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A kinetic study of the early steps in the oxidation of chlorophenols by hydrogen peroxide catalyzed by a water-soluble iron(III) porphyrin†

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The kinetics and mechanism of the initial steps in the oxidation of 2,4,6-trichlorophenol by hydrogen peroxide using iron(III) *meso*-tetra(4-sulfonatophenyl)porphine chloride as a catalyst were studied in this work. The first oxidation step is the formation of a substituted 1,4-benzoquinone. This step was also studied using a selection of differently substituted chlorophenols. It was shown that the rate constants characteristic for the oxidation of the substrate do not follow the pattern of pK_as, but correlate well with the ^{13}C chemical shifts of the carbon atoms directly bonded to the oxygen in chlorophenols. The kinetics of the catalyzed and uncatalyzed oxidation of 2,6-dichloro-1,4-benzoquinone by hydrogen peroxide was also studied. The catalyzed and uncatalyzed pathways give different products.

Introduction

Polychlorinated phenols are used as wood preservatives, pesticides, fungicides, herbicides, insecticides or disinfectants, and they are also present in the waste from paper mills. These compounds are highly toxic, persistent, and regarded as priority pollutants for which efficient chemical treatment processes are needed.[1–3] Oxidative degradation is probably the most advantageous reaction type for this purpose and several different methods have been reported. Chemical methods usually use H_2O_2 or $KHSO_5$ as a stoichiometric oxidant and iron complexes involving mostly N-donor ligands as catalysts.[1,2,4–11] TiO_2-based systems for photodegradation,[12–16] ozonization,[17] heterogeneous catalysis[18,19] and bacterial methods[20,21] have also been thoroughly studied.

Despite the large number of papers published in this field, very few high quality kinetic studies can be found in the literature. Mechanisms for parts of the oxidation process are often proposed, but they are usually based on using chemical common sense and previous knowledge about similar reactions. The largest problem with obtaining high-quality kinetic information is the complexity of the system, which makes the application of on-line detection methods (UV-vis, NMR) complicated. Off-line methods such as LC or GC are sometimes used to analyze the time-dependent composition of reaction mixtures during chlorophenol oxidation.[22] These methods usually require quenching of the original reaction and some kind of sample treatment or derivatization before analysis, both of which are major possible sources of unknown secondary chemical reactions. Used with care, these methods usually provide valuable information on the identity of the intermediate(s) or product(s) present in relatively high concentrations, but it is seldom possible to determine high-quality kinetics because of the inherent errors in concentrations and the time-consuming analysis steps.

In this paper, we present our results using an insightful selection of different chlorophenols, and also report detailed kinetic studies on the second step in the oxidation of 2,4,6-trichlorophenol (TCP), which is one of the most significant pollutants among chlorinated phenols and is often used to test the efficiency of oxidation methods.[1,2] It is also our goal to show that on-line methods (UV-vis spectroscopy and ion-selective potentiometry) can also be used to follow the kinetics of the oxidation process. The chemical structures of the catalyst and the most important two substrates are given in Chart 1.

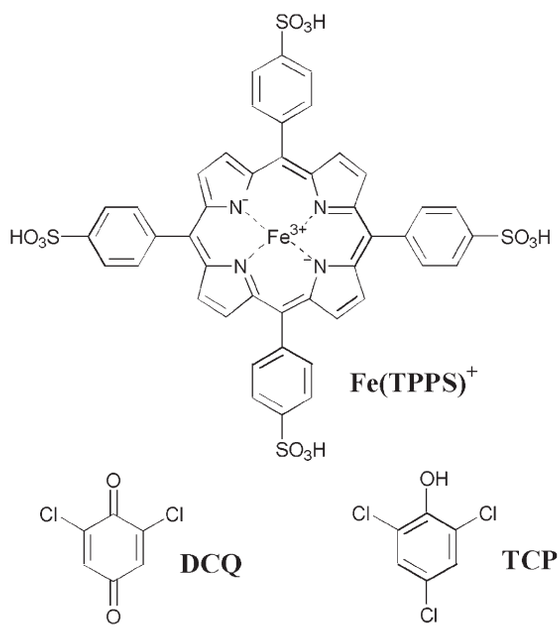

Chart 1 Structural formulas of the catalyst, 2,4,6-trichlorophenol (TCP), and 2,6-dichloro-1,4-benzoquinone (DCQ).

