=○ **Full Paper**

Mechanistic Studies On The Oxidative Polymerization Of 8-Hydroxyquinoline And Diiodohydroxyquinoline In Anti-Diarrhea Tablets

⊠ *Corresponding Author*

Saleh A.Ahmed
Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516, (EGYPT)
E-mail: saleh_63@hotmail.com

Co-Author

Seddique M.Ahmed
Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516, (EGYPT)

ABSTRACT

Mechanistic studies of the oxidative polymerization reaction of 8-hydroxyquinoline(HQ) were studied experimentally using spectrophotometric technique. Molecular mechanics(MM+) calculations showed that the potential energy(PE) and optimum molecular geometric(OMG) energies(kcal/mol) of the proposed structures formed during polymerization process are very low. These calculations supported the proposed mechanism. The oxidation constant(K_{ox}) of the anionic form(HQ-NaOH) is about twice greater than the protonated form(HQ-H$_2$SO$_4$). Molecular mechanics(MM+) calculations showed that the PE (kcal/mol) of the HQ in the anionic(HQ-NaOH) is about two times greater than the PE in the protonated(HQ-HCl) forms. The proposed procedure was followed successfully for the oxidation of HQ in sterptoquin(SQ) (anti-diarrhea) tablets. The oxidation constant(K_{ox}) of HQ in SQ was found also to be lower than the K_{ox} in synthetic(HQ) solution. Kinetic parameters of the oxidative polymerization of the anionic form of HQ(HQ-NaOH) at different concentration were deduced employing a computer-oriented kinetic analysis of the absorbance(A) at 610nm against the time(t/sec) data. The results obtained indicate that the rate controlling process is governed by the Ginstling-Brounshetin-equation three-dimensional diffusion(D4). It is interesting to note from these calculations that the k value calculated by D4 is about eleven, twenty four, and one hindered five times of magnitude lower than the k values obtained by applying first-(F1), second-(F2), and third-order(F3) kinetics under the same conditions. Activation parameters for the rate of oxidation process of HQ have been computed and discussed.   © 2007 Trade Science Inc. - INDIA

Full Paper

INTRODUCTION

The significance of polyhydroxyquinoline(PHQ) in biological systems is widely recognized. It has been reported that the polymers bearing 8-quinolinol have potential applications as antimicrobial surgical materials and ointments for medicinal purposes[1,2]. Moreover, oxidation of some phenols by metal complexes leading to the production of quinones has generated great interest of recent[3-11].

Several authors reviewed the permanganate oxidation of organic compounds and the synthetic applications of permanganate to organic chemistry[12-13].

Recently, we have reported that the electrochemical activity of poly(8-hydroxyquinoline)(PHQ) and its copper ion chelates in different solutions by use of differential pulse polarographic techniques[14]. Also, we have prepared, using several spectroscopic techniques, characterization of the coordination polymers based on PHQ complexed with some metal ion[15].

In the present study, mechanism of the oxidative polymerization process of the cationic and anionic forms of 8-hydroxyquinoline(8-HQ) in synthetic and sterptoquin tablets was investigated practically and theoretically. Activation parameters for the rate of oxidation process of 8-HQ have been computed and discussed. The proposed mechanism was supported by molecular mechanics calculations.

EXPERIMENTAL

Chemicals and solutions

8-HQ was obtained from Aldrich. Chemicals Co.Poly(vinylpyrrolidone)(PVP) K90(PVP; Mwt $=1.2 \times 10^6$) was purchased from Wako chemicals Co. Streptoqin(anti-diarrhea) tablets were purchased from Medical union pharmacy(MUP), Egypt. All other reagents used were of analytical grade or of chemical-pure grade, and double-distilled water was used throughout.

Potassium permanganate solution($KMnO_4$, BDH) was prepared by dissolving the appropriate amount sample in doubly distilled water. This solution was standardized against oxalic acid[13].

