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Thermal and Photochemical Production of Hydrogen Peroxide from Dioxygen and Tannic Acid, Gallic Acid and other related Compounds in Aqueous Solution

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A quantitative study has been made of the formation of hydrogen peroxide when alkaline solutions of tannic acid, gallic acid and a number of other molecules containing the catechol (1,2-dihydroxybenzene) moiety are exposed to air or dioxygen. For gallic acid, from the pH dependence of the initial rates of reaction, it is shown that, over the pH range *ca.* 7.0–8.5, the predominant reactive species is the dianion. The photochemical production of hydrogen peroxide, using 254 nm radiation, has been studied for a variety of air-saturated solutions of phenolic substances at pH 6.0 or below, where the thermal reaction is negligible, and apparent quantum yields are reported. Appreciable formation of hydrogen peroxide is observed with 1,2-, 1,3- and 1,4-benzene diols. Possible mechanisms for the thermal and photochemical reactions are discussed and it is suggested that benzenediol groups may be involved in the natural photochemical production of hydrogen peroxide in surface waters.

Hydrogen peroxide occurs naturally in the environment. It is a common component of cloudwater, being formed by photochemical processes involving atmospheric trace gases,[1] and probably plays an important role in the oxidation of SO_2 to H_2SO_4 in the production of 'acid rain'.[2] It is also present in natural surface waters, with concentrations typically in the range $(1\text{–}100) \times 10^{-8}$ mol dm^{-3}.[3,4] Here, the H_2O_2 is thought to arise mainly from the absorption of sunlight by organic materials such as humic substances. Exposure of natural waters to sunlight or UV in the laboratory normally causes a very considerable increase in the concentration of H_2O_2.[4,5] It has been suggested[4] that either the light-absorbing materials generate free electrons, or that the excited species transfers an electron directly to O_2 to yield the O_2^- ion, which is a common precursor of H_2O_2 by the well known reaction

$$HO_2 + O_2^- \rightarrow HO_2^- + O_2.$$

Very recently, it has been shown that H_2O_2 occurs in some ground-waters,[6] where photochemical production is excluded.

In 1860[7] Schonbein reported that H_2O_2 was formed when weakly alkaline solutions of tannin (tannic acid), pyrogallol, gallic acid (3,4,5-trihydroxybenzoic acid) and haemotoxylin were shaken in air. Tannins of various types occur in almost all plant and vegetable material. The tannic acid from chemical suppliers is a gallotannin (normally Chinese tannin from oak galls), and is a mixture of gallate esters of glucose, containing mono-, di- and tri-galloyl groups, with *ca.* 9–10 gallic acid residues per glucose molecule.[8] Tannic acid and the other compounds studied by Schonbein all contain the catechol (1,2-dihydroxybenzene) moiety. In 1955 Brackman and Havinga[9] showed that H_2O_2 in *ca.* 40% yield was obtained when O_2 was bubbled through an alkaline solution of catechol, provided that morpholine was present to trap 1,2-benzoquinone as soon as it was formed, and prevent its further reaction with the H_2O_2.

In the present work, both the thermal and the photochemical production of H_2O_2 from air or oxygen and aqueous solutions of tannic acid, gallic acid and a variety of related compounds has been studied quantitatively. One of the aims was to elucidate, using relatively simple molecules, the structural features required for H_2O_2 production. Analyses for H_2O_2 were carried out using a recently developed spectrophotometric method,[10] suitable for highly coloured aqueous solutions, in which a proportion of the H_2O_2 is extracted into ethyl acetate and then back-extracted into a Ti^{IV} sulphate solution.

