

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

KINETICS OF THE PHENOL OXIDATION BY PERMANGANATE IN ACIDIC MEDIA. THE INTERMEDIATE OXIDIZED SPECIES 4,4'-BIPHENOQUINONE EVOLUTION

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ABSTRACT. The kinetics of phenol oxidation by permanganate has been carried out in relative strong acidic media, in the presence and in absence of manganese (II) as catalyst. Formation of an intermediate colored species that absorbs light at 400 nm has been observed during the course of reaction. Its formation and decay has been followed spectrophotometrically. The intermediate has been assigned as 4,4'-biphenquinone. Kinetic laws for the formation and consumption of this intermediate have been established. Complicate rate equations of the *one-plus* form were deduced either for building up or for decomposition of the intermediate. Rate constants, pre-equilibrium constants and experimental activation energies were determined. Some mechanistic considerations were made.

Keywords: phenol, permanganate, kinetics, 4,4'-biphenquinone.

INTRODUCTION

The kinetic study of oxidation by permanganate has received a considerable attention because of its importance in analytical [1,2] and organic chemistry [3-5]. Nevertheless, there are still unsolved aspects of the mechanisms of many permanganate oxidation reactions [6]. The reaction mechanisms of oxidation of various substrates, including phenols [7-15], in alkaline solutions are better understood [16-19], but they are more complex in acidic solutions due to ability of manganese to exist in various oxidation states between VII and II, as well as to the auto-catalytic character of numerous permanganate oxidations [20-25]. Knowledge of the phenol oxidation has applications in water purification [26] and some organic syntheses [3,4]. In this paper we report information obtained from a kinetic study by monitoring

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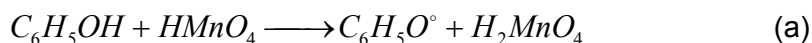
the evolution of 4,4'-biphenoquinone intermediate during the phenol oxidation in acidic solution, either in the absence or in the presence of manganese (II) at the start of reaction.

RESULTS AND DISCUSSION

Spectra and mechanistic considerations. Substantial evidence has been obtained for the formation of an intermediate species that absorbs light within the region 350–450 nm, with a peak located at 400 nm. The mixing of aqueous phenol and permanganate in acidic media leads to solution color changes within an interval of several minutes. It starts purple-violet, rapidly turns yellowish-brown and faded to colorless in a slower pace. When phenol and permanganate were mixed and spectra recorded at 1 second intervals by a diode –array spectrophotometer, an absorption band emerge and then falls to zero around 400 nm. The permanganate ion peak at 525 nm decreases steadily from the start of the process [27]. No isosbestic points have been noticed on time-dependent spectra, suggesting the involvement of some consecutive steps. The same peak position was obtained when the reaction was carried out in the presence of Mn(II) in the reaction mixture. The spectra were presented previously [27] where we performed the reduction of MnO_4^- by Mn^{2+} in large excess. Mn(III) is the single species formed [28]. After complete decay of permanganate ion, a phenol solution was injected into the mixture to achieve a large excess concentration. A yellowish-brown color suddenly appeared during the mixing that further faded to colorless, as time elapses. Successive spectra were recorded and position of the peak is the same as when permanganate was the oxidizing agent. Because Mn(III) is a strong oxidizing agent (redox potential for the Mn(III)/Mn(II) couple of 1.5 - 1.6 V [29]), one can assume it reacts more rapidly with phenol than Mn(VII) does. Such a reaction rate also explains the catalytic effect of Mn(II) in permanganate oxidations. On the other hand, this system involves the same intermediate species as in the case of phenol - permanganate system.

