# Triple Oxidations of Some Polyhydric Phenols by Cerium(IV) in Acid Solutions as observed by Electron Spin Resonance Spectroscopy

By **William T. Dixon** * and **David Murphy**, Bedford College, Regent's Park, London NW1 4NS

A hitherto unobserved radical species has now been obtained from the oxidation of pyrogallol (1,2,3-trihydroxybenzene) by $Ce^{IV}$ in acid solution. Evidence is presented which indicates that this ' new ' radical differs from the semiquinone radical from pyrogallol only by having two fewer electrons, and therefore comes from three consecutive one-electron oxidations. Analogous reactions occur with purpurogallin (2,3,4,6-tetrahydroxy-5*H*-benzocyclohepten-5-one) and with juglone (5-hydroxy-1,4-naphthoquinone). Where there is symmetry, it is clear that the two adjacent molecule orbitals, which may contain the odd electron, depending on whether there has been one- or three-electron oxidation overall, have opposite symmetries.

THE one electron oxidation of pyrogallol (1,2,3-trihydroxybenzene) (A), has been thoroughly investigated by Carrington and Smith,[1] using e.s.r. spectroscopy. The species produced by the action of hydroxyl radicals in a flow system could be satisfactorily identified by means of the hyperfine splittings and was found to exist in different states of protonation at different acidities. In all cases when the spectra corresponded to symmetrical radicals, the largest coupling constant was that of the proton lying in the plane of symmetry, *i.e.* attached to the 5-position [see (I), (II), and (IIa) in the Scheme]. This is also true for the semiquinone from pyrogallol in alkaline solution. These radicals can all be regarded as 2,6-disubstituted phenoxyl radicals,[2,3] rather than as radicals derived from 2-substituted resorcinols,[4] for in the former case, the odd electron goes into a symmetrical orbital, whereas in the latter, it goes into an orbital which is antisymmetrical with respect to the plane of symmetry. At first sight it would appear that the previously observed results [1] are rather unexpected, because 2-substituents in the radicals from resorcinols have little effect on the spin distribution, mainly because they lie on the nodal plane of the odd electron orbital (see Table 1).

We have been able to reproduce the spectra obtained by Carrington and Smith using cerium(IV) ammonium nitrate as the oxidant. However, on further acidification the spectrum of a new radical appears in which there is a completely different splitting pattern, for in this case large spin densities appear on the 4- and 6-positions as in the radicals from resorcinol derivatives.

We naturally became interested in the nature of this ' new ' type of radical, in which the substituents are interrelated in the same way as in the corresponding semiquinone. A number of possibilities present themselves, including ring opening, ring expansion or contraction, *etc.*, but it is difficult to justify such drastic geometrical changes which retain the original symmetry. One clue was the sharpness of the lines (see Figure 1), for the lines of the ' old ' spectrum [1] [*i.e.* of (IIa)] were broadened by incomplete averaging of the hydroxylic proton splittings. This suggested that in the ' new ' radicals, whose spectra were sharp at all the acidities where they were observed, there were no such averaging processes to consider.

---

[1] A. Carrington and I. P. C. Smith, *Mol. Phys.*, 1964, **8**, 101.

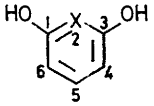
[2] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.

[3] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Faraday II*, 1974, 1713.

[4] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 4302.

TABLE 1

E.s.r. parameters ($a$/mT) for radicals obtained from substituted resorcinols: (a) oxidation by Ce$^{IV}$ in acid solution; (b) autoxidation in aqueous alkali; (c) oxidation in the Ti$^{III}$–H$_2$O$_2$ system in acid solution (calculated values in parentheses)



