

KINETICS OF THE PHENOL OXIDATION BY PERMANGANATE IN ACIDIC MEDIA

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A kinetic study has been carried out on the phenol oxidation by permanganate in relative strong acidic media, in the presence or in absence of manganese (II) as catalyst. A quite complicated rate law has been found as depending on permanganate, manganese (II), substrate and acidity. The stoichiometry indicates the breaking of the aromatic ring. An intermediate colored species, assigned as 4,4'-biphenol that absorbs light in the region of 400 nm, has been involved. Some free radicals, identified by the initiation of polymerization are formed during the oxidation process. A reaction mechanism has been suggested for the formation of the phenoxy radical.

INTRODUCTION

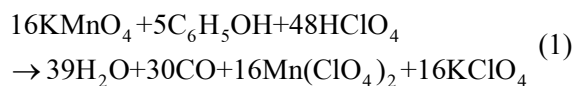
Although the kinetic study of oxidation by permanganate has received a considerable attention because of its usage in analytical and preparative chemistry, there are still unanswered questions concerning the mechanisms of many permanganate oxidation reactions.¹ The reaction mechanisms of oxidation of various substrates, including phenols,²⁻¹⁰ in alkaline solutions¹¹⁻¹⁴ are better understood, but they are more complex in acidic solutions due to ability of manganese to exist in various oxidation states between VII and II, and to autocatalytic character of numerous permanganate oxidations.¹⁵⁻¹⁸ Knowledge of the phenol oxidation is of a potential application in organic synthesis,^{19, 20} water purification,²¹ and analytical chemistry.²²⁻²⁴

In this paper we report information obtained from the kinetic study of phenol oxidation in acidic solution, either in absence or in presence of manganese (II) at the start of reaction.

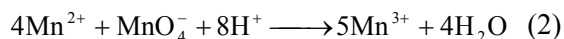
RESULTS AND DISCUSSION

Stoichiometric studies. The phenol – Mn(VII) and Mn(II) – Mn(VII) reaction stoichiometries were determined by colorimetric titration. Various reaction mixtures, having increasing molar ratios,

were allowed to react to completion and the remainder absorbance due to permanganate was recorded at 525 nm. Absorbance vs. the molar ratio exhibits an obvious bend at the ratio 0.32 C₆H₅OH:1 MnO₄⁻. This can be rationalized by the following stoichiometric equation:



It indicates the breaking of the phenyl ring. Such a ring rupture has been mentioned at the oxidation of dinitrophenol by permanganate in strong acidic media.²⁵ Indeed, if the reaction products are extracted into hexane and solvent removed, the recorded IR spectrum corresponds to the one of phenol, which was in excess. No other IR band was obtained, confirming the complete destruction of the ring by oxidation. In the same manner we obtained the ratio of 4 Mn(II):1 Mn(VII), corresponding to the known oxidation of Mn(ClO₄)₂ by permanganic acid.



Spectra. Substantial evidence has been obtained for an intermediate species formation, absorbing light within the region 350-450 nm, with a peak located around 400 nm. The mixing of aqueous phenol and permanganate in acidic media

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leads to a series of changes of solution color. It starts out purple-violet, rapidly turns yellowish-brown and faded to colorless. When phenol and permanganate were mixed and spectra recorded at 1 second intervals by a diode array spectrophotometer, an absorption band emerge at

around 400 nm. The peak intensity increases at the beginning of the reaction, then falls to zero in the later stages. The peak at 525 nm, characteristic to permanganate ion, decreases steadily from the start of the process. Figure 1a presents these recordings.