† Electronic supplementary information (ESI) available: figures providing additional data on the catalytic oxidation of TCP, as well as the calibration curve for the chloride ion selective electrode. See http://www.rsc.org/suppdata/nj/b4/b400482e/

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Experimental

Materials

Chlorophenols and 2,6-dichloro-1,4-benzoquinone were purchased from Aldrich and Lancaster and purified by vacuum sublimation. Iron(III) *meso*-tetra(4-sulfonatophenyl)porphine chloride was used as received from Frontier Scientific (www.porphyrin.com). 2,4,6-Trichlorophenol-3-5-d_2 was synthesized from phenol-d_6, HCl and H_2O_2 using a literature method reported for the preparation of undeuterated 2,4,6-trichlorophenol.[23] Ion-exchanged and ultrafiltered water from a Millipore MILLI-Q purification system was used to prepare the solutions. The concentration of hydrogen peroxide stock solutions was determined iodometrically.

Instrumentation and computations

NMR spectra were recorded in $CDCl_3$ and referenced to the residual proton signal of the deuterated solvent. The pK_a values were determined by a combined pH-metric and UV-vis spectrophotometric technique.[24] In potentiometric experiments, a combination of pH and chloride ion selective electrodes was used, connected to a precision pH-meter. The electrodes were calibrated daily using standard buffers and NaCl solutions. Kinetic experiments with the chloride ion selective electrode were always carried out with a small amount of NaCl added prior to the experiment (referred to as $[Cl^-]_0$ in the figure captions) in order to avoid badly defined voltage readings at the beginning of the kinetic curves. Constant ionic strength was maintained with 0.1 M $NaNO_3$ in both potentiometric and spectrophotometric studies. An oxygen monitor was used to measure the concentration of dissolved oxygen. All experiments were carried out in the dark because light (even fluorescent room light) significantly accelerates further oxidation.[25] Our experience has shown that the monochromatic analyzing light beam of a scanning spectrophotometer or stopped-flow instrument is not intense enough to influence the reaction, but the white light used in a diode-array spectrophotometer corrupts the measurements. Nonlinear least-squares fitting was carried out using the software package Scientist.[26]

Results and discussion

General observations

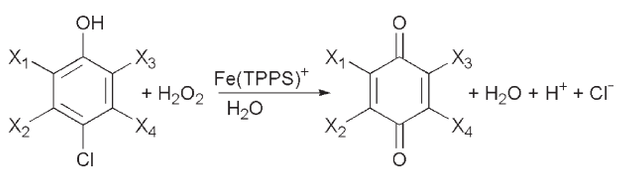
An earlier study on the oxidation of TCP by H_2O_2 using Fe(TPPS)$^+$ as a catalyst found that DCQ was the final product of the oxidation.[7] These experiments were done in citrate buffered CH_3CN. With unbuffered aqueous solution, as explained later, the oxidation is much deeper. Total organic carbon measurements showed that about 40% of the organic carbon content was lost after the completion of the process (about 24 h), indicating the formation of carbon dioxide. Almost all chlorine ($>97\%$) present initially in TCP was transformed onto chloride ion, according to measurements with a chloride ion selective electrode. Citric acid had a slight inhibiting effect on the oxidation of TCP under acidic conditions. Treatment of DCQ with H_2O_2 in the presence of Fe(TPPS)$^+$ also produced chloride ions, showing that DCQ cannot be a stable final product of TCP oxidation under these conditions.

The oxidation process was followed by UV-vis and a chloride ion selective electrode. It was shown that no oxidation occurs in solutions containing hydrogen peroxide and chlorophenols without catalysts. The catalytic experiments were usually carried out in air-saturated solutions. The reaction was tested for the effect of oxygen. The UV-vis curves were the same under air-free and aerobic conditions [see Electronic supplementary information (ESI)]. Experiments with an oxygen measuring system showed that the concentration of dissolved oxygen increases slightly during the first 20 min of the catalyzed reaction, but the overall change was less than 10% (see ESI). The increase in O_2 concentration was somewhat faster when no TCP was present in the solutions, so this effect was rationalized as decomposition of H_2O_2 slightly catalyzed by Fe(TPPS)$^+$. In conclusion, the presence of oxygen does not influence the oxidation reaction.