Stock solution of 8-hydroxyquinoline(HQ) (Ald-rich) was prepared by dissolving the appropriate amount(10mmol) in sodium or potassium hydroxide solutions(10mmol). The final product [poly(8-hydroxyquinoline) (PHQ)] obtained from the oxidative polymerization of HQ was verified experimentally and supported computationally using molecular mechanics (MM+) calculations in our previous work[14,15].

The streptoquin(SQ) tablets used for the oxidative polymerization of diiodohyroxyquinoline in SQ were prepared in the following way. The contents of five tablets of SQ were weighed and powdered. The resulting powder was then dissolved in NaOH(100 mmol). The solution was filtered and diluted to 100ml in a volumetric flask with distilled water.

Instrumentation

A perkin-Elmer Lambada 35 spectrophotometer with 1.0cm quartz cell(scan speed, 8.0nm s^{-1}) was used for normal(zero-or first derivative, $\Delta\lambda=5$nm) spectrophotometric measurements. A heto thermostat(type HMT 200) was used for the accelerated kinetic studies. Molecular mechanics(MM+) calculations include MM2 and MMP2 force field[14-22] were carried out to calculate the potential and geometrical energies in kcal/mol, and dipole moment (μ) in debye units. The search for a minimum energy of the proposed structures, 3D molecular geometry optimization was obtained, dPE=0.10 Cal., method normal.

Procedure

Ten milliliters of the solution containing, oxidant ($KMnO_4$, 0.5mmol L^{-1}) in strong acid(pH 1.0, adjusted by H_2SO_4) or strong alkaline medium(adjusted by standard NaOH(0.1 mol L^{-1})) were placed in the calibrated flask. The background spectrogram of this solution was recorded. A known concentration of the reactant(8-HQ or SQ) was added to the same cell by means of a micropipette(Voaco, UK). The absorption spectra were recorded against the reagent blank. All measured absorption spectra presented here are after the base line corrections for the blank reagent. A reagent blank was prepared in a similar manner but without analyze. All spectral measurements were carried out at room temperature(24 ± 1^0C), except the temperature dependence studies.

RESULTS AND DISCUSSION

UV-Visible absorption spectra of the oxidative polymerization of HQ

Absorption spectra of the oxidant($KMnO_4$, 0.5 mmol) in strong acidic medium(pH 1.0, adjusted by H_2SO_4) shown in figure 1. This absorbance decrease rapidly with increasing the concentration of 8-hydroxyquinoline(HQ). Good linearity(r~0.984) between the decreases of absorbance(at~525nm) and the concentration of HQ was obtained with low standard deviation(SD) as seen in TABLE 1. The number of electrons for this oxidation/reduction process was calculated and it was found to be around 2.5:1 for the monomer(HQ) to oxidant($KMnO_4$) this result could be explained by the following equation:

$$n(5HQ)+2KMnO_4+5H_2SO_4 \rightarrow PHQ+K_2SO_4+3MnSO_4+8H_2O \quad (1)$$

The lower oxidation constant(K_{ox}) was recorded in neutral medium(TABLE 1), while the higher K_{ox} in H_2SO_4. These observation indicate that the K_{ox} is highly dependent on the strength of the acidity of the medium.

The electronic absorption spectra of oxidant ($KMnO_4$, 0.5 mmol) were scanned(Figure 2) in strong alkaline solution(KOH, 0.1 mol). It was found also, the absorbance at~525 nm decrease rapidly with increasing the concentration of monomer(HQ). The K_{ox} for the anionic form(HQ-NaOH) was found to

TABLE 1: Calibration plot data of absorbance vs. concentration of monomer (HQ), at constant oxidant ($KMnO_4$)

