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Effect of β-cyclodextrin on intra and intermolecular Michael addition of some catechol derivatives

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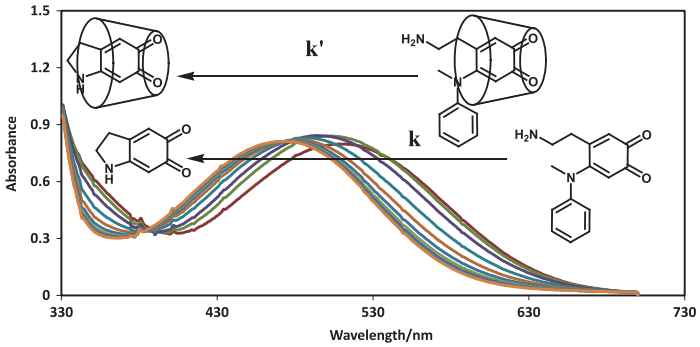
HIGHLIGHTS

- Oxidation of catecholamines were studied in the presence of N-methylaniline.
- Interplay between inter and intramolecular reactions of catecholamines were observed.
- Substituent effect on the absorption band of quinonic products were observed.
- Effect of β-cyclodextrin on the reaction were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

The oxidation reactions of catechol, dopamine and epinephrine have been studied in the absence and presence of N-methylaniline by UV–Vis. Spectrophotometry. A variety of reaction pathways (inter and intramolecular reactions) that followed by this oxidation have been observed depending on the nature of catechol derivatives. The observed homogeneous rate constants of the reactions were estimated by fitting the absorption time profiles for each reaction. The effect of β-cyclodextrin and its inclusion complex has also been studied on the chosen reactions. The formation constants of the complexes of catechol, dopamine and epinephrine with β-cyclodextrin as well as the rate constants of the reactions of free and complexed forms have been obtained by fitting the absorption-time spectra to a proposed kinetic-equilibrium model.

Introduction

Catechol (CA) was first isolated more than 180 years ago by Reinsch through the distilling catechin [1] and nowadays is known as a basic organic compound. It mainly used as precursor of pesticides, flavors and fragrance. CA structure exist also in a variety of naturally occurring polyphenolic compounds as well as neurotransmitters [2,3]. CA and its natural derivatives exist widely in higher plants such as fruits, vegetables, green tea and tobacco. Considering this biological importance CA and its derivatives have been widely studied [4–7]. Moreover catecholamines with a catechol skeleton in their structure are biochemically significant hormones/neurotransmitters. Dopamine (DP) is the most important neurotransmitter and its hydrochloride salt is being used in the treatment of acute congestive failure and renal failure [8]. Epinephrine (EP) or adrenaline is the other most well-known catecholamine which has many functions in the human body; regulating of heart rate, blood vessel and air passage diameters as hormone and neurotransmitter [9].

Upon exposure to many oxidizing agent even the air oxygen; the CA and its derivatives are oxidized to their relative conjugated

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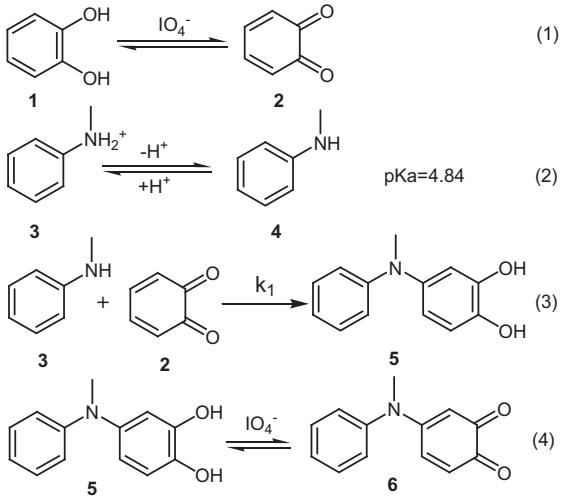
and colored *o*-quinone derivatives. The *o*-quinones as electron-deficient and reactive species undergo some electrophilic reactions [10]. Several studies have reported on the reactivity and reactions of *o*-quinones which have been derived by chemical or electrochemical oxidation of catechols. For example the cyclization of catecholamines via nucleophilic addition of their side chain amine groups is one of the interesting examples of these reactions [11]. CA oxidation that followed by some desired reactions has been utilized as a successful protocol for the derivatization of CA containing molecules and synthesis of more new catechol derivatives [12].