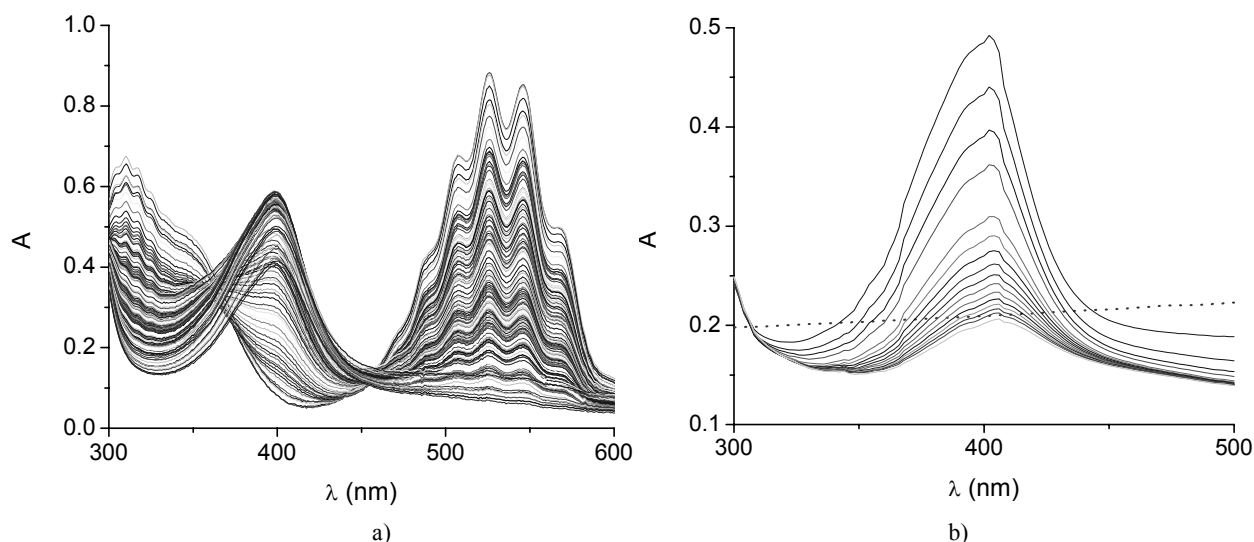
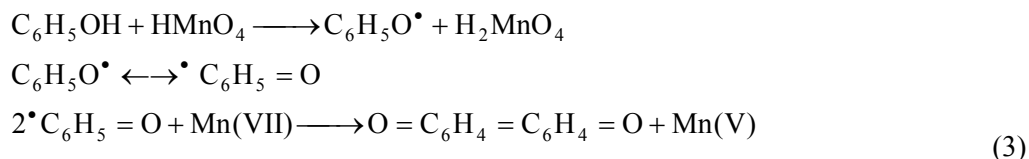


Fig. 1 – a) Absorption spectra recorded as reaction proceeds at each 1 second and b) successive spectra recorded when oxidation is performed by Mn(III) species.

No isosbestic points were noticed on time-dependent spectra, suggesting the involvement of some consecutive steps. The spectra analysis revealed three linearly independent absorbing species present in the mixture.²⁶ Two of them were the permanganate ion and phenol. The third should be either an oxidized species or an intermediate valence state of manganese compound. To assign this peak we analyzed its position and intensity. Both characteristics of the peak differ from the spectra of $\text{Mn}^{3+}(\text{aq})$, and $\text{Mn}(\text{OH})^{2+}$ ions^{27,28} or $\text{Mn}(\text{IV})$.^{17,18,29-31} On the other hand, recorded spectra of *o*- and *p*-quinone, as possible intermediate oxidation species of phenol, do not correspond to the one in Fig. 1a, exhibiting picks below 400 nm. We performed the reduction of MnO_4^- by Mn^{2+} , the latter being in large excess. Mn(III) is the single species formed.²⁸ After complete decay of permanganate ion, a phenol solution was injected into mixture to achieve a concentration in large excess as compared to Mn(III). A yellowish-brown color appeared suddenly during mixing and further faded to colorless. Successive spectra were recorded as presented in Fig. 1b. The position of the peak is at 400 nm.

The same peak position was obtained when the reaction was carried out in the presence of Mn(II). Because Mn(III) is a strong oxidizing agent, with redox potential for the Mn(III)/Mn(II) system of 1.5 - 1.6 V,³² one can assume it reacts more rapidly with phenol than Mn(VII) does. This is the reason for the catalytic effect of Mn(II). Permanganate oxidation yields the same species in appreciable concentration even in the absence of Mn(II) from the start of the reaction and it seems likely that it is an oxidation product of phenol and not an intermediate valence state of manganese compound. We consider that the intermediate is 4,4'-biphenoquinone formed by coupling and successive oxidation of phenoxy radical. This free radical is the primary oxidation product of phenol either by Mn(VII) or Mn(III).

Such a long-lived intermediate has been found in the case of phenol oxidation by ferrate (VI) in phosphate buffered solutions.³³ Lee and Sebastian⁹ showed that phenoxy radicals undergo further coupling and oxidation reactions, which eventually produce a mixture of *o* and *p*-diphenoquinone, the final products of alkaline oxidation.



Our spectra differ slightly from that recorded by Huang and co-workers.³³ In slightly acidic media, this intermediate exhibits a λ_{max} at 418 nm. Because of high acidity in our case, protonated species is involved $[\text{HO}-\text{C}_6\text{H}_4 = \text{C}_6\text{H}_4 = \text{O}]^+$. A small hypsochromic shift may take place and the peak is located at 400 nm. A supplementary argument for the formation of such an intermediate is brought by the oxidation of *o*-cresol, when a similar intermediate with an absorption peak at 408 nm is formed. In the case of *p*-cresol oxidation either by permanganate or Mn(III), no absorption peak was found in this range of wavelength.