Medium	$K_{ox}(10^3)$	a	r	$SD(10^{-4})$
HQ (Neutral)	1.94	1.445	0.979	5.04
HQ (Acidic, λ = 525 nm)				
HQ-HCl	3.44	1.46	0.996	2.91
HQ-HClO$_4$	4.16	1.37	0.993	2.38
HQ-HNO$_3$	5.32	1.37	0.998	1.85
HQ-H$_3$PO$_4$	5.00	1.32	0.994	1.98
HQ-CH$_3$COOH	2.84	1.45	0.991	3.94
HQ-CSA	4.82	1.25	0.994	2.06
HQ-H$_2$SO$_4$	6.537	1.16	0.971	1.48
HQ (alkaline, λ, 525 nm)				
HQ-NaOH	13.21	1.5	0.982	0.742

be twice times greater than the K_{ox} of the cationic form of HQ(HQ-H_2SO_4)(TABLE 1). Molecular mechanics(MM+) calculations(TABLE 2) showed that the potential energy[PE(kcal/mol] of the HQ in NaOH is about two times greater than the PE in acidic solution(HQ-HCl). From these calculations we can concluded that the anionic form of HQ is highly reactive for polymerization than the cationic form. The increases of the absorbance(green, at~ 610 nm) with increasing the concentration of HQ was observed (Figure 2). This absorption is due to the transformation of permanganate(MnO_4^-) to manganate(MnO_4^{2-}) through a one-electron reduction according to the
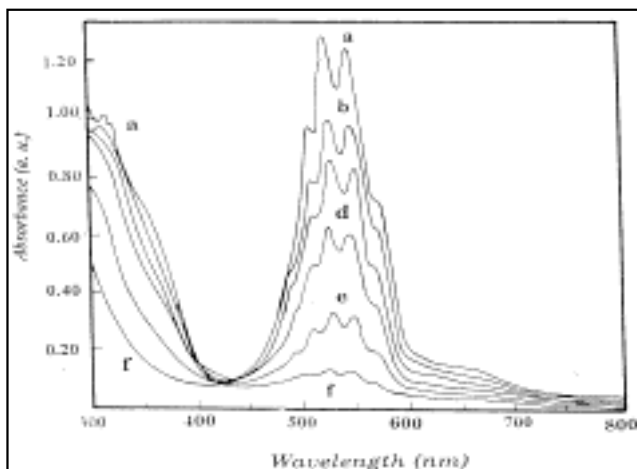

Figure 1: Absorption spectra recorded of the oxidant($KMnO_4$, 0.5 mmol L^{-1}) in strong acid medium(pH 1.0, adjusted by H_2SO_4) during addition of 8-HQ(a-g) as: 0.0, 0.03, 0.05, 0.07, 0.1, 0.15, and 0.20 mmol L^{-1}, respectively
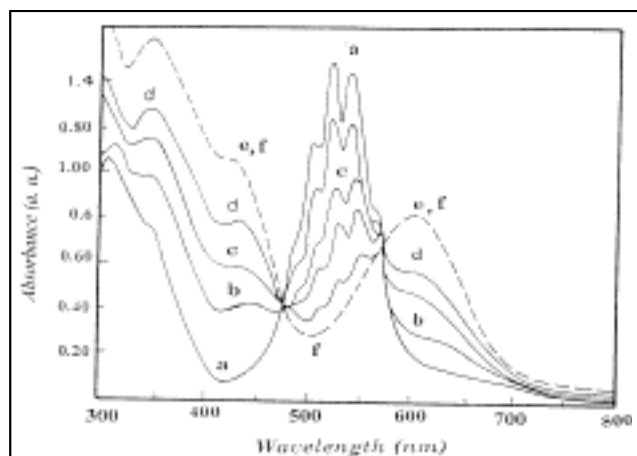

Figure 2: Absorption spectra recorded of the oxidant($KMnO_4$, 0.5 mmol L^{-1}) in strong alkaline medium(NaOH, 0.1 mmol L^{-1}) during different addition of 8-HQ(a-g) as: 0.0, 0.03, 0.05, 0.07, 0.1, 0.15, and 0.20 mmol L^{-1}, respectively