On the other hand, cyclodextrins (CDs) are torus-like macro-rings made from glucopyranose units. They are able to form inclusion complexes with a wide variety of guest molecules [13]. The interaction of solutes with β-cyclodextrin (β-CD) leads to apparent changes in their both equilibrium and kinetic properties [14]. The aim of this research is the oxidation of CA, DP and EP in the presence of N-methylaniline (NM) as a nucleophile and the study of the interplay between inter and intramolecular Michael addition. Moreover the effect of β-CD on the kinetic and patterns of these reactions will be studied.



Scheme 1.

Experimental

Reagents

Catechol, dopamine, epinephrine, N-methylaniline and β-cyclodextrin were purchased from Fluka and were used without further purification. Sodium periodate, sodium acetate, acetic acid, hydrochloric acid, sodium dihydrogen phosphate, disodium hydrogen phosphate and phosphoric acid were reagent-grade materials, from E. Merck. The stock solutions of, CA, DP, EP and NM were prepared fresh, daily by dissolving them in distilled water. The buffered solutions were prepared based on Kolthoff tables, and the concentration of the prepared buffers was 0.15 M [15]. The kinetic experiment was initiated by addition of aliquot amount of stock solution of sodium periodate to the CA, DP and EP solutions with desired pH and β-CD concentrations in a 5 ml volumetric flask. All of the solutions were thermostated at 25 °C before mixing. Measurements were also performed at this temperature. The reaction mixture was shaken and transferred to the spectrophotometer quartz cell immediately. The cell placed in cell holder and reaction monitored by full spectral scan with time. The first spectrum recorded 10 s after mixing for each reaction.

Apparatus

Absorption spectra were obtained with a Scinco UV–Vis. spectrophotometer S2100. In each experiment, the sample placed in a 1 mm path length quartz cells, and the measurements were performed at 25 °C. All of the calculations were performed in MATLAB 7.5 (Math Works, Cochituate Place, MA).

Results and discussion

Kinetic study of the reactions

As the base and model molecule, chemical oxidation of CA has been studied in the absence and presence of NM initially. Fig. 1I, curve a, shows the UV–Vis. spectrum of CA in the presence of periodate (IO_4^-) in acetate buffer solution (pH = 4). In the presence of IO_4^-, as a strong oxidizing agent, the oxidation reaction of CA to its corresponding *o*-quinone took place very fast [16] and an absorption band with the λ_{max} at 390 nm appeared immediately. In the presence of NM and IO_4^-, a new absorption band appeared at 520 nm and reached to its maximum value in 1 min (Fig. 1I, curves b–n). The observed changes are in good agreement with the reaction of NM to *o*-quinone via an intermolecular Michael addition to produce the desired catechol derivative. The reaction product which believed to be also a catechol derivative underwent rapid oxidation with IO_4^- to produce the conjugated and colored final product. The aqueous solution of CA, NM and IO_4^- did not show any absorption at the wavelength region more than 330 nm (Fig. 1I, curves o–q).

Fig. 1II, shows the UV–Vis. spectra of CA in the presence of IO_4^- and NM at pH = 3; the increase in the height of absorption band with λ_{max} 520 nm took place more slowly than pH 4. This pH

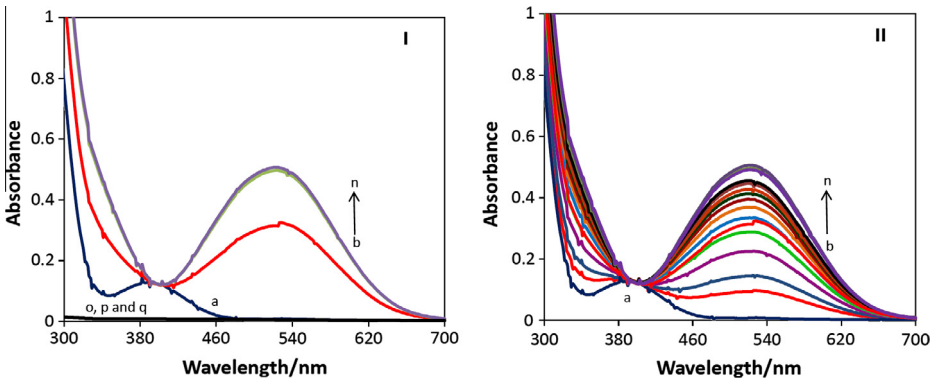


Fig. 1. Absorption spectra for 0.5 mM CA in the presence of 1.5 mM IO_4^- (a) in the absence (b) to (n) in the presence of 0.5 mM NM (I) pH = 4 and (II) pH = 3, interval times from (b) to (n) are 30 s, the absorption spectra of IO_4^-, CA and NM (o) to (q) respectively.

dependence proves that the rate determining step of the overall reaction is the Michael addition reaction. Scheme 1 shows the most probable mechanism for the reaction of CA and NM in the presence of IO_4^-.