The pH was also followed in a few experiments. In an oxidation experiment, the original pH of a TCP test solution (5.2) decreased to a final pH of about 2.8 in 15 h (see ESI). This confirmed that the reaction produces acid. However, as will be explained later, the rate of the reaction did not depend on pH in this region and no buffers were used in this study.

Oxidation of chlorophenols to benzoquinones

The first step of the oxidation of a chlorophenol is the formation of a substituted 1,4-benzoquinone,[22,27] which is a detectable intermediate in the overall oxidation process. Eqn. (1) gives the stoichiometry of the reaction:



(1)

The reactions shown in Scheme 1 allow one to interpret the kinetic observations for all of the chlorophenol substrates used in this study.

This scheme is an extension of an earlier kinetic model postulated using the same catalyst in an oxidation process[28] and is based on measuring chloride ion concentrations using an ion selective electrode and UV-vis measurements carried out at 395 nm, corresponding to the intense Soret band of the catalyst Fe(TPPS)$^+$. Standard steady-state treatment for Cat′ in this scheme, assuming constant concentrations of S (substrate) and H_2O_2, gives the following time-dependent expression for the concentration of Cl^-:[29]

$$[Cl^-] = \frac{k_2}{k_3}[S]_0\left[Fe(TPPS)^+\right]_0 \times \left(1 - e^{-k_\Psi t}\right) \qquad (2)$$

where the pseudo-first-order rate constant k_Ψ is given as:

$$k_\Psi = \frac{k_1[H_2O_2]}{(k_2k_3)[S] + 1} \qquad (3)$$

The initial rate for the concentration of Fe(TPPS)$^+$ can also be calculated from:

$$\left(\frac{d\left[Fe(TPPS)^+\right]}{dt}\right)_{t=0} = -\left(\frac{k_1[H_2O_2]_0}{(k_2k_3)[S]_0+1}\right) \times \left[Fe(TPPS)^+\right]_0 \qquad (4)$$

The chemical sense of the mechanism given in Scheme 1 is that the catalyst reacts with H_2O_2, first forming a highly oxidizing intermediate, Cat′, which oxidizes the substrate (k_2) and gives the original Cat form back, or decomposes to a much less active form, Cat″ (k_3). Catalyst decomposition occurs

$Cat + H_2O_2 \rightarrow Cat'$	$v_1 = k_1[Cat][H_2O_2]$
$Cat' + S \rightarrow Cat + Cl^- + OxS$	$v_2 = k_2[Cat'][S]$
$Cat' \rightarrow Cat''$	$v_3 = k_3[Cat']$

Scheme 1

in competition with oxidation of the substrate and typically 10–15% of the substrate is oxidized in the TCP system before practically all of the catalyst is transformed to the Cat″ form. As pointed out above in this paper, there is evidence for further slow oxidation, but the process is not significant until after the initial period, which usually takes 5–15 min. Under steady-state conditions, one cannot hope to determine all three rate constants appearing in Scheme 1 independently;[29] only k_1 and the ratio k_2/k_3 can be resolved. Another interesting aspect of the scheme is that the reaction rate is independent of the pH in the pH range 2–5, in agreement with experimental results. At higher pH, $Fe(TPPS)^+$ forms a μ-oxo dimer,[30] which seems to be catalytically inactive.

Scheme 1 features only one rate constant, k_2, that is dependent on the identity of the substrate used. As discussed earlier, the value of k_2 cannot be determined, only the k_2/k_3 ratio. The value of this ratio is characteristic of the substrate used and the values were calculated using two different methods. From chloride ion kinetic data, the overall concentration of chloride ion produced ($[Cl^-]_{final}$) in the first stage can be used to estimate the k_2/k_3 value:

$$\frac{k_2}{k_3} = \frac{[Cl^-]_{final}}{[S]_0[Fe(TPPS)^+]_0} \quad (5)$$

From UV-vis curves, the initial rate affords a reliable way to determine k_2/k_3. The initial rate of absorbance change in the presence of substrate (v_0) is measured and then compared to the initial rate measured in a reference experiment, where H_2O_2 and the catalyst is used in the same concentration without any substrate added [v_0(ref)]:

$$\frac{k_2}{k_3} = \frac{1}{[S]_0}\left(\frac{v_0(\text{ref})}{v_0} - 1\right) \quad (6)$$