Experimental

Tannic acid and gallic acid (BDH) were used directly. The tannic acid lost 6.9% by weight of H_2O on heating to 110 °C. 3,4-Dihydroxybenzoic acid, 3-hydroxy-2,4-dimethoxybenzoic acid (syringic acid), 2,3-dihydroxynaphthalene-6-sulphonic acid, 3-hydroxytyramine hydrochloride, 3-hydroxy-2-naphthoic acid, 2,3,4-trihydroxybenzoic acid, 2,3-dihydroxy benzoic acid, 4-hydroxybenzoic acid, benzoic acid, 2-hydroxybenzoic acid (salicylic acid), chlorogenic acid and caffeic acid were recrystallised from water. 3-Methoxy-4,5-dihydroxybenzoic acid (3-*O*-methylgallic acid) was prepared as outlined by Scheline[11] (m.p. 218–220 °C, lit. 220 °C). Catalase (from bovine liver) was obtained from Sigma.

The following buffers were used at 0.05 mol dm^{-3} over the stated pH ranges; 4-(2-hydroxyethyl)-1-piperazine-propanesulphonic acid, EPPS, pH *ca.* 8.5–8.0; 4-morpholine-propanesulphonic acid, MOPS, pH *ca.* 7.5–7.0; succinate, pH *ca.* 6.0–3.6.

For the thermal reactions, air or O_2 was passed first through a pre-saturator, and then through the solution contained in a Dreschel bottle fitted with a sintered glass disc and magnetic follower, immersed in a water bath at 20 ± 0.5 °C. The Dreschel bottle was coated on the outside with Kodak Linagraph Stabilizing Lacquer to absorb ambient UV radiation. Periodically, 10 cm^3 samples were removed and analysed for H_2O_2 as described previously.[10] Blank readings, obtained by treating an aliquot with *ca.* 250 units of catalase and leaving for 10 min before analysing, were normally < 1% of the observed maximum absorbances.

In the photochemical experiments, 20 cm^3 of the phenolic solution in a 10 cm pathlength cylindrical silica cell was exposed along the axis of the cell to 254 nm radiation from a low-pressure mercury lamp whilst air or O_2 was bubbled through using two lengths of 1 mm diameter PTFE tubing. The temperature was maintained at 25 ± 2 °C. Quantum yields, *Q*, for the formation of H_2O_2 were obtained using the ferrioxalate actinometer.[12,13] The solution was replaced by 20 cm^3 of 0.006 mol dm^{-3} $K_3Fe(ox)_3$, and N_2 was bubbled through during irradiation for a known time.

Then

$$Q = \frac{[H_2O_2]t_2 Q'}{[Fe^{2+}]t_1}$$

where

$$Q = \frac{\text{molecules of } H_2O_2 \text{ formed}}{\text{number of quanta absorbed}}.$$

$[H_2O_2]$ and $[Fe^{2+}]$ are the concentrations of these substances formed in times t_1 and t_2, respectively, and Q' is the quantum yield for the formation of Fe^{2+} from $K_3Fe(ox)_3$ (1.25 at 254 nm[12]).

For the measurements, a slight error will be introduced by the presence of the Hg emission lines in the region 313–436 nm, which will be absorbed by the actinometer but only slightly by the phenolic substances. From the known emission of a low-pressure mercury lamp[13] this error should not exceed 5%. Calibration of the output of the lamp in this way was carried out daily before and after each series of photochemical runs. The difference between these two measurements did not exceed 5%.

Results and Discussion

Thermal Production of Hydrogen Peroxide

Tannic Acid

The concentration of hydrogen peroxide produced when air is bubbled through aqueous solutions of tannic acid at various pH values is shown in fig. 1. The molecular weight of the anhydrous tannic acid was taken as 1701, corresponding to one glucose molecule and ten gallate residues, so the maximum yield of H_2O_2 is *ca.* 0.33 mol per gallate residue. When pure O_2 was used instead of air (pH 8.5), the maximum yield was *ca.* 0.40 mol. The rate of production of H_2O_2 increases very markedly as the pH is increased. In view of the complex nature of 'tannic acid', further measurements were made using gallic acid.