The observed considerable Bathochromic shift (130 nm) during the reaction is due to the wider conjugated system of final product (6) rather than the parent *o*-quinone structure (2).

Oxidation of DP has been also performed in the same condition as CA. Fig. 2I, shows that an absorption band with the λ_{max} at 390 nm appeared immediately after mixing of the reagents at pH = 4. It is also related to rapid oxidation of DP to corresponding *o*-quinone as well. Monitoring of the reaction over time showed that new absorption bands appeared (λ_{max} 458 nm) and its height increased with a relatively slow rate. This absorbance change is due to the reaction of side chain amine group of DP with its *o*-quinone moiety via an intramolecular Michael addition [6,11]. The product of this reaction has also a catechol ring, therefore its formation followed by a rapid oxidation by IO_4^- to produce the absorptive final product (Scheme 2). Due to the resonance electron-donating property of the substituted amine group; a bathochromic shift (68 nm) in absorption band of this product (11) is also observed, but the shift is less than those observed for **6**.

The absorption-time of DP and NM in the presence of IO_4^- are shown in Fig. 2II. At the initial time *o*-quinone derivative of DP showed the absorption band with λ_{max} of 390 nm. Upon initiation of the reaction, this absorption peak disappeared whereas an absorption band at 520 nm appeared and its height increased with time up to 2 min.

Thereafter, the height of the peak with λ_{max} of 520 nm decreased slightly and spectral band position shifted to shorter wavelengths. Astonishingly, at the end of the reaction, one peak with λ_{max} of 458 nm remained that its position and half-wave are exactly matched with the λ_{max} of the product of intramolecular cyclization of DP. Based on the above changes; Scheme 2 is proposed for the oxidation of DP in the absence and presence of NM. Based on the proposed mechanism and the observed absorbance with λ_{max} 390, 520 and 458 nm are related to *o*-quinone derivatives of DP (8), the oxidized product of intermolecular (13) and intramolecular reactions (11) respectively.

NM as an aryl-amine has very weak basic character, $pK_b = 9.16$ [17]. At the pH value of 4.5; 68% of NM molecules are in deprotonated form whereas the side chain amine group of DP is fully protonated with good estimation. Therefore the dominant reaction is nucleophilic addition of NM (4) to **8** that produces **13** as the kinetic product. But this product is not the final product, the partially deprotonation of side chain amine group of DP and presence of the equilibrium cause to cyclization reaction and formation of **11** as the final or thermodynamic product. Unfortunately the isolation of the proposed products (11 and 13) and their characterization by spectrophotometric techniques was not possible. However, the electro-active character of products and their different half-wave potentials made it possible to utilize the electrochemical techniques for obtaining further evidences for proposed mechanism. Fig. 3 curves (a–h) show the Differential Pulse Voltammograms (DPV) of 1.0 mM solution of DP and NM in the presence of 3.0 mM IO_4^- those recorded over time.

After the mixing of DP, NM and IO_4^- one cathodic peak appeared in the DPV of solution. The potential of this peak is in good agreement with those obtained for the oxidation of CA in the presence of NM [18]. At longer time, parallel to consecutive decrease of this cathodic peak, a new cathodic peak appeared at more negative potentials and its height increased. The half-wave potential of this peak is exactly same as the previously reported potential for the product of cyclization of DP [11].

Study of the oxidation of EP at the same condition showed an immediate appearance of the absorption band of cyclization product (λ_{max} 482 nm). It clearly shows that the cyclization of EP took place very fast which may be due to the presence of methyl group that enhance the nucleophilicity of amine group [19]. The cyclization reaction of EP takes place very fast at all of the studied pH values, 3–8, and the kinetic study of the reaction is not possible at this pH range. Moreover the absorption changes that followed by oxidation of EP in the presence of NM is exactly same as its absence. It demonstrates that all of the produced oxidized intermediate (*o*-quinone of EP) was consumed completely by the cyclization reaction and NM could not undergo the competitive reaction with side chain amine group of EP. Monitoring of the reaction during longer time periods showed the decrease of absorption due to the degradation of the proposed product (19) (see Fig. 4).

The most probable degradation reaction is the addition of water molecules to the oxidized product of cyclization reaction which is also a quinone derivative [9]. The proposed mechanism for the oxidation of EP is shown in Scheme 3, this mechanism can be considered as the main route in the absence and even in the presence of NM.