| X | Substituents | | $a_2$ | $a_4$ | $a_5$ | $a_6$ |
|---|---|---|---|---|---|---|
| CH | | (a) | 0·375 (0·35) | 1·0 (1·02) | 0·23 (−0·23) | 1·0 |
| | | (b) | 0·07 (−0·08) | 1·12 (1·28) | 0·28 (−0·34) | 1·12 |
| C–CH$_3$ | | (a) | $a_{CH_3}$ = 0·55 | 0·9 | 0·19 | 0·9 |
| C–CO$_2$H | | (a) | | 1·075 | 0·25 | 1·075 |
| C–NO$_2$ | | (a) | $a_N$ = 0·05 | 1·11 | 0·275 | 1·11 |
| N | | (a) | $a_N$ = 0·10 | 1·24 | 0·30 | 1·24 |
| N | 5-CO$_2$H | (a) | $a_N$ = 0·10 | 1·25 | | 1·25 |
| C–OH | | (a) (1) | | 1·23 (1·27) | 0·325 (−0·32) | 1·23 |
| | | (2) | | 0·14 | 0·76 | 0·14 |
| | | (b) | | 0·095 (−0·16) | 0·55 (0·43) | 0·095 |
| | | (c) | | 0·144 | 0·76 | 0·144 |
| C–OH | 5-CO$_2$H | (a) (1) | | 1·23 | | 1·23 |
| | | (2) | | 0·17 | | 0·17 |
| | | (b) | | 0·10 | | 0·10 |
| C–OH | 4-CO$_2$H | (a) (1) | | | 0·32 | 1·22 |
| | | (2) | | | 0·81 | 0·13 |
| | | (b) | | | 0·51 | 0·09 |
| C–OH | 4,6-Bu$^t_2$ | (a) | | $a_{Bu^t}$ = 0·003 | 0·30 | $a_{Bu^t}$ = 0·003 |
| | | (b) | | | 0·545 | |

From the oxidised solutions we were able to isolate purpurogallin (2,3,4,6-tetrahydroxy-5*H*-benzocyclohepten-5-one) (C) which, it is widely accepted, is formed by the dimerisation of pyrogalloquinone [5] (B) in neutral or in acid solution.

This is good evidence for the existence of pyrogalloquinone in our reaction solutions, and suggests that the 'new' radical arises from the oxidation of pyrogalloquinone, as in the Scheme, and that it has two fewer electrons than the initially formed semiquinone.

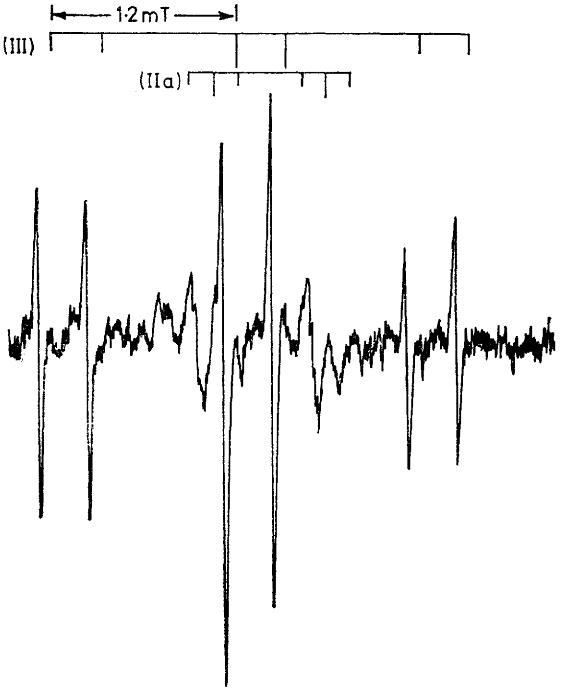
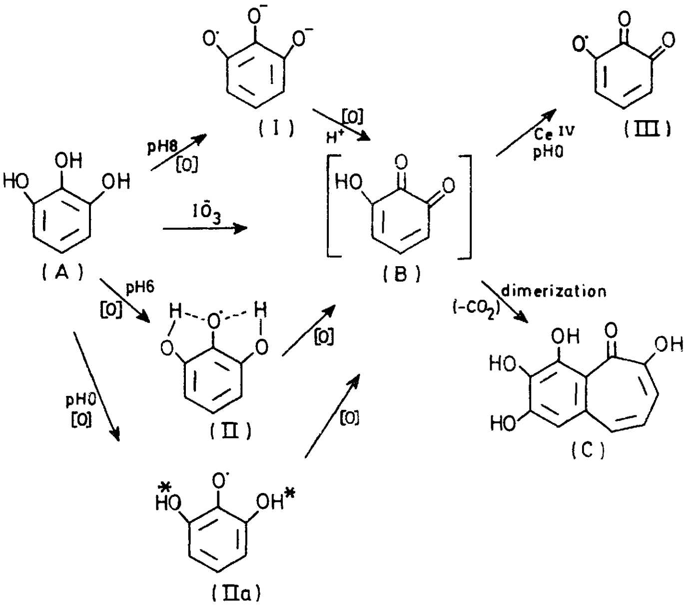