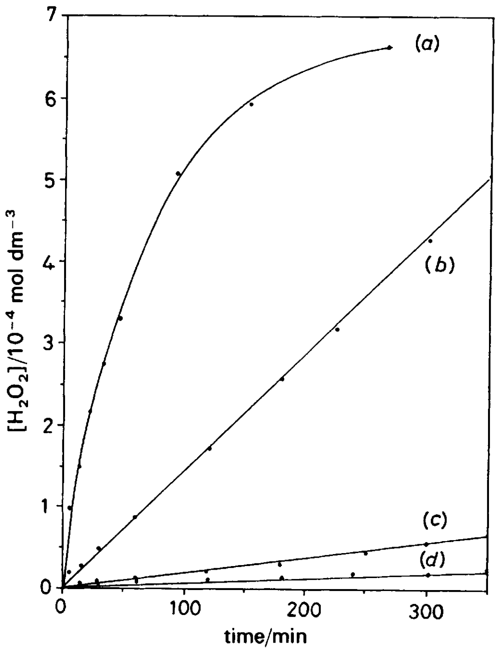

Fig. 1. Concentrations of H_2O_2 produced at various times for 2×10^{-4} mol dm^{-3} aqueous solutions of tannic acid saturated with air at (*a*) pH 8.58, (*b*) pH 7.99, (*c*) pH 7.51, (*d*) pH 7.00.

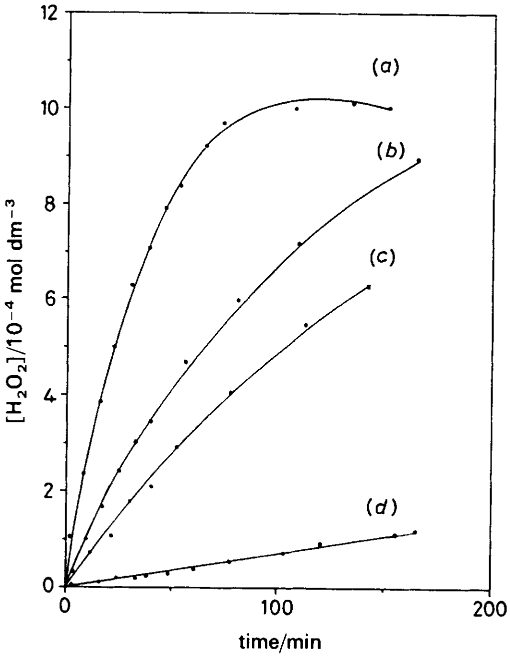

Fig. 2. Concentrations of H_2O_2 produced at various times for 1×10^{-3} mol dm^{-3} aqueous solutions of gallic acid saturated with air at (*a*) pH 8.52, (*b*) pH 8.07, (*c*) pH 7.48, (*d*) pH 7.00.

Gallic Acid

The results obtained in air are shown in fig. 2. The maximum yield of H_2O_2 in the pH range 7.5–8.5 is *ca.* 1.0 mol H_2O_2 per mol of gallic acid. When O_2 is used in place of air, the rate of production of H_2O_2 was considerably increased (at pH 8.5 the initial rate was greater by a factor of *ca.* 3.3), and the maximum yield of H_2O_2 reached a value of *ca.* 1.4 mol. It has been known for many years that oxidation of gallic acid in alkaline solution by air or O_2 gives the highly coloured compound galloflavin[14,15] (fig. 3).

The mechanism involved is unknown, but conversion of two molecules of gallic acid into one molecule of galloflavin involves the loss of '$C_2H_6O_2$'. If all these six H atoms were involved in the formation of H_2O_2, then the maximum possible yield of H_2O_2 would be 1.50 mol per mol of gallic acid. The greater yields obtained with O_2 than with air are presumably due to the faster production of H_2O_2 which allows less time for its subsequent removal by reaction or catalysed decomposition.