Effect of β-CD

As demonstrated above; oxidation of these catechol derivatives followed by a wide variety of chemical reactions. The other aim of this paper was the study of β-CD effect on each reaction pattern. Fig. 5 shows the absorption time profile of CA oxidation in the

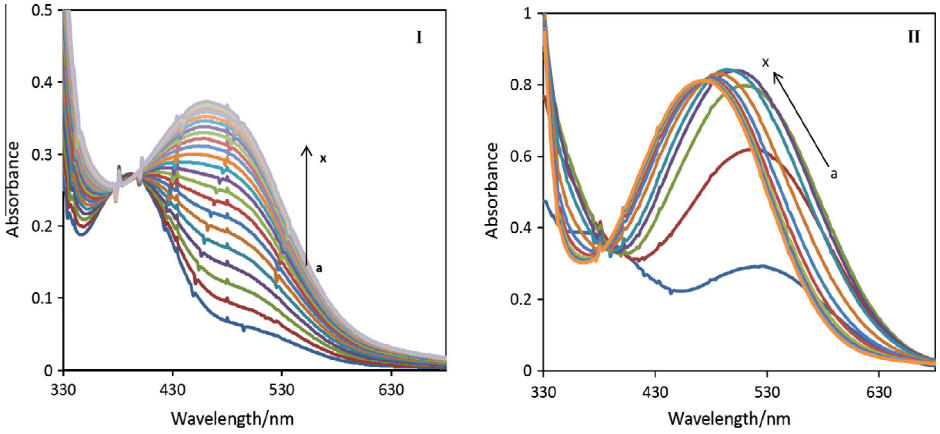
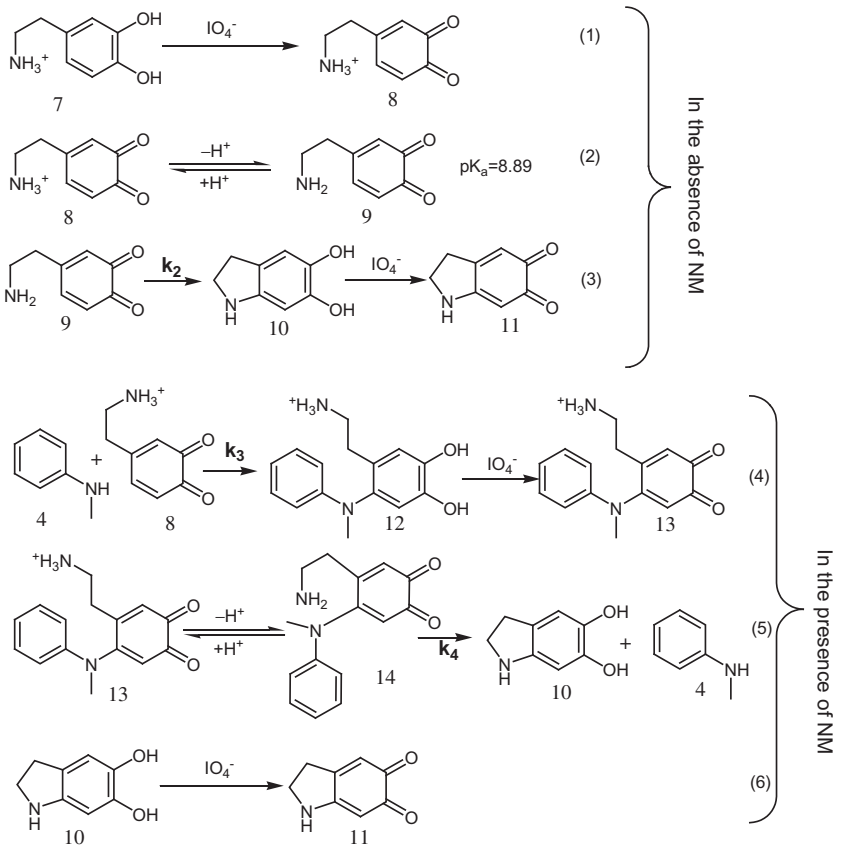


Fig. 2. Absorption spectra for 0.5 mM DP in the presence of 1.5 mM IO_4^- (I) in the absence and (II) in the presence of 0.5 mM NM at pH 4.5, interval times from (a) to (x) are 30 s.



Scheme 2.

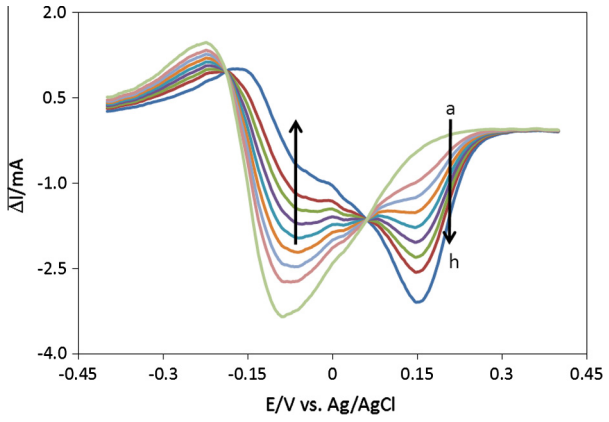


Fig. 3. Differential Pulse Voltammograms of 1.0 mM DP and NM in the presence of 3.0 mM IO_4^- at pH = 4, interval times from (a) to (h) are 120 s.

presence of NM and β-CD at the λ_{max} of **6** (520 nm). The absorption wavelengths and absorption coefficient of the products did not change considerably in the presence of β-CD (Fig. 5 inset).