FIGURE 1 E.s.r. spectrum obtained from acidic oxidation of pyrogallol by Ce$^{IV}$

In order to investigate this proposition further we have conducted parallel series of experiments on purpurogallin and related compounds [6] and as with pyrogallol, different spectra were obtained when the solutions were strongly acidic (Ce$^{IV}$ oxidant) to those observed during alkaline autoxidation.



SCHEME Rapidly exchanging protons are asterisked

However, the quinones from purpurogallin and closely related compounds are stable [7] and could be isolated, then oxidised separately in acid solution to give the same spectra as did the reduced forms, confirming by analogy our explanation for the pyrogallol oxidation.

---

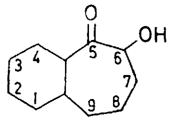
[5] P. L. Pauson, *Chem. Rev.*, 1955, **55**, 9.

[6] W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1974, 1430.

[7] P. D. Collier, *J. Chem. Soc.* (*C*), 1966, 2255.

TABLE 2

E.s.r. spectra ($a$/mT) from 3,4-benztropolones(6-hydroxy-5*H*-benzocyclohepten-5-ones): (a) oxidation by $Ce^{IV}$ in acid solution; (b) autoxidation in aqueous alkali; (c) oxidation by $Ce^{IV}$ in neutral solution



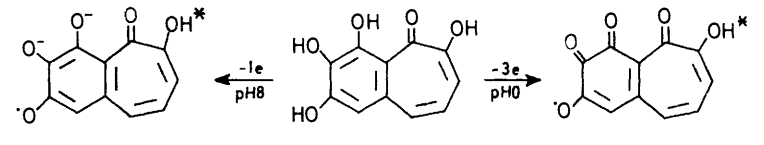
| Substituents | | $a_1$ | $a_2$ | $a_7$ | $a_8$ | $a_9$ |
|---|---|---|---|---|---|---|
| 3,4-(OH)$_2$-7-CO$_2$H | (a) | 0·065 | 0·065 | 0·75 | | 1·00 |
| | (b) | 0·358 | 0·045 | 0·013 | | 0·05 |
| 2,3,4-(OH)$_3$ | (a) | 0·85 | | 0·70 | 0·25 | 0·90 |
| | (b) | 0·11 | | 0·055 | 0·28 | 0·075 |
| | (c) | 0·15 | | 0·17 | 0·43 | 0·17 |

Another example was found with juglone (5-hydroxy-1,4-naphthoquinone) and 1,4,5-trihydroxynaphthalene.

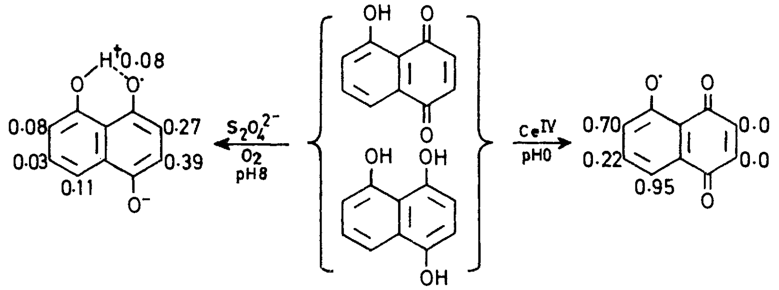
The implication of these findings is that three one-electron oxidations must be taking place well within the dead time (*ca.* 1 ms) of the flow system.[9] This is no precedent however, for multistep reactions are well known with the $Ti^{III}$–$H_2O_2$ system.[10]

