The Kinetics and Mechanism of Oxidation of Hydroquinone and Chlorohydroquinone in the Presence of Nitrous Acid in Aqueous Acid Solution

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Hydroquinone is converted quantitatively into benzoquinone by nitrous acid in air-saturated aqueous acid solution, by a process which is kinetically first order, whether or not the nitrous acid is present in excess. Chlorohydroquinone behaves similarly and substituent effects are discussed. The inorganic and organic steps in the mechanism put forward are shown by numerical integrations to account for all the observations. MOPAC calculations suggest that 4-hydroxy-6-nitrosocyclohexa-2,4-dienone is the first-formed intermediate. Homolysis of this to give the 4-hydroxyphenoxyl radical and nitric oxide is rate determining in the organic sequence and takes place by uncatalysed and acid catalysed pathways. Comparison with previous work on 4-methoxyphenol, where the later step of combination of the 4-methoxyphenoxyl radical with nitrogen dioxide is rate determining, permits an estimate of the relative rate-constants for reaction of the substituted phenoxyl radical with NO and NO_2.

Previous work has demonstrated that the kinetics of the reactions of nitrous acid with 4-phenoxyphenol[1] (giving the 2-nitro-derivative) and 4-methoxyphenol[2] [giving a mixture of the 2-nitro-derivative (NMP) and benzoquinone (BQ)] are very sensitive to the concentration of dissolved oxygen. A mechanism was put forward[2] which accounted for the observations and consisted of five inorganic steps (Scheme 1) and six organic steps (Scheme 2). In the schemes solvent water has been omitted so that the significance of the rate constants is clear. N_2O_4 and N_2O_3, though intermediates in steps (*a*) and (*b*) respectively, can be ignored in the kinetic analysis because under the conditions used their concentrations would at all times be extremely small. At the acidities used, nitric acid is completely dissociated to nitrate ion, but nitrous acid is predominantly undissociated.

$$2NO_2 + \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNO_2 + NO_3^- + H^+ \qquad (a)$$

$$2HNO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO + NO_2 \qquad (b)$$

$$2NO + O_2 \xrightarrow{k_3} 2NO_2 \qquad (c)$$

Scheme 1

$$MeOC_6H_4OH + HNO_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} MeOC_6H_4O^{\bullet} + NO$$

$$MeOC_6H_4O^{\bullet} + NO_2 \xrightarrow{k_5} NMP$$

$$MeOC_6H_4O^{\bullet} + NO_2 \xrightarrow{k_6} BQ + HNO_2 + MeOH$$

$$MeOC_6H_4O^{\bullet} \xrightarrow{k_7} HOC_6H_4O^{\bullet} + MeOH$$

$$HOC_6H_4O^{\bullet} + HNO_2 \xrightarrow{k_8} BQ + NO$$

Scheme 2

The step with rate constant k_4 in Scheme 2 produces the substituted phenoxyl radical. It seemed likely to us that the present substrates might differ from those previously studied in that the k_4 step might be rate-determining in the organic process, because the 4-hydroxyphenoxyl radical is very readily oxidized by loss of a hydrogen atom to give the product benzoquinone. Scheme 2 could then be replaced by Scheme 3 consisting only of the first (slow) and last (fast) steps of Scheme 2. The kinetics would then be simpler because the oxides of nitrogen are not involved prior to the transition state, and dissolved oxygen can exert its influence on the kinetics only through its effect on the concentration of nitrous acid.

$$HOC_6H_4OH + HNO_2 \xrightarrow{k_4} HOC_6H_4O^{\bullet} + NO \qquad (d)$$

$$HOC_6H_4O^{\bullet} + HNO_2 \xrightarrow{k_8} OC_6H_4O + NO \qquad (e)$$

Scheme 3

These predictions were fully borne out by the studies described below. In addition, quantum mechanical calculations are reported which indicate that the kinetically insignificant intermediate[2,3] in step (*d*), not shown in Schemes 2 and 3, is a cyclohexadienone, and the experiments show that its homolysis to the 4-hydroxyphenoxyl radical and nitric oxide is rate-determining and takes place by uncatalysed and acid catalysed pathways.