But comparing the absorption time profile of product with those obtained in the absence of β-CD clearly demonstrates that the overall rate constant of the reaction has been increased in the presence of β-CD. As discussed above the rate determining step of the mechanism is the Michael addition reaction (Scheme 1 Eq. (3)) and then it can be claimed that β-CD accelerates this nucleophilic addition. The catalytic effect of the β-CD on this reaction may be due to the hydrogen bonding between carbonyl group of *o*-benzoquinone with hydroxyl groups of β-CD. It causes electron withdrawing from the *o*-quinone ring and enhances its nucleophilic character and accelerates its reaction [20,21]. It also may be due to the better and real hydrogen bonding between the hyroxy group of product of this step and β-CD.

A catalytic effect was also observed for the cyclization reaction of DP in the presence of β-CD and the same reasons can be considered for the catalytic effect of β-CD on it. This catalytic effect has been discussed in more details in our previous paper [20].

The absorption-time spectra of oxidation of DP in the presence of NM show that the rates of both inter and intramolecular reactions affected and enhanced in the presence of β-CD. But the obtaining of a simple absorption-time profile for each reaction

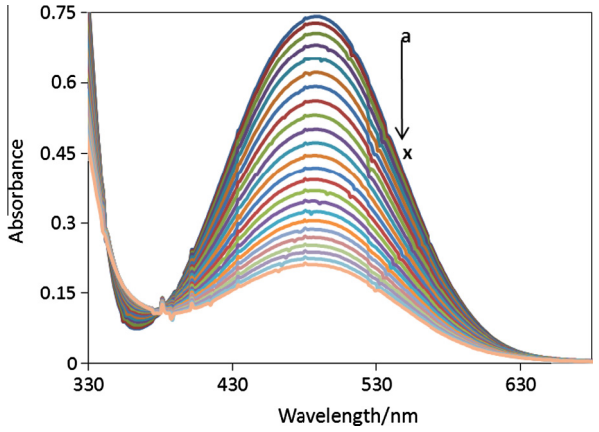
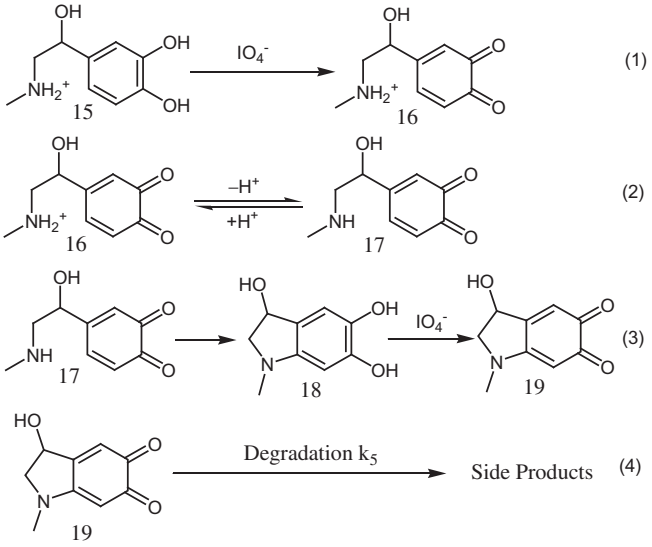


Fig. 4. Absorption spectra for 0.5 mM EP in the presence of 1.5 mM IO_4^- at pH = 4 and interval times from (a) to (x) are 60 s.



Scheme 3.

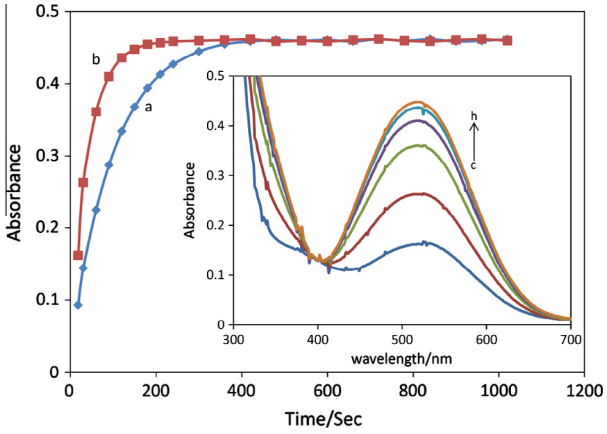


Fig. 5. Absorption-time profiles for 0.5 mM DP and NM in the presence of 1.5 mM periodate (a) in the absence and (b) in the presence of 0.01 M β-CD, inset: (c) to (h) absorbance spectra in the presence of β-CD.