A comparison of the spectra obtained with those of $\text{Mn}_{\text{aq}}^{3+}$, and $\text{Mn}(\text{OH})^{2+}$ ions [30], Mn(IV) with a peak at 418 nm [31–33], identified by Insausti and co-workers [22,23] reveals that the intermediate is an oxidation product of phenol rather than an intermediate valence state of manganese. The spectra of *ortho*- and *para*-quinone differ from the one in discussion. A supplementary argument for the formation of such an intermediate is brought by the oxidation of *ortho*-cresol, when a similar intermediate with an absorption peak at 408 nm is formed. In the case of *para*-cresol oxidation either by permanganate or Mn(III), no absorption peak was found in this range of wavelength.

We consider that the intermediate is 4,4'-biphenoquinone formed by oxidative coupling of phenoxy radicals that is the primary oxidation product of phenol by Mn(VII) or Mn(III). Such a relative long-lived intermediate has been found in the case of phenol oxidation by ferrate (VI) in phosphate buffered solutions [34]. Similar behavior has been found by hexacyanoferrate(III) [35a], *trans*-dioxoruthenium(VI) [35b], oxochromium(IV) ion [35c] in acidic media oxidation. Lee and Sebastian [14] showed that phenoxy radicals undergo further coupling and oxidation reactions, which eventually produce a mixture of *ortho* and *para*- diphenoquinone, the final products of alkaline oxidation. Hay and co-workers described oxidative coupling with 2,6- disubstituted phenols [36]. D.T Yiu and co-workers [35b] showed that either by a hydrogen abstraction or by an electron transfer, the phenoxy radical is produced with ruthenium complex. It undergoes two rapid concurrent reactions. The first is a further three-electron oxidation to give *p*-benzoquinone and other organic products. The second is a coupling and oxidation process to give 4,4'-biphenoquinone, followed by a decay step. Therefore, we consider that the formation of 4,4'-biphenoquinone requires the following sequence of steps:



In the step (b) phenoxy radical switches to a carbon radical. The formation of a covalent bond between one of the limiting structures of the phenoxy radical and the oxidation can take place successively. The involvement of free radicals during the permanganate oxidation of phenols or other organic substrates is supported by the induced polymerization of ethylacrylate [24]. It has been mentioned previously in the case of other phenol oxidation [4,37,38].

Kinetics. Under large hydrogen ion concentration the final reduction product is Mn(II). No MnO₂ precipitate is formed. Our kinetic measurements were carried out under experimental conditions where the induction period was either imperceptible short or it was missing. At least three replicate runs were carried out for each set of experimental conditions, which yield rate constants that do not differ to more than 3 %. Under the excess of phenol, all absorbance recordings could be described by linear kinetics, regardless the absorbance was monitored at 525 nm for Mn(VII), or at 400 nm for the intermediate.

At 400 nm the evolution of absorbance against time, a biphasic curve, obeys the following equation:

$$A = [Mn(VII)]_0 \varepsilon_0 e^{-k_{obsd} t} + s[Mn(VII)]_0 \varepsilon_1 \frac{k'_{obsd}}{k''_{obsd} - k'_{obsd}} (e^{-k'_{obsd} t} - e^{-k''_{obsd} t}) + \varepsilon_2 [C_6H_5OH]_0 e^{-k_{obsd} t} \quad (2)$$

where k'_{obsd} and k''_{obsd} are pseudo-first-order rate coefficients for the formation and decay of the intermediate. ε_0 , ε_1 and ε_2 stand for molar absorptivities of all three absorbing species (permanganate, biphenol intermediate and phenol, respectively), s is a stoichiometry factor. $A_\infty = \varepsilon_2 [C_6H_5OH]_0$ is the final absorbance. Since phenol and permanganate absorb light very weakly in this region of electronic spectrum and $\varepsilon_0, \varepsilon_2 \ll \varepsilon_1$, the first and the last terms in eq. (2) have an insignificant contribution. Therefore,

$$A - A_\infty = C \cdot (e^{-k'_{obsd} t} + e^{-k''_{obsd} t}) \quad (3)$$

The constant C is the factor in front of the parenthesis of the second term in eq. (2).