The p*K* values reported for gallic acid (GH_4) at 20 °C are 4.26, 8.70, 11.45.[16] For the solutions studied here, the carboxylic acid group is effectively completely ionized and it is possible to calculate the concentrations of the species GH_2^{2-} and GH^{3-}, where one and two, respectively, of the hydroxylic protons are removed. Table 1 shows the approximate initial

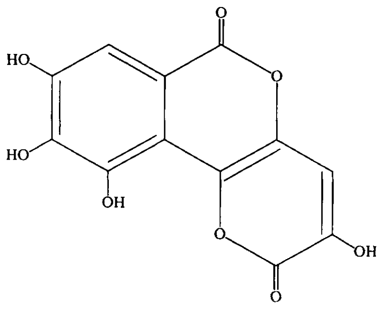

Fig. 3. Galloflavin.

Table 1. Initial rates of production of H_2O_2 as a function of pH for 1×10^{-3} mol dm^{-3} aqueous solutions of gallic acid saturated with air at 20 °C

pH	initial rate /10^{-6} mol dm^{-3} min^{-1}	relative initial rate	relative [GH_2^{2-}]	relative [GH^{3-}]
7.00	0.81	1	1	1
7.48	7.37	2.9	3.2	8.8
8.07	9.36	3.2	9.7	114
8.52	27.5	8.8	20.3	673

rates of production of hydrogen peroxide, and the corresponding concentrations of GH_2^{2-} and GH^{3-}.

It is clear that, over the pH range 7–8.5, the predominant reactive species is GH_2^{2-}. This contrasts with the situation found for tetramethylhydroquinone, which reacts quantitatively with O_2 in alkaline H_2O–EtOH solution to give tetramethylquinone and H_2O_2. Here, the reactive species is apparently the dianion, where both hydroxylic protons have been removed.[17]

Pyrogallol (1,2,3-Trihydroxybenzene) and 1,2,4-Trihydroxybenzene

H_2O_2 is produced even more rapidly with pyrogallol than with gallic acid, and higher yields are obtained (fig. 4). At pH 8.0 with 1,2,4-trihydroxybenzene the reaction was too fast to be studied conveniently. The results obtained at the much lower pH of 6.00 are shown in fig. 4. In spite of the very high reactivity of 1,2,4-trihydroxybenzene towards O_2, the yield of H_2O_2 (0.37 mol) is less than that produced by gallic acid and pyrogallol. Since 1,2,4-trihydroxybenzene itself does not react with H_2O_2, presumably attack by one or more of the reaction products is involved.

Dihydroxybenzenes

Catechols. Fig. 5 shows the production of H_2O_2 by catechol, 3-*O*-methylgallic acid and 3,4-dihydroxybenzoic acid. The observed formation of H_2O_2 by catechol alone, in contradiction of an earlier report,[9] may be partly associated with the low concentration of substrate used in this work. The yields of H_2O_2 are much lower than those found with gallic acid or pyrogallol. This means that the observed initial rates of reaction will be considerably lower than the true values. Nevertheless, it is clear that for the carboxylic acids, the actual reactivities towards oxygen are in the order gallic acid > 3-*O*-methylgallic acid > 3,4-dihydroxybenzoic acid, and also that 1,2,4-trihydroxybenzene and pyrogallol are considerably more reactive than catechol. These differences cannot be accounted for by variations in the p*K* for ionization of the first OH proton. (The actual values at 25 °C are gallic acid 8.64 ± 0.09,[18] 2,4-dihydroxybenzoic acid 8.79 ± 0.07,[19] pyrogallol 8.96 ± 0.02,[20] 1,2,4-trihydroxybenzene 9.02[20] and catechol 9.30 ± 0.01.[21])

With 'tiron' (4,5-dihydroxy-1,3-benzenedisulphonate), which contains two electron-withdrawing sulphonate groups, negligible amounts of H_2O_2 were produced (2×10^{-3} mol dm^{-3}, air, pH 8.5), and also, in contrast to the other catechols studied, the solution remained almost colourless.

Resorcinols. Under similar conditions, 3,5-dihydroxybenzoic acid, resorcinol and phloroglucinol also gave negligible amounts of H_2O_2, whilst a phenol (syringic acid, 4-hydroxy-3,5-dimethoxybenzoic acid) produced only 0.013 mol H_2O_2 after 300 min.