The k_2/k_3 values determined for different chlorophenols are summarized in Table 1. It should be noted that 2,6-dichlorophenol does not have a chlorine substituent in the para position. However, the experimental data showed that the oxidation product in this case is also the corresponding substituted *p*-benzoquinone, that is 2,6-dichloro-1,4-benzoquinone, which was identified from its UV-vis spectrum. No chloride ion was formed in the first stage of the reaction, but k_2/k_3 could be determined spectrophotometrically. 2,2′,6,6′-Tetrachlorodiphenoquinone is another possible, although not particularly likely, product of the oxidation of 2,6-dichlorophenol through the symmetric oxidative coupling of two aromatic rings.[31] This compound absorbs strongly at 400 nm[32] and UV-vis experiments showed that it was not formed at all. We attempted to oxidize unsubstituted phenol as well and determine its k_2/k_3 value, but the product was not the expected 1,4-benzoquinone. The product, most likely diphenoquinone, had a large absorption at the wavelength used for the UV-vis experiments, making quantitative evaluation impossible.

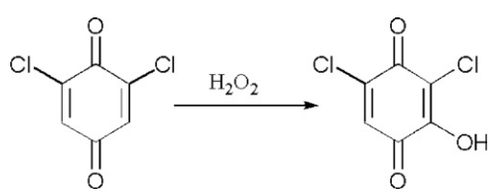
The values listed in Table 1 span a range of two orders of magnitude. It is interesting to note that 2,6-dichlorophenol and 2,4,6-trichlorophenol (TCP) have almost the same k_2/k_3 values. This may be somewhat unexpected because the substituent in the para position must be directly involved in the chemical reaction. However, the ortho substituents, although not involved in the reaction directly, seem to have a large effect on the k_2/k_3 values. TCP-d_2 and TCP also have values that are the same within the error limits, showing the absence of primary deuterium isotope effects in agreement with expectations. Fig. 1 shows that the k_2/k_3 values do not correlate with the pK_a values of the chlorophenols. Fig. 2 shows that the correlation is much better with the ^{13}C chemical shift of the carbon atom directly bonded to the oxygen in the chlorophenol (Chart 2).

One can but speculate that the first step of phenol oxidation might be hydrogen atom abstraction. If this is indeed the case, the k_2/k_3 values should be related to the homolytic O–H bond dissociation energies, which generally do not follow the pattern of pK_as. Unfortunately, no detailed literature data are available on the O–H bond strengths. However, studies of dioxin formation in incinerators suggested that gradual chlorination of phenol should decrease the O–H bond energies and it has been estimated that the O–H bond energy in TCP is about 5 kcal mol^{-1} less than that of the parent phenol.[33] These results are in qualitative agreement with the trend of the k_2/k_3 values observed here; more detailed data would be needed for quantification. The successful correlation shown in Fig. 2 might suggest that ^{13}C chemical shifts, which should be related to the electron density around the carbon nucleus, are in some way indicative of the O–H bond strengths, although this conclusion is highly speculative at this point.

Uncatalyzed oxidation of 2,6-dichloro-1,4-benzoquinone

Previous work and our observations showed without doubt that the first step of the oxidation of TCP is the formation of DCQ.[7,22,25,27] We also confirmed that DCQ was not a final product and made efforts to identify the next step in the oxidation sequence and study its kinetics.

1,4-Benzoquinone is oxidized to 2-hydroxy-1,4-benzoquinone by hydrogen peroxide in basic aqueous solution.[34] Our observations showed that the same product is formed in acidic solution as well. In addition, oxidation of DCQ by H_2O_2 in acidic solution also gave the analogous substituted product, 3-hydroxy-2,6-dichloroquinone [eqn. (7)]:



(7)

Table 1 Values of k_2/k_3 determined for different substrates at 25.0 °C

Substrate	$k_2/k_3/10^4$ M^{-1}	Method[a]	^{13}C δ	pK_a
2,4,6-Trichlorophenol-d_2	16 ± 2	a	147.1	6.10
2,4,6-Trichlorophenol (TCP)	14 ± 1	a	147.1	6.15
2,6-Dichlorophenol	13 ± 1	b	148.1	6.77
2,4-Dichlorophenol	3.7 ± 0.3	c	150.3	7.83
2,6-Dichloro-1,4-benzoquinone (DCQ)	2.1 ± 0.3	a	—	—
2,4,5-Trichlorophenol	1.6 ± 0.1	a	150.8	6.97
3,4-Dichlorophenol	0.32 ± 0.02	c	154.6	8.56
4-Chlorophenol	0.27 ± 0.01	a	153.8	9.34

[a] Key for methods: (a) Cl^- and UV-vis methods together, (b) UV-vis method only, (c) Cl^- method only.