A non-linear regression of equation (3) was used for the data recorded at 400 nm and has fitted well with R^2 between 0.990 and 0.999 and χ^2 of the order of magnitude smaller than 10^{-6} . At constant hydrogen ion concentration, the dependence of the observed first-order rate constants on phenol concentration is presented in Table 1. These data were obtained in the absence and the presence of Mn(II) as catalyst.

Table 1. Observed first-order rate constants (mean values) for the two-step sequence at $[MnO_4^-] = 1.30 \cdot 10^{-4}$, $[HClO_4] = 0.38$, $\mu = 0.4$ and $T = 298K$ in absence and presence of $3.33 \cdot 10^{-4} \text{ mol.L}^{-1}$ Mn(II)

$[C_6H_5OH]$ mmol.L^{-1}	$k'_{obsd} \text{ s}^{-1}$	$k'_{obsd} \text{ s}^{-1}$ Mn(II)	$k''_{obsd} \text{ s}^{-1}$	$k''_{obsd} \text{ s}^{-1}$ Mn(II)
0.33	0.0180	0.032	0.00203	0.0015
0.67	0.0383	0.055	0.00315	0.0024
1.00	0.0526	-	0.00511	-
1.33	-	0.091	-	0.0041
1.67	0.074	0.125	0.00663	0.0050
2.00	0.087	0.150	0.00702	0.0057
2.67	0.120	0.180	0.00782	-
3.33	0.133	0.200	0.00864	0.0075
4.00	0.155	0.224	-	-
5.00	0.179	0.231	0.0091	0.0081
6.67	0.196	0.244	0.0096	0.0087
8.33	0.217	-	0.0100	-

In this paper we focused the attention on the formation and decay of 4,4'-biphenoquinone intermediate that has been followed at 400 nm and exhibits a biphasic behavior concerning the absorbance evolution. Its formation involves a total loss of four electrons from two phenol molecules. On the behalf of permanganate ions it means that 1.25 moles of this condensed compound are formed for each mole of permanganate reduced to Mn(II). Therefore it can be formed at least 1.25 times faster than permanganate consumption. Because of the involvement of the intermediate valence state of Mn, more reactive than Mn(VII), the building of such a species in the early stages of reaction can outpace the rate of disappearance of Mn(VII) reported previously [27].

The rate coefficient for the intermediate formation k'_{obsd} (s^{-1}) exhibits a tendency of leveling off towards larger concentration of phenol as shown in Figure 1. The curve can be described by the following equation:

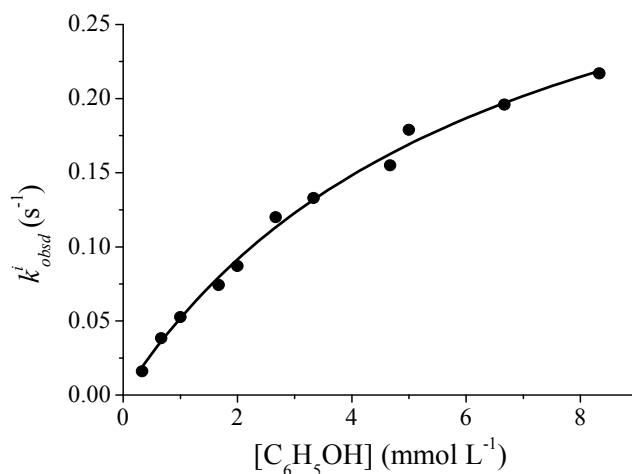


Figure 1. The first-order rate constant dependence on phenol concentration for the formation of intermediate.