DISCUSSION

The most interesting theoretical implication is that, allowing for some possible modification due to protonation, the radicals obtained in alkaline solution differ from those observed in the acidic $Ce^{IV}$ oxidation by two electrons. In molecular orbital language we can therefore say that the two sets of coupling constants give the shapes of two adjacent molecular orbitals. The radicals from pyrogallol are particularly intriguing because it is clear that in radical (I) the odd electron can be said to go into a symmetrical orbital whereas in radical (III) the singly occupied orbital is antisymmetrical with respect to the plane through C(2) and (5), perpendicular to the plane of the nuclei.



* No hydroxylic proton observed in e.s.r. spectrum



†Observed in e.s.r. spectrum [8]

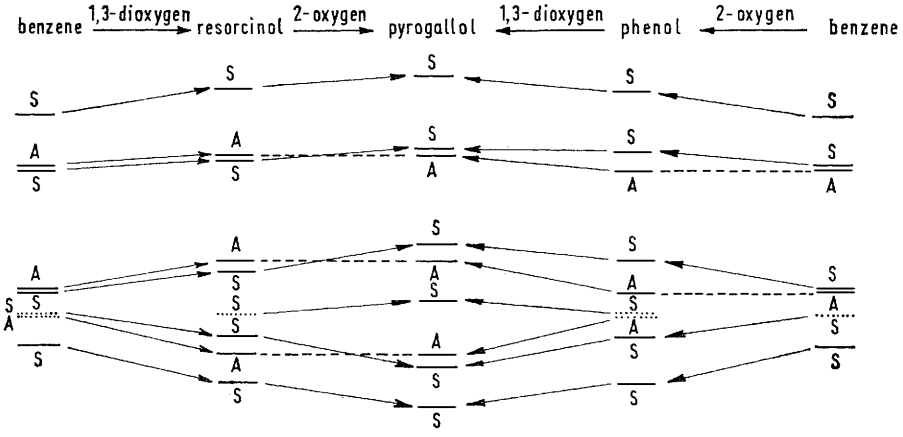


FIGURE 2 Correlation of MO levels in the successive perturbation of benzene by 1,3-di- and 2-oxygen atoms in the formation of pyrogallol: S = symmetrical; A = antisymmetrical orbital; · · · · oxygen atom orbitals

It is instructive to look at the effects of 2-substituents on the orbitals of resorcinol, regarding these sub-

---

[8] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1974, 739.

[9] W. T. Dixon, W. E. J. Foster, and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.

[10] R. O. C. Norman, ' Electron Spin Resonance Studies of Free Radicals and their Reactions in Aqueous Solution,' Chemical Society Special Publication, No. 24, p. 117.

stituents as heteroatoms introducing two more electrons into the π-electron system. Only the symmetrical orbitals will be affected by the perturbation and from a highly simplified orbital diagram we can see that the effect of a strongly interacting group such as $\bar{O}$, is to change the order of the orbitals (see Figure 2).

Confirmation of this assertion was obtained from the results of McLachlan-type calculations in Table 1[3] using the oxygen parameters $\alpha_0 = \alpha + 1{\cdot}6\beta$, $\beta_{CO} = 1{\cdot}3\beta$.

EXPERIMENTAL

The conditions and apparatus used were as previously reported.[1,9,10] The quinones of the 3,4,6-trihydroxybenzocyclohepten-5-one derivatives were made by the methods given in refs. 7 and 11.

[4/2191 *Received, 24th October*, 1974]

---

[11] P. D. Collier, *J. Chem. Soc.* (*C*), 1969, 612.