Search for free radicals. The involvement of free radicals during the permanganate oxidation of phenols is supported by the induced polymerization.¹⁹ When 1 mL of butylacrylate was added to the reaction mixture, a temperature rise of 1.2°C was noticed. It indicates the polymerization. Some polymer was formed and separated. Because of the formation of biphenolquinone involves phenoxy free radical as a precursor, we assume the involvement of at least such a free radical. It has been mentioned previously³³⁻³⁶ in the case of other phenol oxidations and proved by using a spin trap method.

Kinetics. We report here the **kinetics** of permanganate disappearance, followed at 525 nm. It should be mentioned that the oxidation reaction yields some precipitate, indicating that MnO₂ is formed, at acid concentrations lower than 0.03 mol·L⁻¹. Under larger hydrogen ion concentration the final reduction product is Mn(II).

In the absence of Mn(II) in the initial mixture and lower acidity the reaction exhibits an induction period. The sigmoid shape of the absorbance vs time curve indicates it as well as the importance of intermediate valence state of manganese ions.¹⁵ The induction period is diminished and eventually completely removed by increasing the acid concentration and/or by adding Mn²⁺ to the reaction mixture. Our kinetic measurements were carried out under experimental conditions where the induction period was missing. At least three replicate runs were carried out for each set of experimental conditions. Measurements under an inert atmosphere of argon with de-aerated solutions yield the same results as those carried out in air. Consequently, we have given up this precaution.

Under pseudo-first-order conditions, all absorbance recordings could be described by linear kinetics. The absorbance (A) – time curves at 525 nm were well described by an exponential dependence $(A - A_\infty) = (A_0 - A_\infty) \cdot e^{-k_{\text{obsd}}t}$. A_0 and A_∞ correspond to the initial and final readings. Mn(II), the reduction product, is transparent at this wavelength. The linear semi-logarithmic form of first-order integrated equation was well fitted by our data for about 90% of reaction having correlation coefficients of 0.9980 – 0.9990. At constant hydrogen ion concentration, the dependence of the observed first-order rate constants on phenol concentration is presented in Table 1.

Table 1

Observed first-order rate constants at $[\text{MnO}_4^-] = 1.30 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{HClO}_4] = 0.38 \text{ mol}\cdot\text{L}^{-1}$, ionic strength $\mu = 0.4 \text{ mol}\cdot\text{L}^{-1}$ and $T = 298\text{K}$

$10^3[\text{ArOH}]$ mol·L ⁻¹	0.33	0.66	1.00	1.67	2.00	2.67	3.33	4.00	5.00	5.00	8.33
$10 k_{\text{obsd}}$ s ⁻¹	1.6	3.8	5.3	7.4	8.7	12.0	13.3	15.5	17.9	19.6	26.7

The mean value is made of at least three replicate runs, which do not differ to more than 3%. The dependence of the rate coefficient

concerning the consumption of permanganate ion on phenol concentration is linear (eq.4).

$$k_{\text{obsd}} = (3.19 \pm 1.3) \cdot 10^{-3} + (11.8 \pm 0.2)[\text{C}_6\text{H}_5\text{OH}] \tag{4}$$

The intercept can be considered zero. The correlation coefficient is $R = 0.9991$ and $SD = 2.48 \cdot 10^{-3} \text{ s}^{-1}$. In the presence of a constant concentration of $3.33 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ Mn(II), the same linear dependence has been obtained. If observed rate coefficients were compared to those in Table 1, large values were obtained at all acid or phenol concentrations. The slope, representing the apparent second-order rate constant of $(278.1 \pm 7.1) \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, is about 24 times as larger as the one obtained from eq. (4). On the other hand, when perchloric acid, phenol and permanganate were maintained constant and the initial concentration of Mn^{2+} ion was varied within

the range $6.67 \cdot 10^{-4} - 5.00 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, a linear dependence of k_{obsd} has been obtained up to $3.50 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. At higher catalyst concentration than that, the increasing effect seemed to diminish and the proportionality is not longer obeyed.

The influence of hydrogen ion concentration on the reaction rate has been tested at constant phenol concentration. Data are presented in Table 2. The permanganate ion consumption exhibits a complex dependence on the acidity. Pseudo-first-order rate constant is well described by the following equations in the absence (2-nd column) and presence of a constant concentration of $3.33 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ of Mn(II)(3-rd column).