Results

When nitrous acid is added to excess hydroquinone in air-saturated aqueous acid solution, the hydroquinone is converted quantitatively into benzoquinone. Only a catalytic concentration of nitrous acid need be present, and the yield based on nitrous acid can be several hundred percent. In contrast, when nitrous acid is added to excess hydroquinone in aqueous acid solution from which dissolved oxygen has been removed by freeze–thaw cycles under vacuum, the extent of reaction is very small.

Kinetics of reaction in air-saturated solution were studied using full cells as previously[2] to prevent further ingress of oxygen due to phase transfer from the air. Repeat UV scans reveal an isosbestic point. (Towards the end of the reaction there is some small deviation due to slow benzoquinone decomposition as noted previously.[2] We have not investigated this.)

The reaction shows a first-order kinetic form over at least three half-lives; deviations from this form were barely detectable in contrast to what was observed in the previous similar study of 4-methoxyphenol.[2] It is interesting to note that the good first-order kinetic form was observed whether or not the nitrous acid was present in excess. Observed first-order rate constants are in Table 1. These increase more than proportionately with the concentration of nitrous acid (last column in Table 1); the order in nitrous acid appears to be slightly greater than 1. The effect of added nitrate ion is negligible showing that this is not involved in the oxidation process. The reaction is slightly quicker in perchloric acid–sodium perchlorate solution than in the equivalent hydrochloric acid–sodium chloride solution (Table 1), showing that there is no chloride ion catalysis.[4] There is a modest acidity dependence, k_{obs} increasing by about 50% going from 0.1 to 1.0 mol dm^{-3} hydrogen ion concentration.

If excess nitrous acid (as sodium nitrite) is added first rather than last the value of k_{obs} depends upon the length of time allowed to elapse before addition of hydroquinone. During this time the reactions of Scheme 1 can proceed towards equilibrium which includes the consumption of the dissolved oxygen. The reaction is slower than in air-saturated solution, but the diminution in rate is much less than it was in similar experiments with 4-phenoxy- and 4-methoxy-phenol.[1,2] Chlorohydroquinone behaves very similarly, qualitatively and quantitatively (Table 1). The main difference is that the increase in k_{obs} with acidity is relatively smaller.

Table 1 Observed first-order rate constants, k_{obs} (with calculated values[a] in parentheses) for oxidation in dilute aqueous HCl containing nitrous acid at 25 °C

$[H^+]$/ mol dm^{-3}	$[HNO_2]$[b]/ 10^{-4} mol dm^{-3}	k_{obs}/ 10^{-3} s^{-1}	n[c]	$(k_{obs}/[HNO_2])$/ dm^{-3} mol^{-1} s^{-1}
Hydroquinone[d]				
0.0099	1.00	4.26 (4.15)	3	47.3[e]
0.10	1.00	4.72 (4.84)	2	47.6[e]
0.10[f]	1.00	5.35	2	
0.25	1.00	4.93 (5.19)	2	49.3
0.50	1.00	5.64 (5.72)	2	56.4
0.80	1.00	6.14 (6.35)	2	61.4
1.00	1.00	6.59 (6.76)	2	65.9
1.00	0.20	0.98 (0.93)	2	48.8
1.00[g]	0.20	0.99 (0.92)	2	49.4
1.00	0.40	2.31 (2.24)	2	57.8
1.00	0.60	3.68 (3.64)	2	61.3
1.00	0.80	4.96 (5.21)	2	62.0
1.00	1.20	8.11 (8.33)	2	67.6
0.10	10.0	68.8[h] (57.9)	1	69.5[e]
0.10	10.0	35.4[i] (33.4)	2	35.8[e]
Chlorohydroquinone[d]				
0.0099	1.00	4.05 (4.00)	5	45.0[e]
0.10	1.00	4.51 (4.57)	4	45.6[e]
0.30	1.00	4.72 (4.84)	6	47.2
0.50	1.00	4.83 (5.06)	6	48.3
0.8	1.00	5.20 (5.30)	4	52.0
1.00	1.00	5.45 (5.49)	7	54.4
0.10	10.0	52.8[h] (54.9)	4	53.3[e]
0.10	10.0	18.7[i] (31.0)	2	18.9[e]