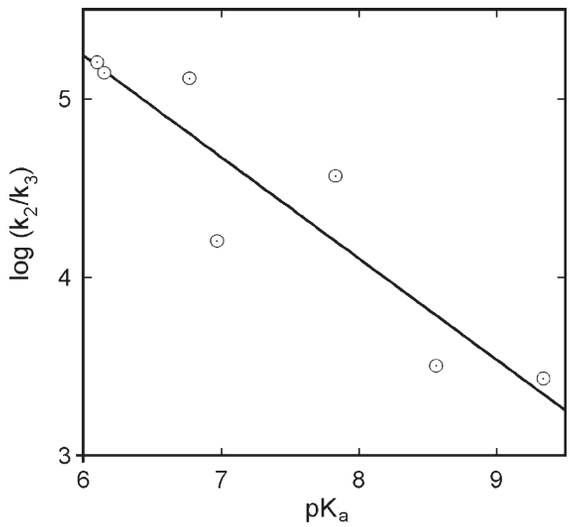


Fig. 1 Ratio of rate constants k_2/k_3 as a function of the pK_a of the chlorophenols (25.0 °C).

To our knowledge, this compound was only characterized in a single previous work as a product of a photochemical reaction.[35] 3-Hydroxy-2,6-dichloroquinone was found to be fairly stable in dilute aqueous solution, but could not be isolated in a pure form due to its reactivity; it is a relatively strong acid with pK_a about 1.6 and the corresponding dissociated anion has a characteristic UV-vis absorption ($\lambda_{max} = 524$ nm; $\varepsilon = 2530$ M^{-1} cm^{-1}),[35] which was used for identification in this work.

The kinetics of the reaction could be easily followed by monitoring the peak of the product anion. The process was complete within 10 s under neutral or basic conditions, but was slower in acidic solutions. Sample kinetic curves are given in Fig. 3. Some absorbance decrease was also detectable at longer times, indicating that the product is not completely stable, in agreement with earlier data obtained for other hydroxybenzoquinone derivatives.[36] The early parts of the kinetic traces (up to 15 minutes), where DCQ was oxidized, were well-separated from the later unexplored secondary reactions (hours) and could be treated independently. Experiments were done at large H_2O_2 excess. These curves gave an excellent fit to an exponential function, indicating that the process is first-order with respect to the limiting reagent DCQ. The pseudo-first-order rate constant at constant pH was proportional to the concentration of H_2O_2 (Fig. 4). The initial rate showed an inverse dependence on the hydrogen ion concentration (Fig. 5). Thus, the experimental rate equation of the process is:

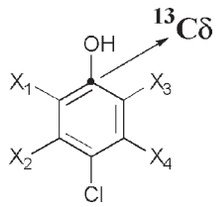


Chart 2

$$v = k_{uncat}\frac{[DCQ][H_2O_2]}{[H^+]} \quad (8)$$

The value $k_{uncat} = (2.7 \pm 0.1) \times 10^{-7}$ s^{-1} was determined with least-squares fitting at 25.0 °C and 0.1 M ionic strength ($NaNO_3$ or acetate buffer). The deprotonation of DCQ is very unlikely and our NMR observation also showed that DCQ does not exchange its hydrogens in D_2O. Therefore, the deprotonation of H_2O_2 is most likely responsible for the inverse hydrogen ion dependence. H_2O_2 is known to have a pK_a of about 12 at 25.0 °C.[37] Because pK_a > pH over the pH range (2–5.5), HO_2^- is present at low concentration levels. However, with pK_a *ca.* 12, one can calculate the actual second-order rate constant for the reaction between DCQ and HO_2^- as *ca.* 3×10^5 M^{-1} s^{-1}, which is clearly not approaching the diffusion-controlled limit and therefore appears to be a reasonable value for the process.