For formation of hydrogen peroxide from oxygen and a catechol, the possible mechanistic pathway shown in fig. 6

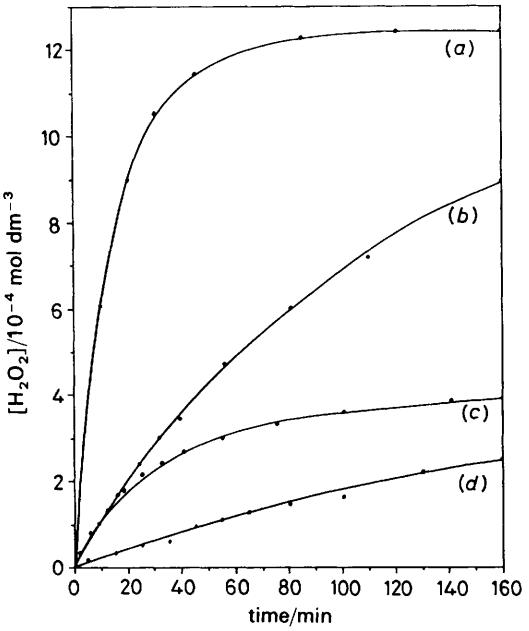

Fig. 4. Concentrations of H_2O_2 produced at various times for air-saturated aqueous solutions of (*a*) 1×10^{-3} mol dm^{-3} pyrogallol at pH 8.00, (*b*) 1×10^{-3} mol dm^{-3} gallic acid at pH 8.07, (*c*) 1×10^{-3} mol dm^{-3} 1,2,4-trihydroxybenzene at pH 6.00, (*d*) 2×10^{-3} mol dm^{-3} catechol at pH 8.50.

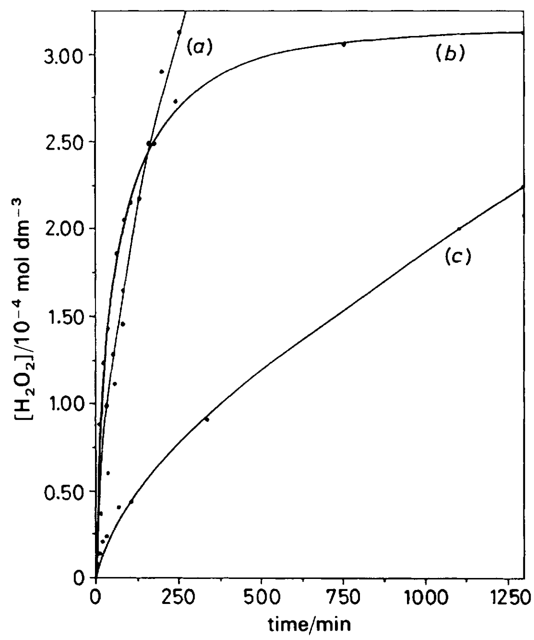

Fig. 5. Concentrations of H_2O_2 produced at various times for air-saturated 2×10^{-3} mol dm^{-3} aqueous solutions of (*a*) catechol at pH 8.50, (*b*) 3-*O*-methyl gallic acid at pH 8.58, (*c*) 3,4-dihydroxybenzoic acid at pH 8.50.