[a] See Discussion for details of the calculation. [b] Stoichiometric concentration of nitrous acid. [c] Number of runs for which the quoted k_{obs} is the mean value. Agreement was always better than ± 2%. [d] Initial concentration 1 × 10^{-4} mol dm^{-3}. Ionic strength of 1.0 mol dm^{-3} maintained with NaCl. Full cells, wavelength 287 nm (hydroquinone) or 292 nm (chlorohydroquinone). Nitrous acid, as sodium nitrite, added last except where indicated. [e] Corrected for acid dissociation of the nitrous acid, calculated assuming a concentration acidity constant of $10^{-3.3}/(0.657)^2$ where 3.3 is the thermodynamic pK_a[5] and 0.657 is the mean ion activity coefficient[6] of the predominant electrolyte, NaCl. [f] $HClO_4$ and $NaClO_4$ used rather than HCl and NaCl. [g] With added nitrate ion (1 × 10^{-3} mol dm^{-3}). [h] Substrate added last, immediately after the sodium nitrite. [i] Substrate added last, approximately 18 h after the sodium nitrite.

Discussion

The fact that the reaction follows a first-order kinetic form even when the concentration of nitrous acid is equal to or smaller than that of the organic substrate indicates that nitrous acid is being regenerated as the reaction proceeds. All the results can be explained in a quantitative way, using numerical integration,[7] on the basis of a combination of Scheme 1 and Scheme 3.

With hydroquinone at a concentration less than twice that of dissolved oxygen, the stoichiometry of reaction (*f*) follows from

$$\text{Hydroquinone} + \tfrac{1}{2}O_2 \longrightarrow \text{benzoquinone} \qquad (f)$$

the addition of steps (*d*), (*e*), (*c*)($\tfrac{1}{2}$) and the subtraction of step (*b*). Rate constants for the steps in Scheme 1 are as before,[1,2] except that we have used the latest[8] measured value for k_3 of 2.1 × 10^6 mol^{-2} dm^6 s^{-1}. The initial concentrations of dissolved oxygen in 1 mol dm^{-3} aqueous HCl and in 1 mol dm^{-3} NaCl, both saturated with air at 25 °C are taken to be 2.4 × 10^{-4} and 1.9 × 10^{-4} mol dm^{-3} respectively.[9] We have linearly interpolated between these two values for mixtures. (The calculations are not sensitive to small changes in the assumed initial concentration of oxygen.) The rate constant k_8 was given an arbitrary value large enough to ensure that the substituted phenoxyl radical did not accumulate. The observed acidity dependence of k_{obs} can only be reproduced if the step with rate constant k_4 is given an uncatalysed and acid catalysed component [eqns. (1) and (2)].

For hydroquinone:

$$k_4/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} = 60 + 26\,\text{dm}^3\,\text{mol}^{-1}\,[H^+] \qquad (1)$$

For chlorohydroquinone:

$$k_4/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} = 58 + 12\,\text{dm}^3\,\text{mol}^{-1}\,[H^+] \qquad (2)$$

With these values the numerical integrations led to calculated variations with time of the concentration of benzoquinone to which first-order curves could be fitted. With the exception of the last entry for each substrate (relating to solutions from which oxygen has been completely removed by conditioning prior to reaction) the fit to a first-order curve was good. The first-order rate constants so obtained are given in parentheses in Table 1. The comparison with k_{obs} over a wide range of concentrations of nitrous acid and hydrogen ion is very satisfactory and the apparent slightly higher than first order dependence on the concentration of nitrous acid is well reproduced.