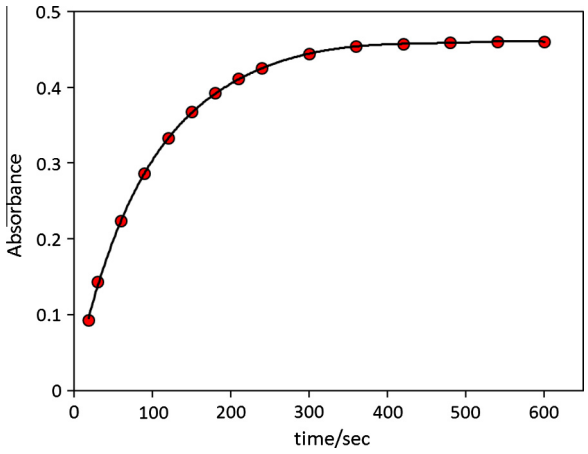


Fig. 7. Experimental (●) and fitted (line) absorption-time profile for 0.5 mM CA and NM in the presence of 1.5 mM IO_4^- at pH 3, wavelength 520 nm.

product was not possible due to the spectral overlaps. More quantitative results will be present after the kinetic evaluation.

Finally the effect of β-CD has been studied on the reaction of EP in the presence of IO_4^-. In the presence of β-CD the rate of cyclization reaction did not show any change, or in better words, the detection of change in reaction rate was not possible using UV–Vis. Spectrophotometry. But the absorption coefficient of the reaction product shows a considerable increase in the presence of β-CD (Fig. 6I) which is a good confirmation for the formation of inclusion complex between EP and β-CD. Moreover there was an interesting and significant effect on degradation reaction of its final quinonic product. Comparing the absorption-time profile at the λ_{max} of reaction product in the absence and presence of β-CD demonstrate that *o*-quinone of EP (19) has found considerable stability in the presence of β-CD (Fig. 6II).

One of the best well-known and effective driving forces of formation of inclusion complex between β-CD and organic molecules is the hydrophobic nature of β-CD interior and affinity of organic molecules for formation of inclusion complex and expulsion of water from the β-CD cavity. In better word during the complex formation, the existing water molecules inside the β-CD cavity are replaced by the desired guest molecule. The hosted organic molecule can be also isolated from the water environment due to formation of inclusion complex. Therefore, the relative stability of **6** may be related to its isolation and protection from the reactive aqueous media by β-CD.

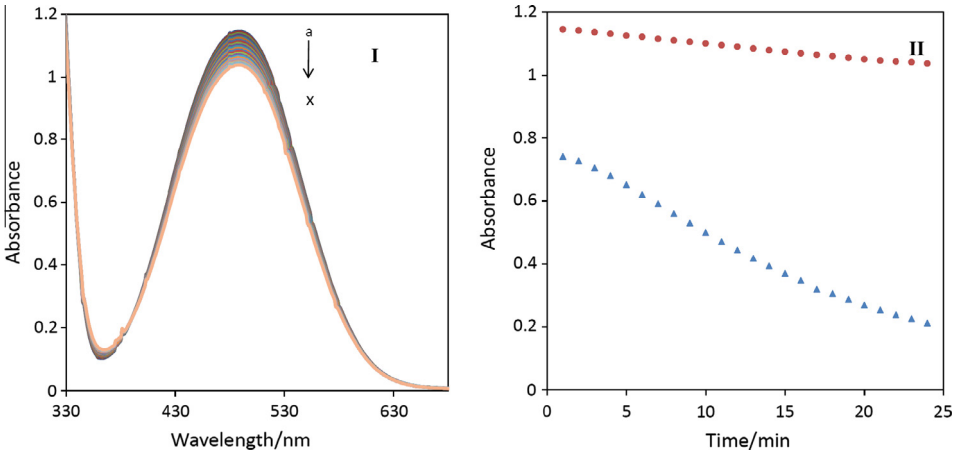


Fig. 6. (I) Absorption spectra for 0.5 mM EP in the presence of 1.5 mM IO_4^- and 0.01 M β-CD at pH = 4, interval times from (a) to (x) are 60 s, (II) absorption-time profile in the absence (▲) and presence (●) of β-CD, wavelength 482 nm.