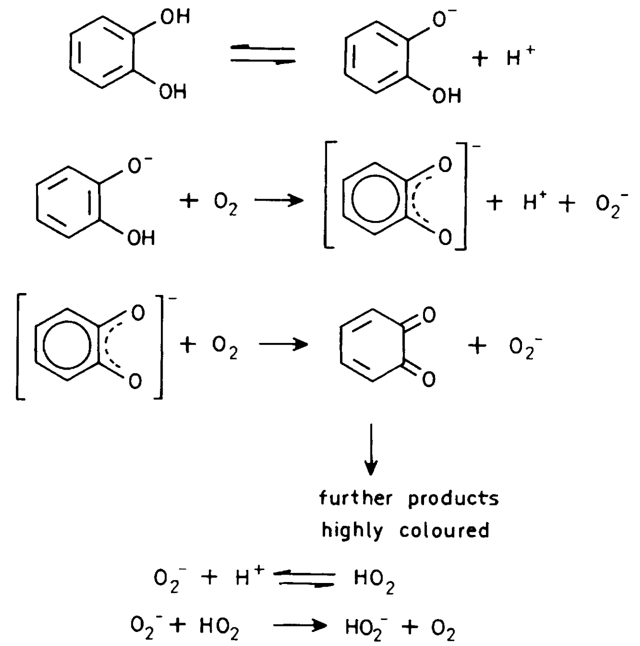

Fig. 6. Possible mechanism for the formation of H_2O_2 from oxygen and a catechol.

can be written. This mechanism can account only for the formation of one mole of H_2O_2 for each mole of the catechol. The higher yields with gallic acid and pyrogallol suggest that H_2O_2 is also produced in the further steps leading to the final product.

The differences in reactivity for substituted catechols can be qualitatively interpreted in terms of the electron density on the O^- of the anion. The CO_2^- group is weakly electron-withdrawing as shown by the Hammett parameters ($\sigma_m = 0.02$, $\sigma_p = 0.11$),[22] which accounts for the greater reactivity of pyrogallol compared to gallic acid. Conversely OH and OCH_3 groups increase the electron density when in a *para* (and also *ortho*) position (OH, $\sigma_m = 0.13$, $\sigma_p = -0.38$, OCH_3, $\sigma_m = 0.10$, $\sigma_p = -0.28$).[22]

The lack of reactivity of resorcinols towards O_2 is presumably because they cannot give a stabilised semiquinone radical-ion.

As mentioned earlier, the main reactive species in hydroquinones seems to be the dianion. This apparent difference from the catechols may be partly due to the difficulty, for electrostatic reasons, of losing two protons from *ortho* OH groups (at 25 °C, pK_2 is 13.3 ± 0.3[21] for catechol, 11.50[23] for hydroquinone).

Finally, the thermal reaction of O_2 with catechol moieties in humic substances could be involved in the reported occurrence of H_2O_2 in groundwaters.[6]

Photochemical Production of Hydrogen Peroxide

Catechols

Aqueous solutions of the catechols (4×10^{-3} mol dm^{-3}, 0.05 mol dm^{-3} succinate buffer) were saturated with air and irradiated at a wavelength of 254 nm. This was done at pH 6.0 or below, where the thermal reaction was normally negligible.

The quantum yields, *Q*, given (see Experimental) as

$$\frac{(\text{molecules } H_2O_2 \text{ formed})}{(\text{quanta incident on the solution})} \times 100\%$$

are effective ones only, being those observed after 30 min irradiation, with the quanta incident upon the solution lying in the range $(2.5\text{–}3.3) \times 10^{-7}$ mol s^{-1}. For gallic acid and pyrogallol, respectively, the pH dependence of the quantum yields are given in tables 2 and 3. The decrease in *Q* as the pH is lowered may arise from protonation of the excited species, leading to lower reactivity, or possibly to changes in reactions subsequent to the primary step.

The effective quantum yields for a wide variety of catechols at pH 6.00 ± 0.01 are given in table 4. In most cases small but definite amounts of H_2O_2 are produced. In spite of the comparatively low quantum yields, appreciable concentrations of H_2O_2 can be formed, for example with gallic acid after 30 min irradiation, $[H_2O_2]$ was 5.6×10^{-4} mol dm^{-3}. For gallic acid, the solution formed on photolysis had an almost identical visible spectrum to that of the product obtained in the thermal reaction (after subsequent adjustment to the same pH).