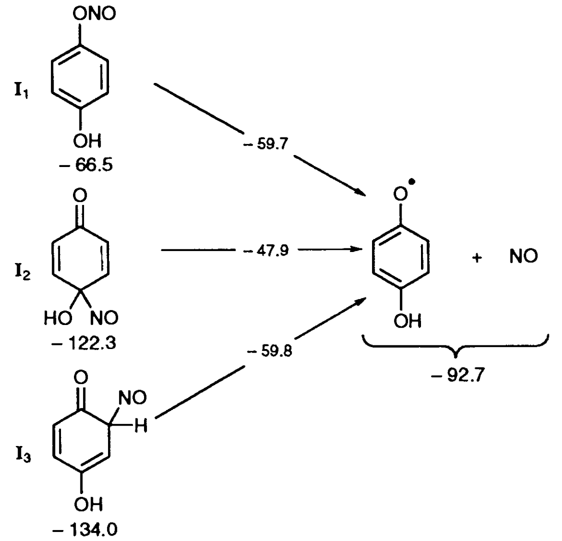
The numerical integrations reveal that the nitrous acid concentration is not constant during a run. It falls, typically under the conditions used by about 20% in the first 40 s, then rises slowly during the course of the reaction due to aerial oxidation of the nitric oxide formed. It is interesting to note that such changes do not lead to any significant deviations from a first order kinetic form.

Step (*d*) in Scheme 3 is an adequate description for kinetic analysis but is likely to consist of two steps with a kinetically insignificant intermediate, reaction (*g*), eqn. (3).

$$HNO_2 + HOC_6H_4OH \overset{K}{\rightleftharpoons} I \xrightarrow{k_4'} HOC_6H_4O^{\bullet} + NO \qquad (g)$$

$$k_2 = Kk_4' \qquad (3)$$

We now report MOPAC[10] calculations of the enthalpies of formation of possible structures for the intermediate **I** in reaction (*g*), and of the transition states formed from them by homolysis to give the 4-hydroxyphenoxyl radical and nitric oxide. These are given in Scheme 4, in which the numbers below the structures are calculated standard enthalpies of formation/kJ mol^{-1}. Calculated transition state energies are also shown. These and other relevant calculations are summarized in Table 2.



Scheme 4

The most stable precursor, **I**, of the 4-hydroxyphenoxyl radical and nitric oxide is clearly not 4-hydroxyphenyl nitrite ($\mathbf{I}_1$) or 4-hydroxy-4-nitrosocyclohexa-2,5-dienone ($\mathbf{I}_2$) but 4-hydroxy-6-nitrosocyclohexa-2,4-dienone, ($\mathbf{I}_3$). The calculations indicate that $\mathbf{I}_1$ is of only marginal stability with regard to homolysis by loss of nitric oxide. In accord with this the calculated O–N bond length in $\mathbf{I}_1$, 0.165 nm, is very long compared with that in, for instance, methyl nitrite,[12] 0.137 nm. The rate constant for its break up by this route must be too large for this to be the rate determining step (*vide infra*) and the transition state formed from it is very close in energy to that formed from $\mathbf{I}_3$. It is best to regard $\mathbf{I}_1$ either as a high energy stopping point or as a *cul-de-sac* during the homolysis of $\mathbf{I}_3$. Formation of $\mathbf{I}_3$ is a nitrosation process and is likely to be acid catalysed.[4] We have considered the possibility that the first step in reaction (*g*) might be partially rate-determining and provide an explanation for the observed acid catalysis but rejected this notion for two reasons. Firstly the plot of k_{obs} against $[\text{H}^+]$ is linear with a substantial intercept, and does not increase proportionately at low acidity then level off as would be expected. Secondly the reaction is not catalysed by chloride ion under conditions which for other nitrosation reactions[4] lead to significant catalysis through equilibrium quantities of NOCl. For these reasons we propose that the homolysis of $\mathbf{I}_3$ is rate-determining, and that k_4 is correctly given as in eqn. (3).

