484. *The Unsaturation Energies of Aroxyl Radicals.*

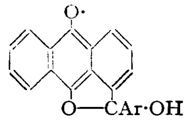
By N. S. Hush.

The changes of unsaturation energy on formation of aroxyl radicals from the corresponding phenols by homolytic fission of the O–H bond are discussed on the basis of assumptions similar to those of Diatkina and Syrkin (*Acta Physicochim., U.R.S.S.*, 1946, **21**, 921) for quinone–quinol systems, and also in terms of a more complete treatment. The results suggest that the critical potentials of phenols determined by Fieser (*J. Amer. Chem. Soc.*, 1930, **52**, 5204) afford a reasonable measure of the differences in normal potential and of $D_{O\cdots H}$ for these molecules.

Formation of Aroxyl Radicals.—Free radicals are formed by oxidation of monohydroxy-aromatic compounds under a variety of conditions, and in some cases can be isolated (Goldschmidt and Stiegerwald, *Annalen*, 1924, **438**, 202; Goldschmidt, Vogt, and Bredig, *ibid.*, 1925, **445**, 123; Scholl, *Ber.*, 1931, **64**, 1158). There is, moreover, considerable chemical evidence for the view (Conant and Pratt, *J. Amer. Chem. Soc.*, 1926, **48**, 3220) that, for a number of oxidants, the initial step in oxidation of phenols in solution under not too drastic conditions usually involves formation in an aroxyl radical (cf. Goldschmidt *et al.*, *Ber.*, 1922, **55**, 3197; Pummerer *et al.*, *Ber.*, 1914, **47**, 1472; 1926, **59**, 2161. For later references, see Cosgrove and Waters, *J.*, 1951, 1726). It is true that most of this evidence involves inferences from the structures of the bimolecular products obtained; recent work by Szwarc and Williams (*J. Chem. Phys.*, 1952, **20**, 1171), however, indicates that $D_{>C\cdots H}$ in aromatic systems is of the same order as $D_{CH_2\cdots H}$, and as $D_{O\cdots H}$ will certainly be less than this in molecules of this type, initial hydrogen abstraction should generally produce an aroxyl rather than a hydroxyaryl radical.

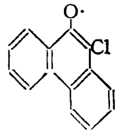
Oxidation Potentials of Hydroxy-aromatic–Aroxyl Systems.—In this paper, we examine the question of how the overall energy change of this initial hydrogen abstraction step varies with change of aromatic structure of the phenol. The energy changes involved in the oxidation of the corresponding dihydroxy-compounds (quinols) to quinones have been discussed from a theoretical point of view by a number of authors (for references, see Evans and de Heer, *Quart. Reviews*, 1950, **4**, 94), connection with the actual magnitudes of these quantities being established by means of the gradation of oxidation potentials of quinone–quinol systems.

(I)



$E_0{}^a = 0{\cdot}360$ v (Ar = phenyl)
$0{\cdot}361$ v (Ar = *m*-xylyl)
$0{\cdot}356$ v (Ar = *p*-methoxyphenyl)

(II)



$E_0{}^b = 0{\cdot}85$ v

[a] Measurements in alcoholic HCl at 25° (Fieser and Young, *J. Amer. Chem. Soc.*, 1932, **54**, 4095).
[b] Measurements in 50% alcohol at 25° (Hush, Morgan, and Oldham, unpublished work).

The oxidation potentials of phenol–aroxyl systems, however, are difficult to measure. For a very few radicals, such as anthroxyls of general formula (I) (Scholl, *loc. cit.*) and for 9-chloro-10-phenanthroxyl (II) (Goldschmidt and Stiegerwald, *loc. cit.*), the oxidation potential can be measured by classical methods, or by simple extensions of them; but, in general, the equilibrium ArO + $\frac{1}{2}H_2 \rightleftharpoons$ ArOH cannot be studied in this way, owing to the lability of the radical. Methods for obtaining a measure of the relative potentials of different phenols were first investigated by Conant (Conant and Lutz, *J. Amer. Chem. Soc.*, 1923, **45**, 1047; 1924, **46**, 1254; 1927, **49**, 1083; Conant and Pratt, *ibid.*, 1926, **48**, 2468, 3178; Conant, Aston, and Tonberg, *ibid.*, 1930, **52**, 407; Conant, *Chem. Reviews*, 1926, **3**, 1), and were developed by Fieser (*J. Amer. Chem. Soc.*, 1930, **52**, 5204). Attention will be confined in this discussion to Fieser's extensive series of comparative measurements.