$$k'_{obsd} = \frac{a_1[C_6H_5OH]}{1 + b_1[C_6H_5OH]} = \frac{(57.5 \pm 2.5)[C_6H_5OH]}{1 + (125 \pm 11)[C_6H_5OH]} \quad (4)$$

with $\chi^2 = 0.000001 \text{ s}^{-1}$ and $R^2 = 0.996$. In the presence of Mn(II) ion, the same pattern has been observed and the equation is:

$$k'_{obsd(Mn)} = \frac{a'_1[C_6H_5OH]}{1 + b'_1[C_6H_5OH]} = \frac{(102 \pm 5)[C_6H_5OH]}{1 + (227 \pm 20)[C_6H_5OH]} \quad (5)$$

The acceleration of reaction rate by Mn(II), which causes a supplementary decrease of Mn(VII) concentration, is due to the intermediate oxidation states of manganese that react faster with reducing organic species. For the case of Mn(II) initially added to the reaction mixture, data presented in columns 3 of Table 1 reveals also that k'_{obsd} increases strongly at smaller concentration of phenol and not so pronounced at higher concentration. A similar tendency of leveling off also appears.

The linear form of this one-plus type equation as a double reciprocal of (4) and (5) also permits the determination of the coefficients.

$$\frac{1}{k'_{obsd}} = \frac{1}{a[C_6H_5OH]} + \frac{b}{a} \quad (6)$$

The effect of the acidity on these rate coefficients was investigated within the range 0.07 – 0.7 mole·L⁻¹ HClO₄. The mean rate coefficients obtained from at least three individual runs are given in Table 2. Data in the second and third columns fitted well with a linear dependence:

$$k'_{obsd} = (3.0 \pm 8.5) \cdot 10^{-3} + (0.34 \pm 0.02)[H^+] \quad (7)$$

with R² = 0.999 and SD = 0.004 in the absence of Mn(II), and

$$k'_{obsd(Mn)} = (1.9 \pm 2.0) \cdot 10^{-2} + (0.52 \pm 0.05)[H^+] \quad (8)$$

in the case of the initial presence of Mn(II) species in the mixture.

Table 2. The effect of acid concentration on the rate. [C₆H₅OH]=3.33·10⁻³, [MnO₄⁻] = 1.30·10⁻⁴, μ = 0.4 and T = 298K in absence and presence of 3.33·10⁻⁴ mol·L⁻¹ Mn(II)

[HClO ₄] mol·L ⁻¹	k'_{obsd} s ⁻¹	k'_{obsd} s ⁻¹ Mn(II)	k''_{obsd} s ⁻¹	k''_{obsd} s ⁻¹ Mn(II)
0.0773	0.0249	0.065	0.00316	0.00319
0.155	0.0559	0.1046	0.0046	0.0049
-0.232	0.0884	0.139	0.00662	0.00572
0.387	0.133	0.200	0.00846	0.00746
0.541	0.189	0.288	0.0098	0.0089
0.619	0.207	0.340	0.0101	0.00908
0.773	0.267	0.428	0.0110	0.00928

The linear dependence of k'_{obsd} as described by eqs (6) and (7) indicates a first-order with respect to hydrogen ion, the intercept of the lines being not statistically different from zero.

By combining equations (4) and (7), the rate coefficient for the intermediate formation can be written as dependent of both phenol and acid concentrations as:

$$k'_{obsd} = \frac{\alpha_1 [C_6H_5OH][H^+]}{1 + \beta_1 [C_6H_5OH]} \quad \text{or} \quad \frac{[H^+]}{k'_{obsd}} = \frac{1}{\alpha_1 [C_6H_5OH]} + \frac{\beta_1}{\alpha_1} \quad (9)$$

The parameters are: $\alpha_1 = (144 \pm 8) \text{ L}^2\text{mol}^{-2}\text{s}^{-1}$ $\beta_1 = (125 \pm 13) \text{ L}\cdot\text{mol}^{-1}$ and $R^2 = 0.997$. By using additionally the data in column 1 of Table 2 in the linear form of eq. (9), the parameters of the line are: slope = 0.0066, the intercept = 0.8696 and $R^2 = 0.9962$ corresponding to $\alpha_1 = (144 \pm 8) \text{ L}^2\text{mol}^{-2}\text{s}^{-1}$, $\beta_1 = (132 \pm 12) \text{ L}\cdot\text{mol}^{-1}$.