Kinetic evaluation

There are two possible situations for obtaining the quantitative study of the reactions and obtaining their related rate constants. The first situation is in the absence of β-CD and the other one is in its presence. Even in the absence of β-CD, the rate determining steps of reaction are coupled with a fast acid base reaction of amines (as nucleophile) and presence of both equilibrium and kinetic reactions follow complicated reaction pathways. For example consumption of NM by the Michael addition reaction (Scheme 1 Eq. (3)) shifts its fast acid–base equilibrium (Scheme 1 Eq. (2)) to the production of NM. Then, the kinetic profiles were obtained by numerical integration using MATLAB's solver, ode45, which is the standard Runge–Kutta algorithm [22]. The values of the rate constants as nonlinear parameters were calculated by fitting the experimental kinetic profile using the Newton–Gauss algorithm. This consists of finding a set of parameters (rate constants) for which the sum of squares over all of the elements of the error matrix (i.e., the differences between the elements of the model and the experimental data) is minimal [23]. The result of this procedure is a set of nonlinear parameters (the best obtained rate constants) which define the concentration profiles of absorptive species. Fig. 7 shows the experimental and fitted absorption-time profile (in the λ_{max} of product) related to the analysis of the data of the oxidation of CA in the presence of NM.

As seen in Fig. 7, the calculated absorption-time profile is consistent with the absorbance change in the collected data. The same method has also been applied for the degradation reaction of the product of oxidation and cyclization of EP (19). However for the reaction of DP in the presence of NM; there was no selective wavelength for the monitoring of the reaction. Then obtaining an absorption time profile and its analysis was not possible. Moreover, there are two consecutive reactions as the rate determining steps and deriving the rate constants of reactions needs more than single wavelength absorption time profile. Therefore the whole absorption time spectra have been used for the quantitative study of the reaction. A two-way data matrix Y can be formed by measuring absorbance under different wavelengths at a series of chosen times (kinetic spectra). This matrix can be decomposed into the product of matrix C, column wise, containing the concentration profiles of the absorbing species and matrix A, row wise, containing their molar absorptivities. Matrix E is the residual.

$$Y = CA + E$$

Purpose of the fitting; consists of finding a set of parameters for which the sum over all the squares, ssq, over all the elements of the error matrix, E, is minimal. The kinetic profiles were obtained same as the above mentioned method and the molar absorptivities of the **13** and **11** were known and have been used during the fitting process. Fig. 8I illustrates the concentration profiles of the absorptive components and kinetic-spectra that obtained during the fitting process for the reaction of DP in the presence of NM. Comparing the simulated (Fig. 8II) and experimental (Fig. 2II) kinetic spectra prove that there is a good consistency between them.

Table 1
Observed rate constant of the desired reactions in the absence of β-CD.

Reagent	Reaction (rate constant)	Rate constant
Catechol	Intermolecular addition of NM (k_1)	0.81 M^{-1} s^{-1}
Dopamine	Intramolecular cyclization (k_2)	11.5 s^{-1}
Dopamine	Intermolecular addition of NM (k_3)	0.65 M^{-1} s^{-1}
Dopamine	Intramolecular cyclization of intermediate (k_4)	3.91 s^{-1}
Epinephrine	Degradation of cyclization product (k_5)	0.07 s^{-1}

Table 1 shows the rate determining step of each reaction(s) and obtained rate constants for it (them).

As the final aim of the paper, the quantitative studies have been performed in the presence of β-CD. As shown above, presence of β-CD can have changed the rate of reactions due to formation of inclusion complex. Formation of inclusion complex as an equilibrium reaction and difference in the rate of reaction for complexed and free forms can be considered again as a "kinetic-equilibrium" model. For example the following model (Scheme 4) can be considered for the cyclization reaction of oxidized form of DP in the presence of β-CD. Based on the proposed reaction mechanism and difference in the rate of reactions, the observed reaction rates are roughly proportional to the equilibrium concentration of free and complex forms.

Consumption of each reactant shifts the equilibriums to counteract the imposed changes. The rate constants of the desired reactions and the formation constant of the reactants that involved in these reactions have been obtained based on the proposed model. The observed rate constants of the chemical reactions in the absence of β-CD entered as known parameters during this step of fitting process. The obtained values are listed in Table 2, the small lack of fits, they were less than 3% for all of the fitting processes are also good evidences for the validity of the underlying models.