For a large number of unstable oxidation–reduction systems, Fieser determined a reproducible quantity which was termed the critical potential (E_c) of the system, and it was suggested that the critical potential measures the reversible potential of the system at a small fixed percentage oxidation, α. The relation between the critical potential and the normal potential E_0 on this hypothesis is then

$$E_c = E_0 + (\boldsymbol{R}T/n\boldsymbol{F}) \ln \alpha/(100 - \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the reversible step involves the transfer of n electrons. There is reasonably good evidence in support of this for systems involving two-electron transfer; in all cases studied for which both E_c and E_0 are known, α is approximately 0·5%, corresponding to a value for $(\boldsymbol{R}T/n\boldsymbol{F}) \ln \alpha/(100 - \alpha)$—subsequently referred to for brevity as a—of −0·068 v.

There is unfortunately less direct evidence that equation (1) is also obeyed in the case of one-electron systems. It should be noted, however, that the temperature coefficients of E_c for the phenols are consistent with equation (1) (cf. discussion by Conant and Fieser, *J. Amer. Chem. Soc.*, 1922, **44**, 2480, of entropies of reduction in quinone–quinol systems), and that independent evidence in favour of this relationship is provided by the parallelism between the E_c values of phenols and their chain-breaking capacity as antioxidants in reactions of the type RO•O + ArOH ⟶ ROOH + ArO (Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 242). More qualitatively, the separation of normal potentials of (I) and (II) roughly parallels that of the E_c values of 9-anthrol and 9-phenanthrol if allowance is made (*e.g.*, by the use of equation 11, below) for the effect of the anthrol–anthrone equilibrium in the former molecule, as would be expected if the difference of aromatic structure is the main reason for the separations both of E_0 and E_c.

Summarizing the position, it appears that the interpretation of the E_c data embodied in equation (1) has some experimental support, but it is by no means conclusive; consequently, these values cannot be used as an unequivocal test of theoretical predictions of the energy changes involved in phenol oxidations. In deciding how to proceed, we must bear in mind that theoretical treatments of the energy changes in quinol ⟶ quinone reactions have been highly successful. It is therefore reasonable to expect that in these simpler and closely analogous systems similar arguments will be equally successful in accounting for the actual variations of the overall energy changes. These calculations may be regarded, in fact, as providing evidence for or against the general applicability of equation (1) to phenol–aroxyl systems.

Energy Changes in the Reaction ArO ⟶ ArOH.—It is necessary to relate the free-energy change ΔG of reaction (a) to the change of potential energy ΔE accompanying the

$$ArO_{soln.} + \tfrac{1}{2}H_2 \longrightarrow ArOH_{soln.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

corresponding reaction in the gas phase. Since the structural relation between all ArOH–ArO pairs is very similar, and the members of any pair differ little in mass and in moment of inertia, it can be assumed that

$$\Delta G_1 - \Delta G_2 \simeq \Delta E_1 - \Delta E_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

over the range being considered; the corresponding assumption for quinone–quinol systems appears to be well based (cf. Evans and de Heer, *loc. cit.*). The relation between ΔG and ΔE is discussed more fully on p. 2379; here we require only equation (2), from which it is immediately derivable that

$$\boldsymbol{F}E_0 \simeq -\Delta G + \text{const.} \simeq -\Delta E + \text{const.}' \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where E_0 is the normal potential of the system.

Total Energy and π-Electron Energy.—The phenoxyl radical and phenol are isoconjugate with (*i.e.*, contain the same number of π-electrons in approximately the same geometrical configuration of atomic *p*-orbitals as) benzyl and the benzyl anion respectively, and the energy change for reaction (*a*) is

$$\Delta E = \Delta D_\sigma - \tfrac{1}{2}D_{\mathrm{H}_2} + E_{(n+1)\pi} - E_{n\pi} - 2E_{p_y} \quad . \quad . \quad . \quad . \quad (4)$$

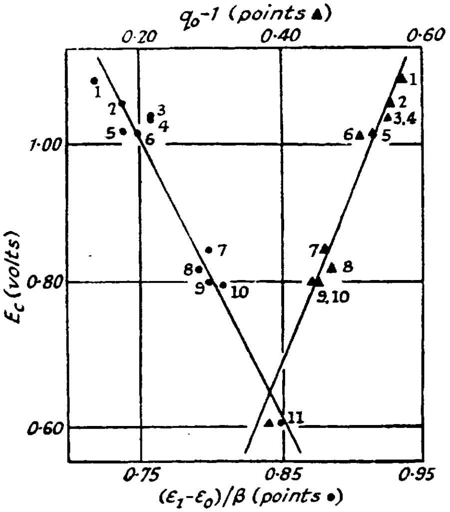
where ΔD_σ is the total change in σ-bond energy of the molecules, E_{p_y} is the energy of an electron in the oxygen p_y orbital with axis of symmetry in the aromatic plane, *n* is the number of conjugated atomic orbitals, and $E_{(n+1)\pi}$ and $E_{n\pi}$ are the energies of the $n + 1$ and *n* π-electrons of the phenol or aroxyl respectively. Variation in all but these last terms is assumed to be small over a series of conjugated molecules (cf. Evans, Gergely, and de Heer, *Trans. Faraday Soc.*, 1949, **45**, 312); with this assumption, we have

$$\Delta E = E_{(n+1)\pi} - E_{n\pi} + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