The observed acid catalysis [eqns. (1) and (2)] must relate to the second step in reaction (*g*). We note that acid catalysis has been demonstrated in the rather similar homolysis of 4-methyl-4-nitrocyclohexa-2,5-dienone to the 4-methylphenoxyl radical and NO_2.[13]

The calculations indicate (Table 2) firstly that the preferred site of protonation is as expected the carbonyl oxygen, and secondly that the activation energy for homolysis of carbonyl-protonated 4-hydroxy-6-nitrosocyclohexa-2,4-dienone is less than for the unprotonated molecule. This may account for the observed contribution from acid catalysis. (Uncertainties about the pK_a of the protonated form and about solvation of hydrogen bonding cations preclude definite conclusions from the calculations relating to the protonated form.)

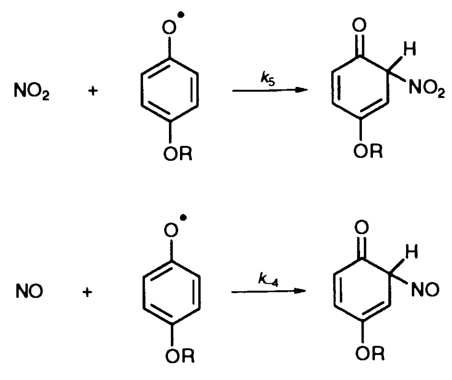
Table 2 Standard enthalpies of formation calculated by MOPAC (Version 6.0; PM3 Hamiltonian)

	Ground state/ kJ mol^{-1}	Transition state[a]/kJ mol^{-1}
4-Hydroxyphenyl nitrite	−66.5	−59.7
4-Hydroxy-4-nitrosocyclohexa-2,5-dienone	−122.3	−47.9
4-Hydroxy-6-nitrosocyclohexa-2,4-dienone	−134.0	−59.8
4-Hydroxy-2-nitrocyclohexa-3,5-dienone	−222.9	−130.2
4-Hydroxyphenoxyl radical	−183.0	
NO_2	33.2[b]	
NO	90.3[b]	
4-Hydroxy-6-nitrosocyclohexa-2,4-dienone protonated on carbonyl oxygen	601.5	631.8

[a] Formed from the ground state by homolysis to give NO. [b] Experimental values used, following precedents.[11]

The uncatalysed process is insensitive to chloro substitution [first terms in eqns. (1) and (2)] but the rate constant for the acid catalysed process is diminished by a factor of 2.2 [second terms in eqns. (1) and (2)]. It is to be expected that the chlorosubstituent would reduce the basicity of $\mathbf{I}_3$ and therefore the rate of the acid catalysed process. That there is almost no effect of chloro substitution on the uncatalysed process is surprising; presumably the favourable effect on the homolysis is balanced by the unfavourable effect on the pre-equilibrium extent of nitrosation [first step of reaction (*g*)].