As demonstrated in Table 2 and comparing those appeared in Table 1; it can be concluded that β-CD has a catalytic effect on Michael addition of the *o*-quinones and their conversion to catechol derivatives. It has been demonstrated that the difference in hydrogen bond formation of reactants and product is an important deriving force for this effect. The catalytic effect is more significant for the intramolecular reactions. It seems that the cavity of β-CD as a

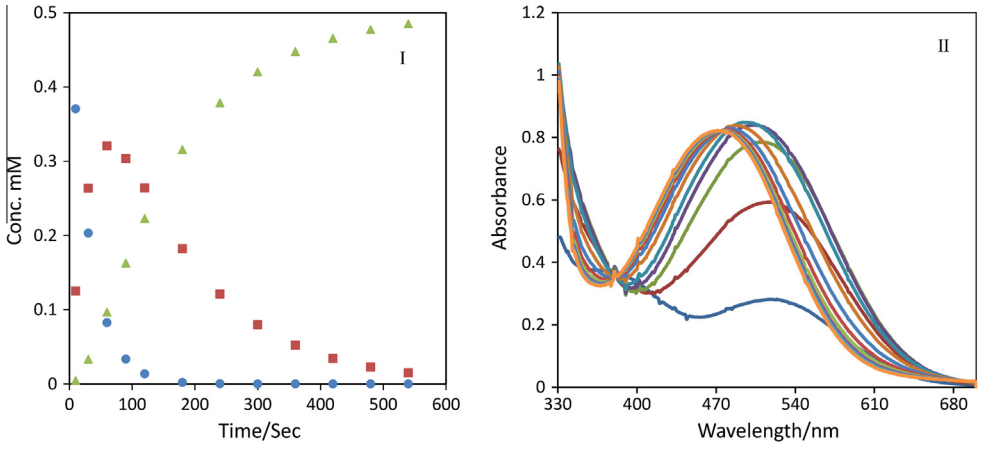
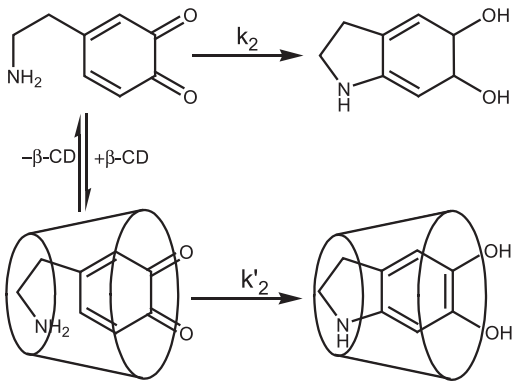


Fig. 8. (I) Simulated absorption spectra of DP and NM in the presence of IO_4^- and concentration profiles of absorptive components **8** (●), **14** (■) and **11**(▲).



Scheme 4.

Table 2
Observed rate constant of the desired reactions in the presence of β-CD.

Reagent	Reaction (rate constant)	Rate constant
Catechol	Intermolecular addition of NM (k'_1)	1.12 M^{-1} s^{-1}
Dopamine	Intramolecular cyclization (k'_2)	14.6 s^{-1}
Dopamine	Intermolecular addition of NM (k'_3)	0.84 M^{-1} s^{-1}
Dopamine	Intramolecular cyclization of intermediate (k'_4)	5.32 s^{-1}
Epinephrine	Degradation of cyclization product (k'_5)	0.009 s^{-1}

"molecular reactor" provide a better media for the intramolecular reaction in which both reactive site located on one included molecule. Among the whole inter and intramolecular reactions which have studied here; the degradation of the product of EP oxidation have been slow down considerably in the presence of β-CD. It may be due to this fact that encapsulated guest in the hydrophobe cavity of β-CD is isolated from the aqueous media and protected from the nucleophilic addition of water molecules.

Conclusion

Spectrophotometric study of oxidation of CA, DP and EP has been performed in the presence IO_4^- as strong oxidizing agent and NM as nucleophile. In the presence of strong oxidizing agents such as IO_4^-, the oxidation reaction of the chosen catechol derivatives to their corresponding *o*-quinones took place very fast. The in situ generation of *o*-quinone and three patterns of reactivities were observed depending on the structure of catechol derivatives. Oxidation of CA in the presence of NM followed only by an intermolecular nucleophilic addition. Two steps consecutive inter and intramolecular reactions were observed for oxidation of DP in the presence of NM. An intramolecular cyclization reaction were detected for EP as the main route in the absence and presence of NM that followed by the degradation of final product with relatively slow rate. The effect of β-CD has been studied on all of the observed reaction mechanism. Overally, conversion of *o*-quinone to the desired catechol derivatives, through nucleophilic addition, accelerated in the presence of β-CD whereas, the degradation reaction of the products by water molecules slow-down in its presence. In conclusion, the kinetic-spectrophotometric method has been proposed for the study of the weak and reversible complexation β-CD and the effect of inclusion on various reaction pathways.**Acknowledgements**This work was supported by Iran National Science Foundation (INSF).

Acknowledgements

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