Catalytic oxidation of 2,6-dichloro-1,4-benzoquinone

In the presence of the $Fe(TPPS)^+$ catalyst, the oxidation of DCQ with H_2O_2 gave a product different from the one obtained in the uncatalyzed process. As shown in Fig. 6, chloride ion was clearly produced during the reaction. Fig. 7 shows absorbance traces at two wavelengths: 395 nm, where primarily the catalyst is monitored, and 524 nm, where 2,6-dichloro-3-hydroxy-1,4-benzoquinone is the dominant absorbing species but the catalyst also provides some absorbance contribution. It can again be seen that 2,6-dichloro-3-hydroxy-1,4-benzoquinone is not a product of the catalyzed pathway. If it were, an absorbance increase of about 0.2 units would

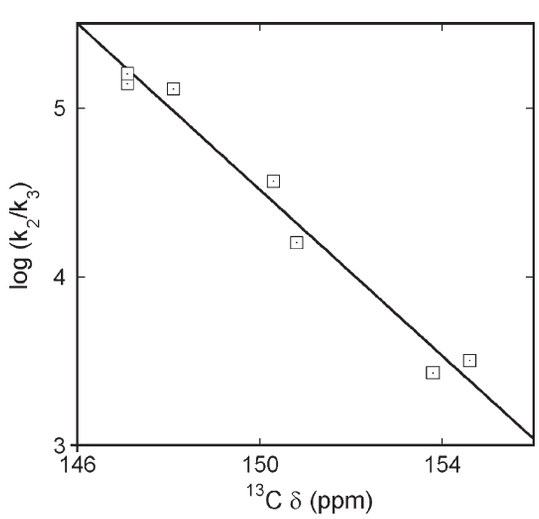


Fig. 2 Ratio of rate constants k_2/k_3 as a function of the ^{13}C chemical shift of the carbon atom bonded to the oxygen in chlorophenols (25.0 °C).

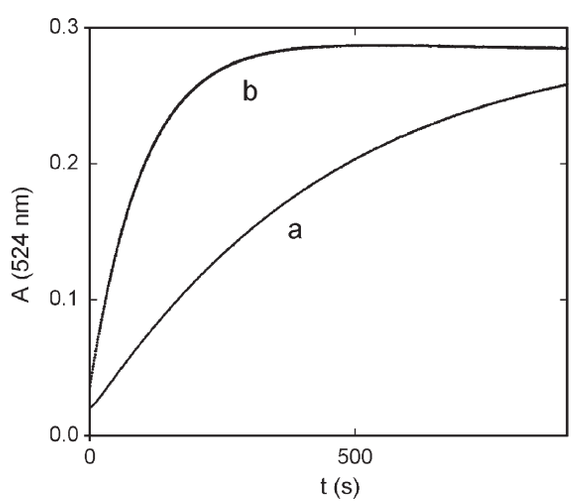


Fig. 3 Kinetic traces taken during the reaction of 0.28 mM 2,6-dichloro-1,4-benzoquinone with a $[H_2O_2]$ of (a) 37 and (b) 187 mM at pH = 5.25, $\mu = 0.1$ M (acetate buffer), 25.0 °C, $\lambda = 524$ nm and path length of 1 cm.

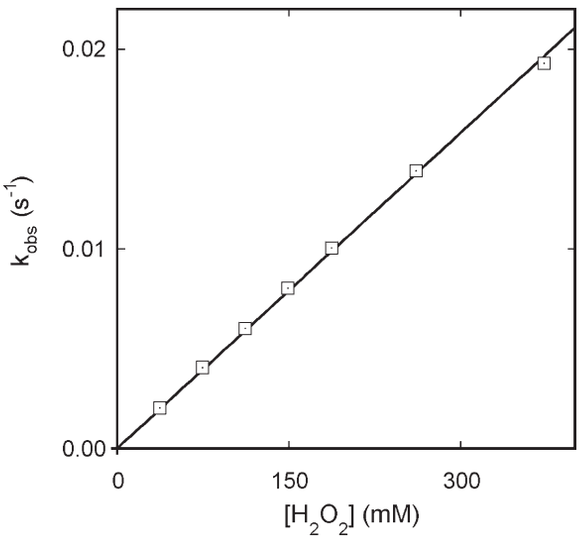


Fig. 4 Pseudo-first-order rate constants as a function of the concentration of H_2O_2 during the reaction of 2,6-dichloro-1,4-benzoquinone with H_2O_2: pH = 5.25, μ = 0.1 M (acetate buffer), 25.0 °C.