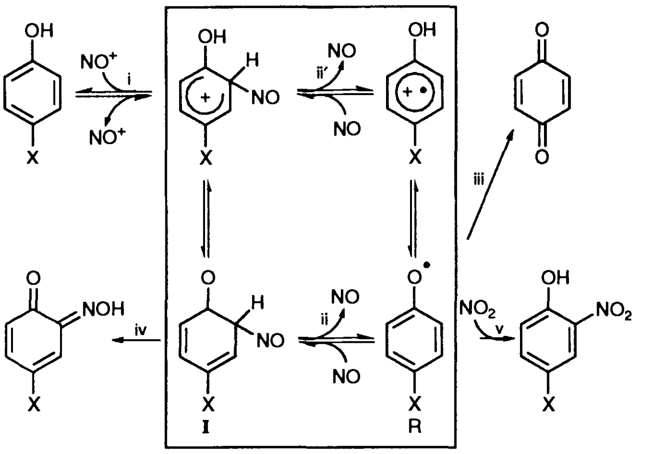
The values of the rate constants k_4, k_5 and k_{-4} (Scheme 2) are likely to be very similar for the reactions of hydroquinone and 4-methoxyphenol. Combination of the estimated value of k_4k_5/k_{-4} for 4-methoxyphenol[2] of 3×10^4 dm^3 mol^{-1} s^{-1} with the value of k_4 for hydroquinone of 60 dm^3 mol^{-1} s^{-1} [eqn. (1), non acid-catalysed term] then leads to an estimate of 500 for the value of k_5/k_{-4} for the ratio of the rate constants for uncatalysed attack by NO_2 and NO at the 2-position of the substituted phenoxyl radical, Scheme 5. (The magnitude of this ratio is larger than expected but does not invalidate the assumed inequality $k_{-4}[\text{NO}] > k_5[\text{NO}_2]$ in ref. 2 because the numerical integrations indicate that $[\text{NO}]/[\text{NO}_2]$ is generally greater than 500.)



Scheme 5

The difference in the calculated enthalpies of activation for these two reactions is −13.3 kJ mol^{-1} (using data in Table 2). If the entropies of activation are assumed to be the same this leads to an expected ratio of rate constants k_5/k_{-4} at 25 °C of 220. In view of the approximations involved the agreement is satisfactory.

It is now possible to present a more complete picture of the reactions which can occur when 4-X-phenols and nitrite are mixed in air-saturated aqueous acid. Along with the inorganic reactions of Scheme 1 and associated protonic equilibria there are the possibilities of the organic reactions shown in Scheme 6.



Scheme 6

6-Nitroso-4-X-cyclohexa-2,4-dienone (**I**) is first formed by a reversible, acid catalysed, process, *via* the nitrosonium ion or a carrier (step i). Under acid conditions the preferred fate of this intermediate is reversion to starting materials *via* its protonated form (reverse of i). The alternative is homolysis (uncatalysed, step ii, or acid catalysed, step ii') to give the 4-X-phenoxyl radical (R) and nitric oxide. If X = OH this process is effectively irreversible because loss of hydrogen atom to give the product, benzoquinone, step iii, is rapid. If X is not OH, no such rapid exit from the boxed section exists. Other exits are C-proton loss from **I** to give the nitroso compound, or its oxime tautomer as shown here,[4] step iv, formation from R of benzoquinone (if X = OR) in two ways not detailed here but described previously,[2] and combination of R with NO_2 [1,2] at C2, step v. The preferred exit from the boxed section will depend, not only on the nature of the substituent X, but also on the concentrations of NO and NO_2.

Experimental

Materials.—Sodium nitrite, sodium nitrate, benzoquinone, 2-chloro-1,4-benzoquinone and acetonitrile were AR reagents. Hydroquinone (ex Aldrich) and chlorohydroquinone (ex Kodak Eastman) were high purity reagents (99+%). Hydrochloric acid solutions were prepared by dilution of AR grade HCl and maintained at an ionic strength of 1.0 mol dm^{-3} with addition of AR sodium chloride. Perchloric acid solutions were prepared by dilution of 70% AR grade perchloric acid, and the molarity determined by titration. The perchloric acid solutions were (then) maintained at an ionic strength of 1.0 mol dm^{-3} with addition of AR sodium perchlorate. Benzoquinone was purified by recrystallisation.

Kinetics.—These were studied as previously described.[2]

Acknowledgements

We thank the SERC for financial support.

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Paper 4/00119B
Received 10*th January* 1994
Accepted 9*th February* 1994