It is obvious that the *p*-diphenoquinone intermediate is formed on the account of permanganate in the early stages of the reaction. Therefore, in the initial absence of Mn(II) ion, its formation is caused by the oxidation of phenol by permanganate, or when considering the first-order with respect to hydrogen ion, by permanganic acid. Indeed, when the process was followed at 400 nm and various initial concentrations of permanganate were used, always as limiting reactant, a linear dependence of k'_{obsd} on permanganate has been found:

$$k'_{obsd} = (9.2 \pm 5.4) \cdot 10^{-3} + (9.1 \pm 0.4) \cdot 10^2 [MnO_4^-] \quad (10)$$

Note that in the early stages of reaction, under the larger concentration of oxidizing agent, the larger concentration of phenoxy free radicals is formed and the larger rate of biphenoquinone would be. The intercept is quite small and can be considered zero. It clearly justifies the use of equation (4), which is first order with respect to the colored oxidizing agent. Another possibility of the proton involvement could be its rapid bounding to phenol.

If one compares k_{obsd} at the permanganate consumption ($\lambda = 525 \text{ nm}$), as obtained previously [27], with the apparent first-order rate coefficient k'_{obsd} , the latter is greater than $1.25 \cdot k_{obsd}$. The stoichiometric factor of 1.25 comes out from the need of 4-electron removal from reducing species to form a molecule of biphenoquinone. The involvement of intermediate valence-state of Mn, which react faster than Mn(VII) is apparent. The dependence in Table 1 proves the involvement of at least Mn(III) species revealing the autocatalysis/catalysis by Mn(II). On the other hand, the involvement of two terms in the denominator of rate equation (9) indicates also the presence of a fast reversible process.

The effect of temperature on the apparent first-order rate constant k'_{obsd} in the range of 15 – 40°C yielded an experimental activation energy of 67 ± 2 kJ.mol⁻¹. A comparison with the smaller value of 12.5 ± 1.9 kJ.mol⁻¹ when permanganate consumption was monitored [27], indicates that the step of formation of phenoxy radical is not the rate-determining step for 4,4'-biphenol formation, but its further oxidation or coupling. The switch from oxy free radical to a carbon free radical (eq. 1.b) seems also to take place rapidly within the π -conjugated electronic system. The coupling and further oxidation (or further oxidation of C-free radical and coupling) could also justify the linear dependence of k^i_{obsd} on permanganate.

Concerning the decay of the intermediate species, the same pattern of the one-plus type rate law has been found as dependent of the substrate concentration. The apparent first-order rate constant is:

$$k''_{obsd} = \frac{a_2[C_6H_5OH]}{1 + b_2[C_6H_5OH]} = \frac{(7.1 \pm 0.3)[C_6H_5OH]}{1 + (547 \pm 33)[C_6H_5OH]} \quad (11)$$

with $\chi^2 = 1.5 \cdot 10^{-7}$ s⁻¹ and $R^2 = 0.997$ for the consumption of the intermediate in the absence of Mn(II) ion. The linear form of eq.(10), as a double reciprocal, is presented in Figure 2.

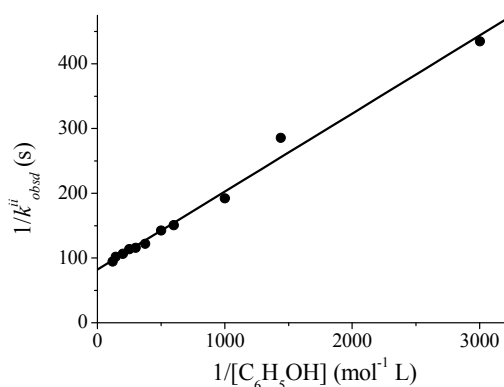


Figure 2. Double reciprocal plot of equation (5) with the data in Table 1

The parameters of the line are: slope = $1/a_2 = 0.141$, intercept = $b_2/a_2 = 77.1$, $R^2 = 0.9877$. The constants are $a_2 = 7.1 \pm 0.3$ L.mol⁻¹s⁻¹ and $b_2 = 547 \pm 33$ L.mol⁻¹ (errors statistically counted). On the other hand, as presented in the last two columns of table 1, a small decline of k''_{obsd} , as compared to