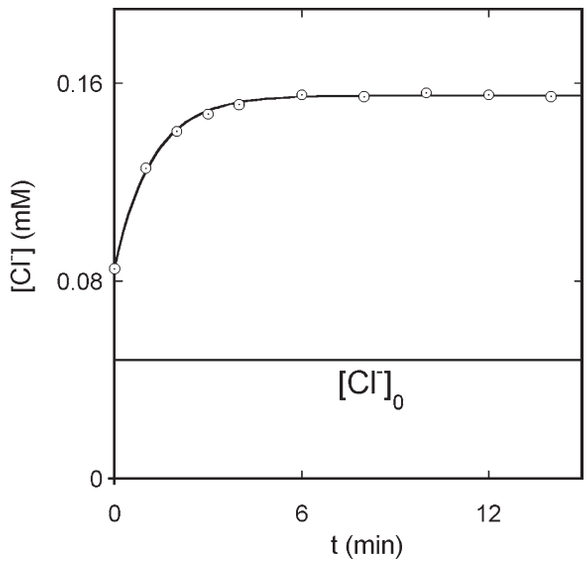


Fig. 6 Chloride ion concentration as a function of time during the reaction of 2,6-dichloro-1,4-benzoquinone with H_2O_2 catalyzed by $Fe(TPPS)^+$: [DCQ] = 1.63 mM, [H_2O_2] = 139 mM, [$Fe(TPPS)^+$] = 2.9 μM, μ = 0.1 M ($NaNO_3$), 25.0 °C, [Cl^-]$_0$ = 48 μM.

be expected at 524 nm in the first 3 min rather than the small decrease observed experimentally. At later times, relatively slow formation of 2,6-dichloro-3-hydroxy-1,4-benzoquinone produced in the uncatalyzed pathway is observed at 524 nm. The kinetic observations in the catalytic oxidation of DCQ are in agreement with Scheme 1. The value of k_2/k_3 was determined both with the chloride selective (2.3×10^4 M^{-1}) and the spectrophotometric (1.9×10^4 M^{-1}) methods. The agreement of the two values, which is not obvious in this case, shows that one Cl^- is produced for every DCQ consumed in the process. The identity of the product formed in the catalytic reaction is not very easily confirmed. One possibility is that one of the chlorine atoms in DCQ might be substituted with a hydroxyl group in this process. However, based on the UV-vis observations, the product is not a substituted hydroxy-1,4-benzoquinone, which has strong absorption in the visible range around 500 nm.[35,38] The product is only formed in relatively small concentrations and the 2,6-dichloro-3-hydroxy-1,4-benzoquinone formed simultaneously in the uncatalyzed pathway hindered our attempts to characterize it more thoroughly.

Later steps in the oxidation of 2,4,6-trichlorophenol

From the data collected in Table 1, it is possible to draw further conclusions for the catalytic oxidation of TCP, which has a k_2/k_3 value that is about an order of magnitude larger than that for DCQ. Consequently, when TCP is present in the oxidation system, DCQ is not oxidized. In other words, DCQ accumulates during the oxidation and becomes a detectable intermediate. However, DCQ is slowly oxidized by H_2O_2 under the somewhat acidic conditions of TCP oxidation in the direct pathway without the involvement of the catalyst. Therefore, 2,6-dichloro-3-hydroxy-1,4-benzoquinone, the oxidation product of the uncatalyzed DCQ oxidation pathway, should be observable in the system. An experimental confirmation of this prediction is shown in Fig. 8. This figure shows an experiment where a sample was taken 1 h after starting the catalyzed oxidation of TCP in the dark; this sample was titrated with strong acid as quickly as possible. The pH and UV-vis spectra were measured simultaneously. The original

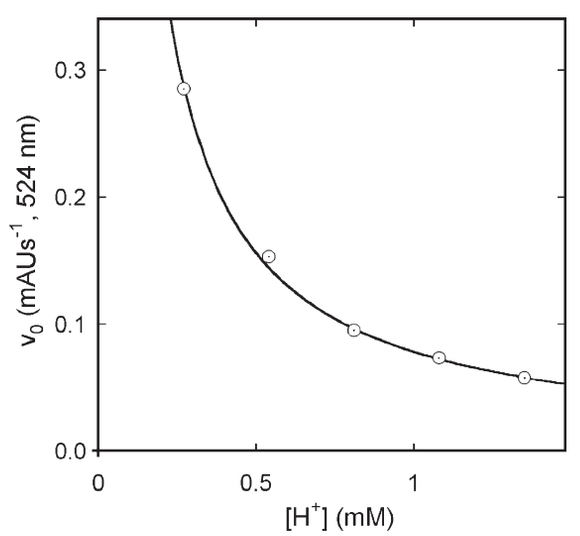


Fig. 5 Initial rate as a function of the concentration of hydrogen ion during the reaction of 2,6-dichloro-1,4-benzoquinone with H_2O_2: [DCQ] = 0.38 mM, [H_2O_2] = 373 mM, μ = 0.1 M (acetate buffer or $NaNO_3$), 25.0 °C, λ = 524 nm and path length of 1 cm.