Absorption of 254 nm radiation will normally result in a π–π^* transition to the lowest excited singlet state of the molecule, which corresponds to the $^1B_{2u}$ level in benzene shifted to lower energies by the substituents.[24] This singlet state can react directly or it can undergo rapid radiationless conversion to the lowest triplet. It has been shown that phenols are more acidic in the lowest excited singlet state than in the ground state (or the lowest triplet). For phenol itself, p*K*s are 10.00, *ca.* 4.0 and *ca.* 8.5 for the ground state, the lowest excited singlet state and the lowest excited triplet state, respectively.[25] Flash photolysis of aqueous phenol solutions is known to produce hydrated electrons,[26,27] although continuous photolysis using low-intensity radiation apparently does not.[28]

One possible mechanism for the photochemical formation of H_2O_2 from oxygen and a catechol is given in fig. 7.

4-Hydroxybenzoic acid, a substituted phenol, gave negligible yields of H_2O_2 (table 4). The greater reactivity of catechols in their excited states, as compared to phenols, may be

Table 2. Variation of quantum efficiency with pH for an air-saturated 4×10^{-3} mol dm^{-3} aqueous solution of gallic acid

pH	efficiency (%)
6.02	2.40
4.98	1.72
4.80	1.48
4.61	1.32
4.42	1.03
4.04	0.67
3.91	0.63
3.85	0.54
3.80	0.47
3.70	0.43
3.60	0.34

30 min irradiation at 254 nm.

Table 3. Variation of quantum efficiency with pH for an air-saturated 4×10^{-3} mol dm^{-3} aqueous solution of pyrogallol

pH	efficiency (%)
6.00	2.18
5.60	1.96
5.20	1.85
5.00	1.60
4.80	1.54
4.40	1.33
4.00	1.13
3.60	1.02

30 min irradiation at 254 nm.

Table 4. Quantum efficiences for the production of hydrogen peroxide for air-saturated 4 × 10^{-3} mol dm^{-3} aqueous solutions of aromatic compounds at pH 6.00 ± 0.01

compound	quantum efficiency (%)
3,5-dihydroxybenzoic acid	3.29
gallic acid	2.40[a]
pyrogallol	2.20
2,5-dihydroxybenzoic acid	1.22
3-*O*-methylgallic acid	0.89
2,3-dihydroxynaphthalene -6-sulphonic acid	0.80
tannic acid	0.72[b]
DL-DOPA	0.71
3,4-dihydroxybenzoic acid	0.66
resorcinol	0.57
2,3-dihydroxybenzoic acid	0.55
phloroglucinol	0.50
3-hydroxy-5-methoxybenzoic acid	0.48
1,2,4-trihydroxybenzene	0.46[c]
2,3,4-trihydroxybenzoic acid	0.42
3-hydroxytyramine hydrochloride	0.40
5-bromo-3,4-dihydroxybenzoic acid	0.31
2,4-dihydroxybenzoic acid	0.30
tiron	0.30
3,4-dihydroxyhydrocinnamic acid	0.25
syringic acid	0.24
methyl-2,3,4-trihydroxybenzoate	0.22
catechol	0.21
chlorogenic acid	0.11
benzoic acid	<0.10%
2,6-dihydroxybenzoic acid	
3,4-dihydroxycinnamic acid	
4-hydroxybenzoic acid	
3-hydroxy-2-naphthoic acid	
salicylic acid	

30 min irradiation at 254 nm.
[a] 4 × 10^{-3} mol dm^{-3} solution with oxygen 3.40%. [b] 4 × 10^{-3} mol dm^{-3} solution with oxygen 0.83%. [c] At pH 4.00 owing to appreciable thermal reaction at pH 6.00.

due to the increased stability of the semiquinone radicals formed by the loss of an electron. This would allow some of the electrons to escape from the solvent cage before recombination occurs.