Full Paper

TABLE 2: Optimum molecular geometric(OMG), and potential(PE) energies in kcal/mol and dipole moment(μ) in Debye units of the neutral(HQ), protonated(HQ-HCl) and ionized(HQ-NaOH) forms of HQ

Structure	OMG (kJ mol^{-1})	PE (kJ mol^{-1})	μ (debye)
HQ	-2.80	-5.93	5.85
HQ-HCl	-4.35	-9.07	6.10
HQ-NaOH	-8.86	-18.11	7.53

mechanism illustrated in equation (2):

$$n(2HQ)+2KMnO_4+2KOH \rightarrow PHQ+ 2K_2MnO_4+2H_2O \qquad (2)$$
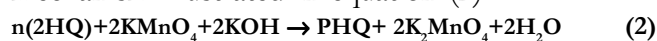
It was reported that, in strong alkaline medium the stable reduction product of permanganate ion (MnO_4^-) is manganate ion(MnO_4^{2-})[23]. The oxidative polymerization mechanism of HQ in strong alkaline (NaOH or KOH, 0.1 mol/l) medium was also supported by MM+ calculations(TABLE 3). Its noticeable from the data presented in TABLE 3 that, the lower energy value of PE substantiated our proposed mechanism(SCHEME 1). The obtained results and the proposed mechanism were found to in a good

TABLE 3: OMG and PE energies in kvcal/mol and ı in Debye units of the possible configuration structures formed during polymerization of HQ. Using MM+ calculations

Matrix	I	II	III	IV	V	VI
OMG	0.68	-1.02	-0.03	-3.39	-3.52	-3.03
PE	0.66	-2.13	-0.64	-7.25	-7.98	-14.15
μ	5.78	10.58	7.08	6.32	6.32	9.52

agreements with our former studies[14,15].

UV-Visible absorption spectra of the polymerization of HQ in SQ tablets

The electronic absorption spectra of the oxidant (KMnO4, 0.5 mmol) were recorded. A prounced decrease of the absorbance at around 525 nm by increasing the concentration of sterptoquin (SQ) in strong acid or alkaline media was observed (TABLE 4). The oxidation constant(K_{ox}) was found to be strongly dependent on the pH medium. Higher value of the oxidation constant was found in strong H_2SO_4 for a series of acids(TABLE 4). The K_{ox} value in
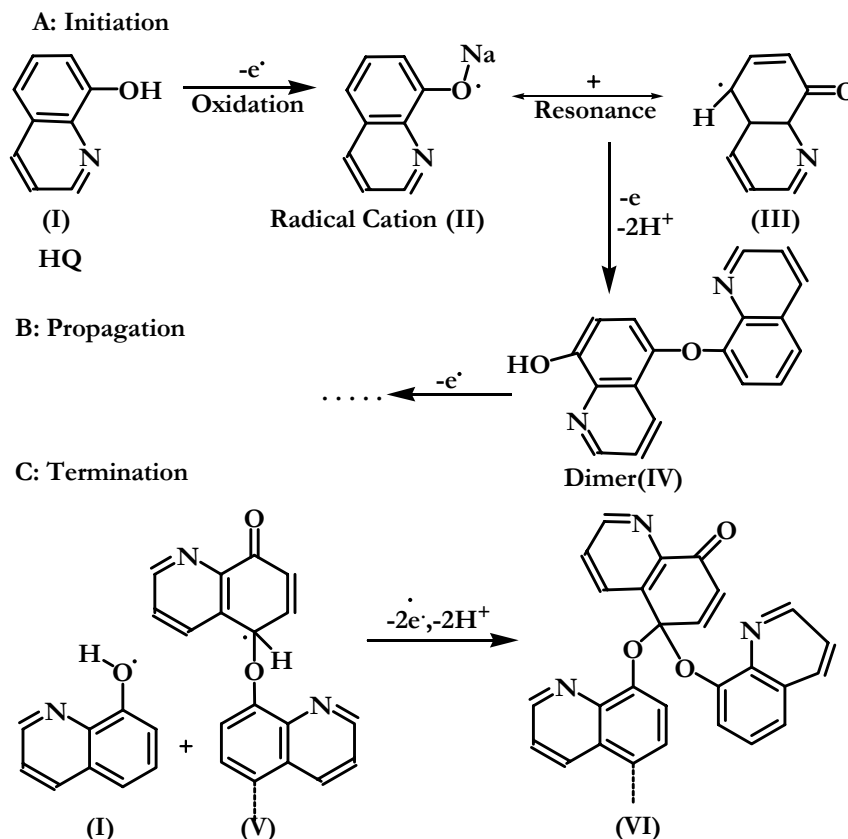
SCHEME 1: Optimum molecular geometric(OMG) possible configuration structures formed during oxidative polymerization of HQ as anionic(HQ-NaOH) form, using MM+ calculations