the values in the absence of Mn(II) in the mixture has been noticed for the disappearance of the biphenol intermediate.

A more complex behavior has been found at the decay of the intermediate as dependent on the mineral acid in solution as compared to that of the intermediate formation. A one-plus type equation describes hydrogen ion effect on the observed rate. It infers the involvement of a rapid protonation pre-equilibrium. The apparent first-order rate constant is:

$$k_{obsd}'' = \frac{a_2'[H^+]}{1 + b_2'[H^+]} = \frac{(0.051 \pm 0.0023)[H^+]}{1 + (3.47 \pm 0.25)[H^+]} \quad \frac{1}{k_{obsd}''} = \frac{1}{a_2'[H^+]} + \frac{b_2'}{a_2'} \quad (12)$$

It is characterized by $\chi^2 = 3.68 \cdot 10^{-8}$, $R^2 = 0.998$ and $R^2 = 0.9968$ for the line. In the presence of Mn(II) the corresponding values are: $a_2' = (5.6 \pm 0.3) \cdot 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $b_2' = 4.79 \pm 0.23 \text{ L} \cdot \text{mol}^{-1}$ and $R^2 = 0.993$. These last values are not far from those in the absence of Mn(II), suggesting the interaction between phenol and 4,4'-biphenol is not significantly influenced by the catalyst.

When combining equations (11) and (12), the decay rate of the intermediate is described by the following rate equation:

$$-\frac{d[OC_6H_4 = C_6H_4O]}{dt} = \frac{\alpha_2[C_6H_5OH][H^+]}{1 + \beta_2[C_6H_5OH][H^+]} [OC_6H_4 = C_6H_4O] \quad (13)$$

and the first-order rate coefficient is:

$$k_{obsd}'' = \frac{\alpha_2[C_6H_5OH][H^+]}{1 + \beta_2[C_6H_5OH][H^+]} \quad (14)$$

with the parameters $\alpha_2 = (17.9 \pm 0.7) \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ and $\beta_2 = (1.32 \pm 0.12) \cdot 10^3 \text{ L}^2 \cdot \text{mol}^{-2}$. It can be assigned to the reaction of the protonated *p*-diphenol with the excess phenol molecule.

If this equation describes well the data, it should be applied to both series of measurements, when either phenol, or the acid has been maintained constant and the other was varied. Indeed, we obtained such a correlation in the linear form, as presented in Figure 3.

$$\frac{1}{k_{obsd}''} = \frac{1}{\alpha_2''} \frac{1}{[C_6H_5OH][H^+]} + \frac{\beta_2''}{\alpha_2''} \quad (15)$$

with $R^2 = 0.993$, $(\beta_2 / \alpha_2 = 74 \pm 4)$ and $(1 / \alpha_2 = 0.056 \pm 0.002) \text{ mol}^2 \cdot \text{s} \cdot \text{L}^{-2}$.

