-sphere coordination adducts possessing a catalytic activity. Adv. Synth. Catal. **346**, 1449–1456 (2004)

19. Fenyvesi, E., Szente, L., Russel, N.R., McNamara, M.: In: Szejtli, J., Osa, T. (eds.) Comprehensive Supramolecular Chemistry, vol. 3, p. 305. Pergamon Press, Oxford, UK (1996)

20. Soldaini, G., Cardona, F., Goti, A.: Catalytic oxidation of imines based on methyltrioxorhenium/urea hyrogen peroxide: a mild and easy chemo- and regioselective entry to nitrones. Org. Lett. **9**, 473–476 (2007)

21. Yin, G., Busch, D.H.: Mechanistic details of facilitate applications of an exceptional catalyst, methyltrioxorhenium: encouraging results from oxygen-18 isotopic probes. Catal. Lett. **130**, 52–55 (2009)

22. Abu-Omar, M.M., Hansen, P.J., Espenson, J.H.: Deactivation of methylrhenium trioxide-peroxide catalysts by diverse and competing pathways. J. Am. Chem. Soc. **118**, 4966–4974 (1996)

23. Matusi, Y., Sunouchi, A., Yamamato, T.: Inhibitory effect of cyclodextrins on the discoloration reaction of an anthocyanide, pelargonidin chloride in acidic media. J. Incl. Phenom. Mol. Recognit. Chem. **32**, 57–67 (1998)

24. Hapiot, F., Tilloy, S., Monflier, E.: Cyclodextrins as supramolecular hosts for organometallic complexes. Chem. Rev. **106**, 767–781 (2006)

25. Harada, A.: Preparation, properties and stereochemical aspects of inclusion compounds of organometallic complexes with cyclodextrins. In: Zanello, P. (ed.) Chain, Clusters, Inclusion Compounds, Paramagnetic Labels and Organic Rings; Stereochemisty

of Organometallic and Inorganic Compounds, vol. 5, pp. 411–455. Elsevier, Amsterdam (1994)

26. Ramusino, M.C., Bartolomei, M., Rufini, L.: H-NMR and UV-spectroscopic study of the inclusion complex formation between pyridoxine and β- and γ-cyclodextrin. J. Incl. Phenom. Mol. Recognit. Chem. **25**, 113–116 (1996)

27. Kanagaraj, K., Pitchumani, K.: Solvent-free multicomponent synthesis of pyranopyrazoles: per-6-amino-β-cyclodextrin as a remarkable catalyst and host. Tetrahedron Lett. **51**, 3312–3316 (2010)

28. Narayana Murthy, S., Madhav, B., Prakash Reddy, V., Nageswar, Y.V.D.: One-pot synthesis of 2-amino-4H-chromen-4-yl phosphonate derivatives using β-cyclodextrin as reusable catalyst in water. Tetrahedron Lett. **51**, 3649–3653 (2010)

29. Cassez, A., Ponchel, A., Bricout, H., Fourmentin, S., Landy, D., Monflier, E.: Eco-efficient catalytic hydrodechlorination of carbon tetrachloride in aqueous cyclodextrin solutions. Catal. Lett. **108**, 209–214 (2006)

30. Szejtli, J.: Introuction and general over view of cyclodextrin chemistry. Chem. Rev. **98**, 1743–1753 (1998)

31. Al-Ajlouni, A.M., Espenson, J.H.: Epoxidation of styrenes by hydrogen peroxide as catalyzed by methylrhenium trioxide. J. Am. Chem. Soc. **117**, 9243–9250 (1995)

32. Eyring, H.: The activated complex in chemical reactions. J. Chem. Phys. **3**, 107–115 (1935)

33. Al-Ajlouni, A.M., Espenson, J.H., Bakac, A.: Reaction of hydrogen peroxide with the oxochromium(IV) ion by hydride transfer. Inorg. Chem. **32**, 3162–3165 (1993)

34. Gemeay, A.H., Mansour, I.A., El-Sharkawy, R.G., Zaki, A.B.: Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine. J. Mol. Catal. A Chem. **193**, 109–120 (2003)