TABLE 4: Calibration plot data of absorbance vs. concentration of SQ, at constant oxidant(KMnO$_4$)

Medium	$K_{ox}(10^3)$	a	r	SD(10^{-4})
SQ (Neutral)	0.397	1.44	0.943	0.23
SQ (Acidic, λ, 525 nm)				
SQ-HCl	2.96	1.38	0.994	3.35
SQ-HClO$_4$	3.70	1.39	0.984	3.17
SQ-HNO$_3$	3.18	1.41	0.993	2.99
SQ-CSA	1.25	1.37	0.994	7.79
SQ-H$_2$SO$_4$	3.89	1.34	0.998	2.95
SQ (alkaline, λ = 525 nm)				
SQ-NaOH (λ, 525 nm)	6.82	1.31	0.963	3.41
(λ, 605 nm)	(10.95)	(0.16)	(0.989)	(5.06)

strong alkaline is about twice times greater than the K_{ox} in acidic(TABLE 4), revealing again the anionic form of HQ in SQ is also profitable form for polymerization process(TABLE 4). The value of K_{ox} of the polymerization of HQ in real sample(SQ, TABLE 4)) is lower than the K_{ox} in synthetic medium (TABLE 1). This may be attributed to the presence of many additives in streptoquin Tablets.

Kinetics of the oxidative polymerization of HQ in strong alkaline medium

Figure 3 respresents the computer drawing of the absorbance of the oxidant(KMnO$_4$, 0.5 mmol) (green, λ~610 nm), at different addition of HQ in strong alkaline medium(NaOH, 0.1 mol) versus oxidative polymerization time(t/min) by keeping other parameters constant. The rate constant(k/min) is dependent on the oxidative polymerization time(t/min) and so, g(A)=kt. A plot of g(A) against time should thus, gave a straight line if the corrected form of g(A) is used. Analysis of the kinetic data obtained was proceeded by determining which rate equation derived from different models[20,25]. The kinetic analysis was carried out for each set of A and t data according to the variant kinetic equations[16-18]. From these calculations, it was found that the Ginstling-Bronstein equation(D4) gives the best fit of the experimental data, with a correlation coefficient(r) close to unity and a very low standard deviation. The ginstling-bronstein equation(D4) can be expressed as:

$$(1-2A/3)-(1-A)^{2/3} = kt \qquad (3)$$
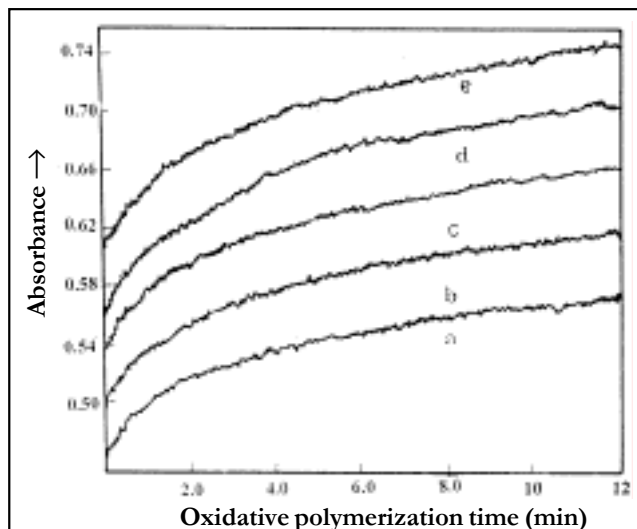
Where A is the absorbance(a. u.), k is the rate