This relation, together with (3), leads to the general equation for phenol–aroxyl systems:

$$-\boldsymbol{F}E_0 = \varepsilon_{(n+1)\pi} - \varepsilon_{n\pi} + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the terms in ε are now total π-electron binding energies; and where Fieser's postulate (1) holds, the left-hand side of (5) may be replaced by $\boldsymbol{F}E_c$ + const.′. Equation (5) thus permits of a correlation between the oxidation–reduction potential of a monohydroxy-aromatic molecule and the change in π-electron energy accompanying its formation from the corresponding aroxyl radical.



Potentials measured in 37% EtOH at 25°, referred to the normal hydrogen electrode in this solvent. Directly calculated values of $(\varepsilon_1 - \varepsilon_0)$ were taken from the collections of Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025) and of Diatkina and Syrkin (*Acta Physiochim. U.R.S.S.*, 1946, **21**, 641); where direct values are not available, those obtained from the linear relationship between $(\varepsilon_1 - \varepsilon_0)$ and the coefficient of the non-bonding M.O. at the extracyclic atom (Hush, *J.*, 1953, 684) have been employed.

The phenols are numbered as follows: (1), phenol; (2), 2-phenanthrol; (3), *o*-hydroxydiphenyl; (4), *p*-hydroxydiphenyl; (5), 2-naphthol; (6), 4-phenanthrol; (7), 1-phenanthrol; (8), 2-anthranol; (9), 9-phenanthrol; (10), 1-naphthol; (11), 1-anthranol.

Aromatic Methyl Approximation.—As a first approximation to the calculation of Δε,* the unsaturation energy of the aroxyl radical will be set equal to that of the corresponding aromatic methyl radical (ε_1), and the conjugation energy of the hydroxyl group to the aromatic nucleus will be taken to be roughly constant, so that the unsaturation energy of the phenol will be set equal to that of the aromatic residue (ε_0) plus a constant term. The required difference in unsaturation energy on this approximation is thus

$$\Delta\varepsilon = \varepsilon_{\text{phenol}} - \varepsilon_{\text{aroxyl}} = (\varepsilon_0 - \varepsilon_1) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

On combination with equation (3), this yields

$$\boldsymbol{F}E_0 = (\varepsilon_1 - \varepsilon_0) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The plot of E_c against $(\varepsilon_1 - \varepsilon_0)$, in units of the C–C resonance integral, β_{CC}, is shown in the Figure. As would be expected in the relation (1) is valid, this is reasonably linear, and the sign of the slope is in agreement with equation (7); the more highly stabilized the

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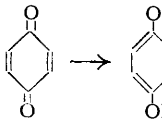
* Unsaturation energies are calculated on the basis of L.C.A.O. M.O. assumptions, with neglect of non-orthogonality of adjacent atomic orbitals.

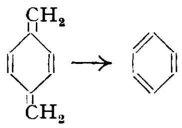
radical, the lower the O–H bond-dissociation energy (and E_c) for the phenol. The trend parallels that of quinone–quinol potentials on the similar " quinonedimethane " approximation of Syrkin and Diatkina (*loc. cit.*), in which $\Delta\varepsilon$ for reactions of the type (III) ⟶ (IV) is taken to be identical with that for (V) ⟶ (VI). It is important that the experimental slopes $n\boldsymbol{F}\delta E/\delta(\Delta\varepsilon)$ for the two types of systems are in reasonable agreement with each other.

(III)



(IV)

(V)



(VI)

Influence of Perturbation Terms.—Absolute calculations of unsaturation energies of ArOH and ArO molecules within the framework of M.O. theory are not possible unless the values of all coulomb and resonance integrals for the systems are known. There is, however, much uncertainty as to the correct values of these terms for hetero-atoms, so complete solution of the secular equations would not be particularly informative.