Resorcinols

It has been shown earlier that, as expected, resorcinols in alkaline solution do not react thermally with O_2 to give H_2O_2. However, in the photochemical reactions, the highest quantum yield for the formation of H_2O_2 is found with 3,5-dihydroxybenzoic acid (table 4) and smaller but significant yields are obtained with other resorcinols. There is thus a complete contrast between the ground state and excited state reactivity of the resorcinol moiety. This may be associated with the much greater interaction which is known to occur between *meta* substituents in the excited states of substituted benzenes, compared to the ground states.[29] In the thermal production of H_2O_2, trihydroxy compounds such as gallic acid and pyrogallol are clearly best regarded as OH substituted catechols. In the photochemical production of H_2O_2, this is not necessarily so, and they could equally well be considered as OH-substituted resorcinols. The negligible quantum yield for 2,6-dihydroxy benzoic acid may arise from hydrogen bonding of both OH groups with the carboxylate anion, which can result in rapid radiationless conversion of the excited state to the ground level [*cf.* ref. (30)]. 2,5-dihydroxybenzoic acid was the only hydroquinone studied, and an appreciable yield of H_2O_2 was obtained (table 4).

The wavelength of the radiation used in this work (254 nm) is shorter than that corresponding to the solar-energy 'cut-off' at sea-level (*ca.* 295 nm).[31] However, most of the compounds studied here have absorption bands which extend beyond 295 nm (*e.g.* ε = 50 dm^3 mol^{-1} cm^{-1} for gallic acid at 316 nm, 3,4-dihydroxybenzoic acid at 314 nm, 3,5-dihydroxy benzoic acid at 353 nm and tannic acid at 436 nm, while ε = 10 dm^3 mol^{-1} cm^{-1} for resorcinol at 295 nm and catechol at 299 nm).

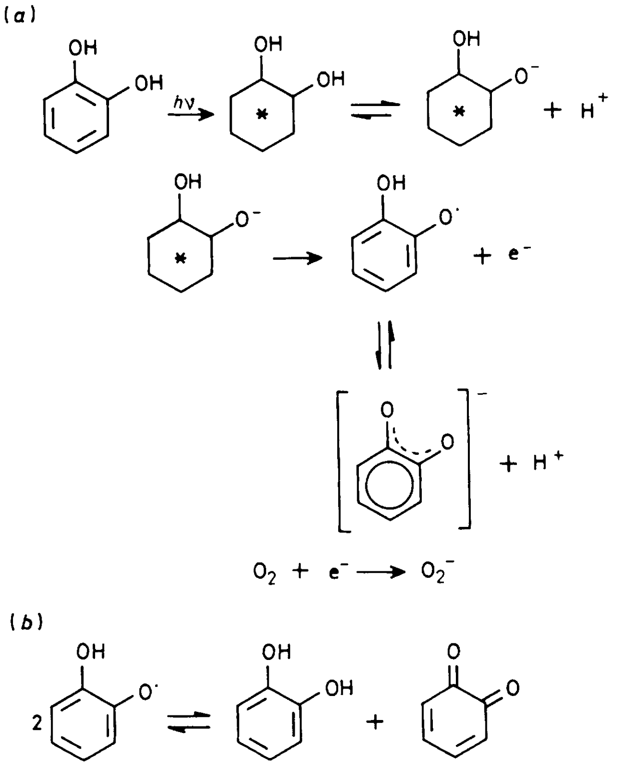

Fig. 7. (*a*) Possible mechanism for the photochemical formation of H_2O_2 from oxygen and a catechol. Alternatively the electron can be transferred directly from the excited state to the O_2. The remaining steps are as for the thermal reaction, except that in these more acidic solutions disproportionation (*b*) of the semiquinone radicals may occur.

Conclusion

A number of catechol derivatives, including the ubiquitous 'tannic acid', react with O_2 in weakly alkaline aqueous solution to give H_2O_2, sometimes in surprisingly high yields. Loss of only one of the OH protons seems to be required for reaction. At pH 6.0 or below, photochemical production of H_2O_2 has been demonstrated, using 254 nm radiation. Unexpectedly, the highest yield of H_2O_2 was obtained with a resorcinol derivative, 3,5-dihydroxybenzoic acid.

1,2-, 1,3- and 1,4-benzenediol residues are found quite commonly in plant materials including humic substances.[32] The present work suggests that the photochemical production of H_2O_2 in the environment could well involve these species, possibly in conjunction with other groups which would shift the absorption to longer wavelengths.

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