Figure 3: Computer drawing of the absorbance (λ~605 nm) vs. oxidative polymerization time(min), at different addition of HQ(a-e) as: 40, 45, 50, 55, and 60 μmol L^{-1}, respectively, temperature(20^{0}C)

constant(sec^{-1}), and t is the oxidation time(sec). By applying D4 for the oxidation of hydroxyquinoline (HQ)(0.03 mmol) oxidant(KMnO$_4$, 0.5 mmol)(for example). Interestingly, the rate constant k and other statistical parameters were as follows: k=2.039×10^{-5} (s^{-1}); r=0.987; a(initial absorbance at 610 nm)= 0.036; and SD=2.13×10^{-5}.

It is interesting to note from these calculations that the k value calculated by D4 is about eleven, twenty four, and one hindered five times of magnitude lower than thee k values obtained by applying first-(F$_1$), second-(F$_2$), and third-order(F$_3$) kinetics under the same conditions. The same conclusion (TABLE 3) was reached for the oxidation of HQ with other acids.

Activation parameters of the oxidative polymerization of HQ

Rate constants(k/s) for the oxidation of HQ in strong alkaline solution(NaOH, 0.1 mol) were determined at different temperatures(283-323 K) by keeping all other conditions the same. Activation parameters (TABLE 5) for the oxidation of HQ were computed from arrhenius and eyring plots[16-18] of -ln k or -ln k′ against 1/T(K). Good linearity(r > 0.97) between -ln k(Arrhenius plot) or -ln k′/T(Eyring plot) against 1/T(K) for the oxidation of HQ was obtained (Figure 4). The proposed mechanism(SCHEME 1)
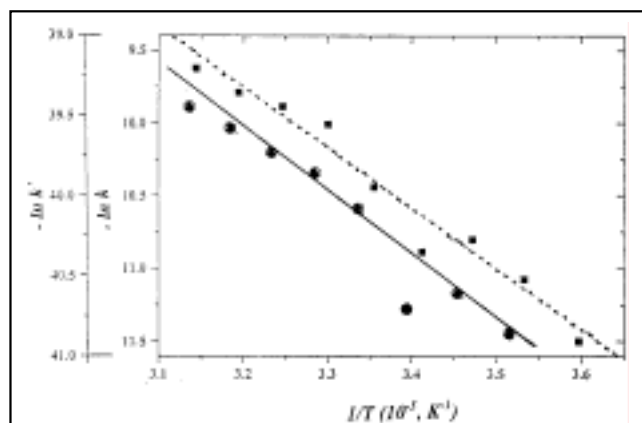
Full Paper

Figure 4: Plot of -ln k(Arrhenius, dashed line) and -ln k′(Eyring, solid line) plots vs. 1/T(K) of the oxidative polymerization of 8-HQ

Figure 5: Plot of $\Delta S^{\#}$ vs. $\Delta H^{\#}$ for the oxidative polymerization of 8-HQ at different concentrations(TABLE 5)

for the oxidative polymerization of HQ is also supported by the moderate values of the energy of activation(TABLE 5).