As a first approach to a more complete treatment, the approximate $\Delta\varepsilon$ change accompanying reaction (*a*) will be calculated by a first-order perturbation method. Where $\varepsilon_0{}^j$ is the energy of a π-electron in the M.O. Ψ^j of the isoconjugate hydrocarbon ($\Psi^j = \sum_r c_r{}^j\phi_r$), the energy ε^j in the oxygen-containing molecule is, to first-order approximation (cf. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265),

$$\varepsilon^j = \varepsilon_0{}^j + \sum_r \sum_s c_r{}^{*j} c_s{}^j \int \phi_r{}^* H' \phi_s d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

H' being the perturbation applied to the one-electron Hamiltonian of the hydrocarbon by oxygen substitution. Of the energy integrals under the double sum, only three will have values which are significantly greater than zero in each molecule; these are, for the phenol and its isoconjugate analogue : (x), the difference in coulomb integral between –OH and $-CH_2{}^-$, (y), the difference in resonance integral for $>C-OH$ and $>C-CH_2{}^-$, and (z), the difference in coulomb integral between a ring carbon atom in the isoconjugate hydrocarbon and at the point of attachment of –OH in the oxygen-substituted molecule. For the aroxyl radical, we have a corresponding set (x'), (y'), (z'), where the oxygen centre is now –O instead of –OH. Since we are interested in the change of unsaturation energy when an electron is placed in the lowest available orbital of an aroxyl, only those terms which contribute to variations in $\Delta\varepsilon$ need be taken into account; this orbital, in the isoconjugate hydrocarbon, is non-bonding, and it follows immediately * that of the above six perturbation terms, the only one contributing to variation in $\Delta\varepsilon$ is that in x; summing over all π-electrons, we obtain the very simple relationship

$$\varepsilon_{\text{phenol}} - \varepsilon_{\text{aroxyl}} = q_0 x + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where q_0 is the π-electron density at the extracyclic position in the carbanion isoconjugate with the phenol. On combination with equation (5), this yields

$$\boldsymbol{F}E_0 = -q_0 x + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If the connection between the critical potential and the normal potential of phenol–aroxyl systems embodied in Fieser's postulate (1), and equation (10), are valid, the plot of E_c against q_0 should be linear, with a slope of $-x/\boldsymbol{F}$; since –OH is more electron-attracting than $-CH_2{}^-$, x will be negative, so the slope will be positive. The plot of q_0 against E_c for all systems for which potential data are available is shown in the Figure; it is seen that there are no serious deviations from linearity over this range of molecules, and that the slope is indeed positive, as predicted. The relationship between E_c and q_0 is best satisfied by

$$E_c = 3{\cdot}0(q_0 - 1) - 0{\cdot}55 \text{ v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The use of first-order perturbation theory limits the discussion to small values of the hetero-parameters. It can easily be shown, however, that a treatment which is valid over

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* The properties of non-bonding orbitals have been described by Longuet-Higgins (*loc. cit.*). Only alternant molecules are considered here.

a larger range of these terms leads to a similar prediction of simple dependence of E_0 on q_0, with the difference that the parameter x of equation (10) becomes a more complex quantity. The conjugation of a hetero-atom to an alternant system has been discussed in detail by Coulson and de Heer (*Trans. Faraday Soc.*, 1951, **47**, 681; *J.*, 1952, 483). Where the hetero-atom is $-$O(H), contributing two π-electrons, then on the assumptions that x is not too small and that the inductive effect of the hetero-atom on the coulomb term of the carbon atom to which it is attached is approximately constant over a series of structures, it may be derived from the work of these authors that

$$\varepsilon_{\text{conj.}}(-\text{OH}) = 0{\cdot}67\ \sqrt{\pi_{\text{ii}}}\ (y + 1)^2/x^{\frac{1}{2}} + \text{const.} \quad . \quad . \quad . \quad . \quad (12)$$

where $\varepsilon_{\text{conj.}}(-\text{OH})$ is the conjugation energy across the $>$C–OH bond and π_{ii} is the self-polarizability of the carbon centre (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39) to which the hetero-atom is attached. (All energy terms are in units of β_{CC}.)

Where the hetero-atom contributes only one π-electron to the system (as does $-$O) and where the parameters are of the same order of magnitude as for $-$OH, the conjugation energy should be given by an expression of the same form as (12), but with a different

$$\varepsilon_{\text{conj.}}(-\text{O}) = 0{\cdot}67\ \xi\ \sqrt{\pi_{\text{ii}}}\ (y' + 1)^2/(x')^{\frac{1}{2}} + \text{const.} \quad . \quad . \quad . \quad . \quad (12')$$

numerical constant; thus, for $-$O, the relation (12′), where ξ is a constant, will be expected to hold, the important variable terms being assumed to be those in x' and y'. This leads to

$$\varepsilon_{\text{phenol}} - \varepsilon_{\text{aroxyl}} = 0{\cdot}67\ \sqrt{\pi_{\text{ii}}}\left\{\frac{(y + 1)^2}{x^{\frac{1}{2}}} - \frac{\xi\ (y' + 1)^2}{(x')^{\frac{1}{2}}}\right\} \quad . \quad . \quad . \quad (13)$$