Table 2

The effect of acid concentration on the rate. $[\text{C}_6\text{H}_5\text{OH}] = 3.33 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{MnO}_4^-] = 1.30 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $\mu(\text{ionic strength}) = 0.4 \text{ mol} \cdot \text{L}^{-1}$ and $T = 298\text{K}$ and $[\text{Mn(II)}]^{**} = 3.33 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$

$[\text{HClO}_4]$ $\text{mol} \cdot \text{L}^{-1}$	k_{obsd} s^{-1} *)	k_{obsd} s^{-1} **)
0.077	0.018	0.030
0.155	0.033	0.046
0.232	0.038	0.058
0.387	0.046	0.091
0.541	0.047	0.110
0.619	0.050	0.115
0.773	0.053	0.120

*) without Mn(II) as catalyst;

**) in the presence of Mn(II) in the initial reaction mixture

$$k_{\text{obsd}} = \frac{(0.38 \pm 0.03)[\text{H}^+]}{1 + (6.1 \pm 0.6)[\text{H}^+]}$$

$$\chi^2 = 2.12 \cdot 10^{-6} \text{ and } R^2 = 0.9946$$

$$k_{\text{obsd}} = \frac{(0.394 \pm 0.03)[\text{H}^+]}{1 + (1.9 \pm 0.23)[\text{H}^+]}$$

$$\chi^2 = 1.0 \cdot 10^{-5} \text{ and } R^2 = 0.9942.$$

The small values of χ^2 and good correlation coefficient argue the description model of experimental data. The similar dependence for the two sets of experiments suggests the same pattern of hydrogen ion involvement. From the data

$$-\frac{d[\text{MnO}_4^-]}{dt} = \left[\frac{\alpha[\text{H}^+]}{1 + \beta[\text{H}^+]} + \frac{\alpha^*[\text{H}^+]}{1 + \beta^*[\text{H}^+]} [\text{Mn}^{2+}] \right] [\text{C}_6\text{H}_5\text{OH}][\text{MnO}_4^-] \quad (6)$$

Increased reaction rate with increasing $[\text{H}^+]$ can be assigned to greater reactivity of HMnO_4 as compared to MnO_4^- , since phenol is completely un-dissociated under acidic conditions employed. If k_{obsd} values in tables 1 and 2 are divided by phenol concentration, a second-order rate constant

obtained in the absence of catalyst or in its presence the rate law, describing the decrease of permanganate ion concentration, can be written as follows:

k_2 can be computed, as dependent on the acidity. A plot of $1/k_2$ as a function of $1/[\text{H}^+]$ should be linear, and the constants α and β can be obtained for uncatalyzed reaction (small contribution of the second term in parenthesis).

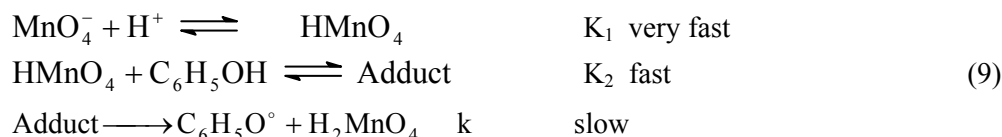
$$\frac{1}{k_2} = \frac{1}{\alpha} \frac{1}{[\text{H}^+]} + \frac{\beta}{\alpha} \quad (7)$$

This plot gave a straight line with $R^2 = 0.9850$ and $SD = 0.007 \text{ L}^{-1}\cdot\text{mol}\cdot\text{s}$. Because of the scatter of the points, the correlation coefficient is not as good as previously obtained. From the intercept and the slope, the corresponding constants are $\alpha = (98.2 \pm 6.1) \text{ L}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$ and $\beta = (4.7 \pm 0.7) \text{ L}\cdot\text{mol}^{-1}$. These

$$\frac{1}{\Delta k_2} = \frac{\beta^*}{\alpha^*} + \frac{1}{\alpha^*[H^+]} \quad \frac{1}{\Delta k_2} = (2.6 \pm 0.5) \cdot 10^{-3} + (1.2 \pm 0.1) \cdot 10^{-3} \frac{1}{[H^+]} \quad (8)$$

From here, considering the Mn(II) concentration, $\alpha^* = (2.5 \pm 0.2) \cdot 106 \text{ L}^3\cdot\text{mol}^{-3}\cdot\text{s}^{-1}$ and $\beta^* = (2.6 \pm 0.5) \text{ L}\cdot\text{mol}^{-1}$, respectively for the manganese ion catalyzed reaction.