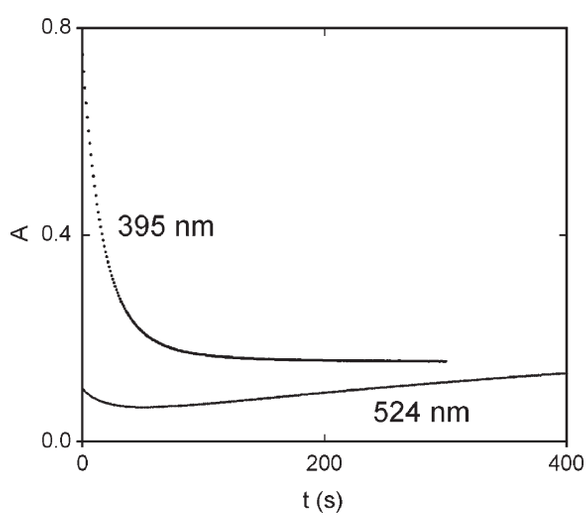


Fig. 7 Kinetic traces during the reaction of 2,6-dichloro-1,4-benzoquinone with H_2O_2 catalyzed by $Fe(TPPS)^+$: [DCQ] = 0.51 mM, [H_2O_2] = 75 mM, [$Fe(TPPS)^+$] = 6.2 μM, μ = 0.1 M ($NaNO_3$), 25.0 °C and path length of 1 cm.

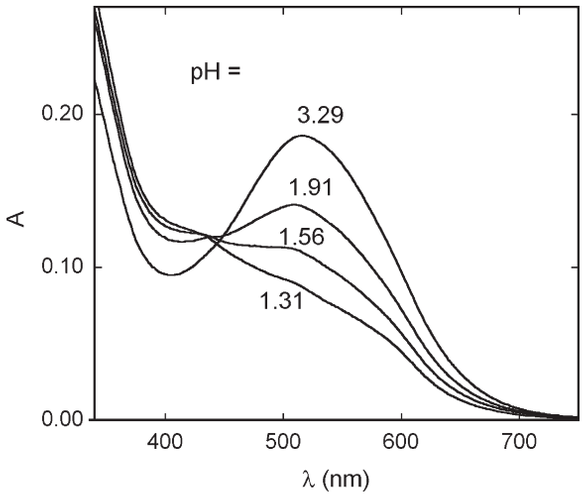


Fig. 8 UV-vis spectrophotometric identification of 2,6-dichloro-3-hydroxy-1,4-benzoquinone in a sample taken from the $Fe(TPPS)^{+}$ catalyzed oxidation of 2,4,6-trichlorophenol by H_2O_2. The sample was titrated with HCl. $\mu = 0.1$ M ($NaNO_3$), 25.0 °C and path length of 1 cm. pH values are shown on the figure itself.

sample had a pH of 3.29 and the UV-vis spectrum was the same as the independently known spectrum of dissociated 2,6-dichloro-3-hydroxy-1,4-benzoquinone. Furthermore, quantitative evaluation of the titration data gave a characteristic pK_a of 1.7 ± 0.1. This is also in good agreement with the pK_a of 2,6-dichloro-3-hydroxy-1,4-benzoquinone (1.57) known independently from the earlier photochemical study.[35]

Conclusions

An important conclusion from the results presented in this paper is that the rate constants characteristic for the catalytic oxidation of different chlorophenols do not follow the pattern of pK_as, but correlate well with the ^{13}C chemical shifts of the carbon atoms directly bonded to the oxygen in chlorophenols. In addition, a study of the catalyzed and uncatalyzed oxidations of 2,6-dichloro-1,4-benzoquinone by hydrogen peroxide showed that the two pathways give different products. In the oxidation sequence starting from a chlorophenol, the uncatalyzed pathway of this process, which produces a substituted hydroxybenzoquinone, is much more important than the catalyzed pathway.

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