Combining this with equations (1) and (5), we should therefore expect E_c to be approximately linear with $\sqrt{\pi_{\text{ii}}}$ over a series of aromatic structures, and this is indeed found to be the case. This relation does not need to be discussed further, for over the range of structures considered here, π_{ii} is related to q_0 by $\sqrt{\pi_{\text{ii}}} \simeq 1{\cdot}182 - 0{\cdot}357q_0$, so that the plot in the Figure can also be regarded as a test of this prediction. In this case it is, of course, difficult to predict the sign of the slope, but there is no reason to believe that the observed sign is inconsistent with the theory.

Discussion of O–H *Bond-dissociation Energies in Phenols.*—These considerations of the energetics of the oxidation reactions support the view that the order of critical potentials for the phenols discussed is, within reasonable limits of error, the order of their standard oxidation–reduction potentials. These quantities are of some interest, as it is possible, with their use, to derive approximate values of the O–H bond-dissociation energies in phenol molecules; we note that a (large) error of 0·1 v in E_0 will contribute only $\pm$ 0·1 e.v. to the probable error in $D_{\text{O}\cdots\text{H}}$.

The heat Q_a of reaction (*a*) is related to $D_{\text{O}\cdots\text{H}}$ by

$$Q_a = D_{\text{O}\cdots\text{H}} - \tfrac{1}{2}D_{\text{H}_2} + (Q^s{}_{\text{ArOH}} - Q^s{}_{\text{ArO}}) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $Q^s{}_{\text{ArOH}}$ and $Q^s{}_{\text{ArO}}$ are the heats of solution of gaseous phenol and aroxyl, respectively. The term involving these heats of solution will be small; from the data for quinols and quinones (cf. Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 293), and with allowance for the fact that the oxidant possesses only one $-$OH group, the difference $Q^s{}_{\text{ArOH}} - Q^s{}_{\text{ArO}}$ is estimated at 3 kcal. mole^{-1}. From equation 2, the mean entropy change in reaction (*a*) may be taken to be $\sim -$ 16 e.u. mole^{-1}, so that $D_{\text{O}\cdots\text{H}}$ can be estimated to a reasonable approximation from the free energy of the oxidation–reduction reaction in solution. For the term *a* (equation 1) connecting E_c and E_0, Fieser's proposed value (*loc. cit.*, 1930) * $-$ 0·14 v is employed. On substitution in (14), this gives

$$D_{\text{O}\cdots\text{H}} \simeq \boldsymbol{F}E_c + 57\ \text{kcal. mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

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* The value of $\frac{1}{2}D_{\text{H}_2}$ is taken as 52·0 kcal. mole^{-1} (Rossini *et al.*, "Selected Values of Properties of Hydrocarbons," 1948).

Typical values of $D_{O\cdots H}$ (in kcal. mole^{-1}) obtained by the use of equation (15) for the more important molecules are shown below :

Molecule	$D_{O\cdots H-}$	Molecule	$D_{O\cdots H-}$
Phenol	(82) 84 †	2-Naphthol	80
2-Phenanthrol	81	1-Naphthol	75
p-Hydroxydiphenyl	81	1-Anthrol	71

† The point for phenol lies somewhat off the line in the Figure; the value of 84 kcal. mole^{-1} calculated from (11) and (15) is probably a better approximation in this case.

Although the absolute uncertainty is difficult to estimate, these values are unlikely to be seriously in error. It may be noted that extrapolation in the Figure leads to a value of $D_{O\cdots H}$ for the case $(q_0 - 1) = 1$ of 110 kcal. mole^{-1}. In order to connect this approximately with $D_{O\cdots H}$ for methanol, we need to know the difference in hyperconjugation energy between the ethyl radical and the ethyl anion; calculations by Matsen, Robertson, and Chuoke (*Chem. Rev.*, 1947, **41**, 273) lead to a value ≈ -9 kcal. mole^{-1} for this quantity, and on this crude approximation, this would correspond to $D_{O\cdots H}$ in methanol ≈ 101 kcal. mole^{-1}. This is certainly of a reasonable order of magnitude, as $D_{O\cdots H}$ in ethanol is known to be 101 kcal. mole^{-1} (Laidler and Rebbert, *J. Chem. Phys.*, 1952, **20**, 574).

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