The effect of temperature on the reaction has been investigated in the range of 15 - 40°C on the observed first-order rate constant. A straight line Arrhenius plot has been obtained (correlation coefficient 0.9972). The apparent activation energy for permanganate consumption is $12.5 \pm 1.4 \text{ kJ}\cdot\text{mol}^{-1}$,



One question that remains, concerns the nature of the adduct intermediate that is formed from permanganic acid and phenol. It seems likely to consider this as an inner-complex $\text{C}_6\text{H}_5\text{OMnO}_2(\text{OH})_2$, with a covalent bond between phenol oxygen and manganese (VII) atom. Sharpless *et al.*³⁸ have presented evidence that all oxidation reactions by transition metal oxy anions could be initiated by formation of similar intermediates. Oxidation by Cr(VI) of various organic or inorganic substrates proceeds by

$$\text{rate} = \frac{d[\text{Mn(VII)}]_t}{dt} = \frac{kK_1K_2[H^+][\text{C}_6\text{H}_5\text{OH}]}{1 + K_1[H^+]\{1 + K_2[\text{C}_6\text{H}_5\text{OH}]\}} [\text{Mn(VII)}]_t \quad (10)$$

K_1 is the reciprocal value of the acid dissociation constant of permanganic acid⁴⁰ and should be of the order of magnitude of 10^{-2} , K_2 is the adduct formation constant and k is the rate

$$k_{\text{obsd}} = \frac{kK_1K_2[H^+][\text{C}_6\text{H}_5\text{OH}]}{1 + K_1[H^+]\{1 + K_2[\text{C}_6\text{H}_5\text{OH}]\}} \quad (11)$$

In acidic media, the intermediate states of manganese, formed from the beginning of the run, react faster with the initial organic substrate or its

values are close to those obtained by fitting the data in eq.(5). To calculate α^* and β^* in eq.(6) a similar plot can be used. It contains the differences between k_{obsd} in the presence and absence of Mn(II) divided by phenol concentration, to account for catalyzed reaction. The linear equation is:

a value quite small for the removal of a hydrogen atom from phenol. It indicates the involvement of some exothermic pre-equilibrium.

The "one-plus" form³⁷ of the pseudo-first-order rate constant in eq.(6) also suggests the involvement of at least two consecutive reaction steps (two terms in the denominator). Kinetic data fit well with the following reaction scheme, for the start of the process:

formation of such intermediates.³⁹ The manganic acid is unstable in acidic media and reacts faster, either by auto-oxidation-reduction, or by oxidation of any reducing species in solution. The phenoxy radicals generate rapidly 4,4'-biphenolquinone. At 525 nm all compounds of Mn(VII) have some contribution to the absorbance monitored as function of reaction time. Therefore, based on the mechanism (9), the concentration balance and pre-equilibria, the rate of Mn(VII) consumption is:

constant for phenoxy radical formation. The first-order rate constant expression (11) is in agreement with eq. (6).

oxidized successors. This explains the increased values of k_{obsd} in the presence of the catalyst.

The stoichiometry found implies that the partial oxidized products of phenol should react rapidly further, up to the ring rupture, even in the presence of phenol excess with any oxidizing species in solution. The complexity of the system needs more data for a complete elucidation. A separate approach of the reaction of the intermediate oxidized species of phenol may be undertaken. Research is in progress in our laboratory, and new data will hopefully illuminate these aspects of the process.

EXPERIMENTAL

Materials. Chemicals of analytical grade and de-ionized and tetra-distilled water were used in this study. Stock solutions of HClO_4 and NaClO_4 were prepared from Merk's 70% HClO_4 solution and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ respectively and standardized by titration (after passing through Vionit -100C H-form cationic resin in the case of NaClO_4). Solution of KMnO_4 was prepared before each set of runs and standardized by titration with oxalic acid. The phenol solution was freshly prepared from purified stuff (distillation under low pressure; m.p. 40.5 – 41.5°C).

Spectra. Electronic absorption spectra were recorded either by using a M-40 Diode-Array Spectrophotometer or a Jasko UV-VIS V-530 spectrophotometer.

Kinetic measurements. The reaction was followed spectrophotometrically at constant temperature and at wavelength of 525 nm, where permanganate ion exhibits an absorption peak. The reaction was performed in a 5-cm path length quartz cuvette. It was started by injection of 5 mL permanganate solution (within at most 1 s) over the mixture of the other reactants. Pseudo-first-order conditions were employed with phenol and mineral acid taken in large excesses. Some kinetic measurements were carried out in the presence of Mn(II) ions.

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