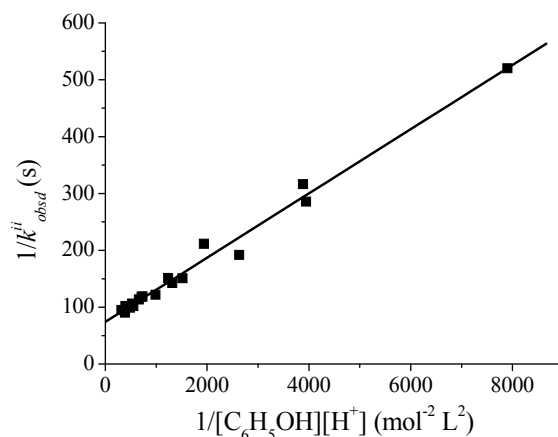
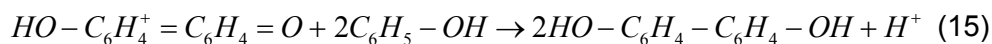


Figure 3. Linear presentation of all data (eq.14) of the two series of measurements (Tables 1 and 2) in the absence of Mn(II).

Accounting for the acid effects, interaction of protonated 4,4'-biphenoquinone is involved in the phenol oxidation to generate biphenols [39] with the stoichiometry:



It could proceed by two successive one-equivalent electron-transfer yielding free oxy radicals from phenol and biphenol. The apparent activation energy determined over the same range of temperature by the effects on k_{obsd}'' is $50 \pm 1 \text{ kJ.mol}^{-1}$, a value smaller than that of the intermediate formation, and could be attributed to the first one- equivalent electron-transfer step (or first hydrogen abstraction from phenol by protonated 4,4'-biphenoquinone). The second step involves a free oxy radical of biphenol, which would react faster with the second phenol molecule.

The overall stoichiometry of phenol – permanganate reaction found previously [27] implies that the partial oxidized products of phenol react further, and probably faster, up to the ring rupture, even in the presence of phenol excess with any oxidizing species in relative strong acid solution. A possible route could be by means of traces of benzoquinone formed by phenoxy radical oxidation. All intermediate oxidation states of manganese are able to bring about oxidative ring breakage of *o*- or *p*-benzoquinone. The complexity of the system needs more data for a better elucidation of the elementary steps network.

CONCLUSIONS

The formation and decay of 4,4'-biphenoquinone, as an active intermediate, has been followed and the corresponding rate laws have been determined.

The presence of Mn(II) in the solution has a catalytic effect on the formation and practically no influence on the consumption of intermediate.

The one-plus rate laws revealed complex mechanisms with the involvement of some pre-equilibrium concerning the proton intervention. Third-order rate constants α and equilibrium constants β were estimated from the kinetics.

The apparent activation energies were also obtained, which argue the rate determining steps implied in the formation and redox consumption of 4,4'-biphenoquinone.

EXPERIMENTAL SECTION

Materials. Chemicals of analytical grade and ultra-pure water (de-ionised and tetra-distilled) were used throughout this study. A stock solution of HClO₄ was prepared from Merk's 70 % HClO₄ and standardized by titration. Stock solution of NaClO₄ was prepared from Merk's NaClO₄·H₂O and standardized by titration after passing a measured volume over Vionit –100C (H-form) cationic resin. Working solution of KMnO₄ was prepared before each set of runs and standardized by titration with oxalic acid. The phenol solution was also prepared freshly from purified staff (distillation under low pressure; m.p. 40.5 – 41.5°C).

Kinetic measurements. Electronic absorption spectra were recorded either by using a M-40 Diode-Array Spectrophotometer or a Jasco UV-VIS V-530 spectrophotometer. A conventional spectrophotometrical method was used to monitor the progress of the reaction at constant temperature. Two wavelengths could be used: either at 525 nm, where permanganate ion exhibits an absorption peak and its disappearance was recorded, or 400 nm, where a biphasic plot has been obtained, the formation and the decay of a yellowish-brown colored intermediate species. The reaction was performed in a quartz 5-cm path length cuvette. It was started by injecting of 5 mL permanganate solution over the mixture of the other reactants. The mixing time does not exceed 1 second. Pseudo-first-order conditions were employed. Both the phenol and mineral acid were taken in excess as compared to permanganate oxidizing agent. Kinetic measurements were also carried out in the presence of Mn(II) ions, in a small excess as compared to permanganate.

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