Plot of $\Delta H^{\#}$ against $\Delta S^{\#}$ for the different concentration from HQ gave a good linearity(r~0.991) as shown in figure 5. The presented data suggests existence of a compensation or isokinetic effect. In addition, there are several others that have been proposed to check the existence of an isokinetic or equilibrium relationship[24-27]. The most important application of the compensation and/or isokinetic effect that such behaviors constitute evidence for a dominant mechanism throughout out the correlated series chemical catalysis, cooperative relaxation kinetics in thermally simulated process, the sorption and browning of garlic[25-27]. etc. The higher positive value of $\Delta G^{\#}$ indicates that the transition state is highly solvated. Negative value of $\Delta S^{\#}$ within the range of radical reactions have been ascribed to the nature of

Figure 6: Plot of $\Delta H^{\#}$ (solid line) and $\Delta S^{\#}$ (dashed line) vs. concentration of HQ

electron pairing and electron unpairing processes and to the loss of degree of freedom, formerly available to the reactions on the formation of rigid transition state. Also, this is consistent with an SN_2 or associative mechanism the transition state.

On plotting $\Delta H^{\#}$ and $\Delta S^{\#}$ against monomer(HQ) concentration(Figure 6) and extrapolating to C=0.0. $\Delta H^{\#0}$ and $\Delta S^{\#0}$ values were obtained and hence $\Delta G^{\#0}$ was computed at any given temperature. The values seem to be almost independent of HQ concentration. These values are 108.16±0.1 at 25^0C and 68.352±0.3 kJ mol^{-1} for $\Delta H^{\#0}$ and $\Delta G^{\#0}$ respectively. The value of $\Delta S^{\# 0}$ is equal to -133.599±0.5 J mol^{-1}. This $\Delta H^{\#0}$ is somewhat close to 17 kJ mol^{-1} a characteristic value of spherocolloids[30].

TABLE 5: Activation parameters for the oxidative polymerization of 8-HQ in strong alkaline(NaOH, 0.1 mmol) medium

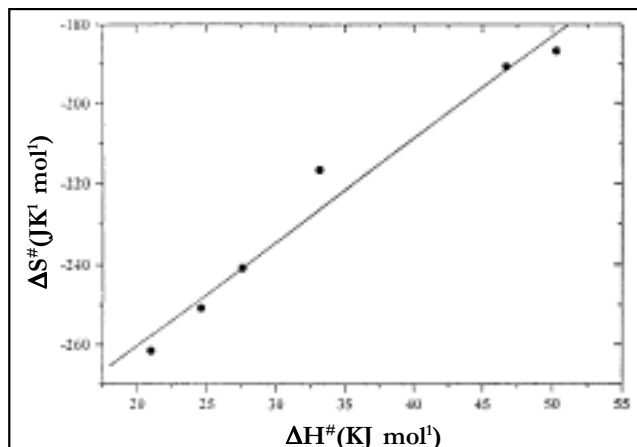| HQ (μmol L^{-1})	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	r
30	44.56	50.301	186.70	105.94	0.973
40	38.57	46.72	190.72	108.55	0.995
50	32.59	33.13	216.75	79.72	0.981
60	28.61	29.55	240.77	99.28	0.977
70	23.62	24.56	250.79	99.29	0.991
80	20.03	20.97	261.62	98.93	0.982

Full Paper

CONCLUSIONS

Oxidative polymerization process of 8-hydroxy-quinoline(HQ) was studied in both experimentally using spectrophotometric technique and computational using molecular mechanics(MM+) calculations. The proposed procedure was applied successfully for the oxidation of diiodohydroxy-quinoline in sterptoquin(SQ) tablets. The proposed mechanism was successfully proved both experimentally and theoretically. It was observed that the method proposed was simple, precise, inexpensive, unique and require neither sophisticated instrumentation such as spectro-electrochemical equipment nor transparent electrodes such as metal oxide anodes of the type indium-doped tin oxide coated glass-working electrode. The results obtained encourage the applicability of the proposed method for oxidation of some other organic compounds in different fields such as wastewater treatment than the Fenton or Electro-Fenton processes[28,29]. Both of these methods require the addition of ferric chloride($FeCl_3$) to the solution, which, in turn, invokes consecutive separation steps.

ACKNOWLEDGMENTS

REFERENCES

[1] M.Bankova, N.Monlova, N.Markova, T.Radoucheva, K.Dilova, I.Rashkov; Eur.Polym.J., **34**, 247 **(1998)**.

[2] M.Bankova, T.Petrova, N.Monlova, I.Rashkov; Eur. Polym.J., **34**, 247 **(1996)**.

[3] E.T.Kaiser, S.W.Weidman; J.Am.Chem.Soc., **87**, 4354 **(1964)**.

[4] J.F.Iyun, H.M.Lawal, O.T.Olagbemiro; Indian J. Chem., **14**, 446 **(1995)**.

[5] J.F.Iyun, K.Y.Musa, G.A.Ayoko; Science in New Guinea, **22(1)**, 10 **(1996)**.

[6] A.Mc Aulley, I.Spencer, P.R.West; Can, J.Chem., **63**, 1198 **(1985)**.

[7] D.F.C.Morris, J.J.Ritter; Int.J.Chem.Kinetics, XI, 1081 **(1979)**.

[8] G.Davies, K.Kustin; Trans.Faraday.Soc, **65**, 1630 **(1989)**.

[9] C.F.Wells, I.V.Kuritsyn; J.Chem.Soc., A, 1372 **(1970)**.

[10] E.Mentasti, E.Pellizzetti; J.Chem.Soc.Dalton, 2605 **(1973)**.

[11] E.Mentasti, E.Pellizzetti, G.Saini; J.Chem.Soc.Dalton, 2609 **(1973)**.

[12] F.J.Alexander; Synthesis, **21**, 85 **(1987)**.

[13] A.I.Vogel; 'A Text book of Quantitative Chemical Analysis, ELBS, Longman Essex, UK, 5th Ed., 371 **(1989)**.

[14] M.M.Kamal, S.M.Ahmed, M.M.Shahata, Y.M.Temerk; Anal. and Bioanal.Chem., **372**, 843 **(2002)**.

[15] S.M.Ahmed, M.M.Kamal, M.M.Shahata; J.Inorg. and Organometalic Polym., **13(3)**, 171 **(2003)**.

[16] S.M.Ahmed; Polym.Deg. and Stability, **85**, 605 **(2004)**.

[17] S.M.Ahmed; Int.J.Chem.Kinetics, **35**, 260 **(2003)**.

[18] S.M.Ahmed, B.M.Abu-Zied; J.Anal. and Appl.Pyrolysis, **70**, 277 **(2003)**.

[19] J.T.Sprague, J.C.Tai, Y.Yuh, N.L.Allinger; Comput. Chem., **8**, 581 **(1987)**.

[20] W.Hasel, T.F.Hendrichkson, W.C.Still; Tet.Comput. Meth, **1**, 103 **(1988)**.

[21] G.Chang, W.C.Guida Still; J.Am.Chem.Soc., **111**, 4379 **(1989)**.

[22] K.Miller; J.Am.Chem.Soc., **112**, 8533 **(1990)**.

[23] A.L.Harihar, M.R.Kembhavi, S.T.Nandibewoor; Indian J.Chem., **39A**, 769 **(2000)**.

[24] Y.J.Jtang, L.M.Zhou, Q.H.Wang, D.Q.Zhu, X.L.Liu; Chin J.Anal.Chem., **28**, 106 **(2000)**.

[25] R.Ranganathan, N.N.Bakhshi, J.F.Mathews; Can.J. Chem.Eng., **55**, 544 **(1977)**.

[26] J.P.Ibar; Thermochim.Acta, **192**, 91 **(1991)**.

[27] P.S.Madamba, R.H.Driscoll, K.A.Buckle; Food Eng., **28**, 109 **(1996)**.

[28] C.Walling; Acc.Chem.Res., **8**, 125 **(1975)**.

[29] E.Brillas, R.C.Sauleda; Electrochem.Soc., **145**, 737 **(1998)**.

[30] ChD.Prarsad, H.N.Singh; Colloid Surf, **59**, 27 **(1991)**.