622. *Hydrogen Transfer. Part X.* The Dehydrogenation of Hydroaromatic Hydrocarbons by Quinones: Theoretical Calculations for Possible Intermediates.*

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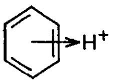
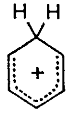
The L.C.A.O. M.O. method with various refinements has been used to afford the relative energies of stabilisation of σ-complexes believed to be involved in the dehydrogenation of hydroaromatic hydrocarbons by quinones. The qualitative order of these energies is consistent with the two-step ionic mechanism postulated in earlier papers. The preference for an ionic rather than a free-radical mechanism is discussed. A perturbation method, taking hyperconjugation into account, has been used for calculation of the energies of ionic intermediates.

THE results of the kinetic survey, described in Part II,[1] of the thermal dehydrogenation of 1,4-dihydronaphthalene by various quinones led to the postulation of an ionic mechanism, and more intimate details of this mechanism were considered in Part III.[2] In particular, an attempt was made to determine the nature of the intermediate (RH^+) involved in the two-step process (1). Two extreme ionic species were considered. They were the π-complex (I) and the σ-complex (II). It was suggested that the σ-complex could not be involved as such since the observed order of reactivity of three hydrocarbons, *viz.*, 1,4-dihydrobenzene > 1,4-dihydronaphthalene > 9,10-dihydroanthracene, was opposite to that expected for the stabilities of the σ-complexes. That the relative stabilities of these ions should be in the reverse order to that of the parent dihydro-compounds was concluded partly on intuitive grounds and partly from a consideration of " resonance " structures. The method of counting resonance structures is, however, known to be inherently unsound.[3] In this paper it is shown that molecular-orbital calculations lead to the opposite conclusion and indicate that the observed order of reactivities is compatible with that of the relative stabilities of the σ-complexes for the three examples quoted.

$$RH_2 + Q \longrightarrow QH^- + RH^+ \longrightarrow QH_2 + R \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

(I) 

 (II).

We have sought to establish the sequence of stabilities by direct calculation using the L.C.A.O. M.O. method with various refinements. Since within the series of hydroaromatic systems under consideration the changes in bond-type remain the same, the relative driving force of the reaction for each member of the series will be a function of the difference in resonance energies of the hydroaromatic system and the σ-complex. The resonance energies of the hydroaromatic compounds have been assessed from experimental data. Magnus and Becker[4] give values, obtained from heats of combustion data, of 75·3,† 36·7, and 35·9 kcal. mole^{-1} for 9,10-dihydroanthracene, 1,4-dihydronaphthalene, and benzene respectively, while from heats of hydrogenation[5] values of 37·0 and 36·0 for 1,4-dihydronaphthalene and benzene are obtained. The extra resonance energies above

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* Part IX, *J.*, 1956, 3070.

† The redetermined[4] heat of combustion of 9,10-dihydroanthracene makes this value 76·6. We have used the lower value although the higher value is more favourable for our purpose.

[1] Braude, Jackman, and Linstead, *J.*, 1954, 3548.

[2] Braude, Jackman, and Linstead, *J.*, 1954, 3564.

[3] Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, 1952, *A*, **214**, 482.

[4] Magnus and Becker, *Erdöl u. Kohle*, 1951, **4**, 115.

[5] Williams, *J. Amer. Chem. Soc.*, 1942, **64**, 1395.

that of the benzene nuclei of 9,10-dihydroanthracene and 1,4-dihydronaphthalene are 3·5 and 0·8—1·0 respectively. It is reasonable to suppose that the corresponding value for 1,4-dihydrobenzene is smaller and probably negligible. We shall assume, therefore, that the resonance energies of the three systems, compared with the value of 36·0 for benzene, are 0·0 for 1,4-dihydrobenzene, 36·9 for 1,4-dihydronaphthalene, and 75·5 for 9,10-dihydroanthracene. Unless otherwise stated, all calculated resonance energies of the σ-complexes given below have been obtained by using parameters which give the value of 36·0 for the resonance energy of benzene. The driving forces for the reactions are then conveniently presented by taking the value for the 9,10-dihydroanthracene system as an arbitrary zero.

Carbonium ions of the type (II) are believed to be the intermediates involved in electrophilic aromatic substitution [6] and some attempts to estimate their π-electron energies have been made.[7,8,9] Gold and Tye [9] have extended Wheland's original calculations [7] to a number of polycyclic aromatic hydrocarbons, using the M.O. approximation in its simplest form. Their results of interest in the present connection are reproduced in Table 1 and are seen to agree with the experimental sequence of reactivities.

Gold and Tye's method does not take into account a number of factors which could have a significant effect on the calculated energies. In systems such as (II) the contribution of methylene hyperconjugation to the total π-electron energy is probably considerable. Mulliken and his co-workers [10] have sought to introduce hyperconjugation explicitly into the energy calculation by treating the methylene group as a quasi-double bond ($-C=H_2$), assigning to it a resonance integral, 2β, twice that of the benzene bonds. The coulomb integral associated with terminal H_2 was made equl to $\alpha + \delta\beta$ (α being the value for $2p\pi$-carbon atom) where δ was given values from $-0{\cdot}5$ to $0{\cdot}5$. The calculations which were confined to the benzenium ion were carried out with various refinements. In the most detailed treatment the energies were made self-consistent to variations of β's and α's with bond orders, and with charge densities respectively, several functional relations being assumed for the latter. Overlap was included and correction made for compressional energy. In applying Mulliken's model to higher members of the series we have corrected for overlap and compressional energy, but because of the complexity of the problem we have not made the calculations self-consistent. The results for various stages of refinement may be found in Table 1 and again they exhibit the same qualitative order as the experimental reactivities.

While the calculations by Mulliken and his co-workers represent quite a high order of refinement they do not explicitly include electron-interaction terms. Ideally this should be done in such a way as to obtain the self-consistent molecular orbitals in the manner described by Pople.[11] The difficulty arises as to how to handle the electron repulsion terms ($\gamma_{\mu\nu}$'s) associated with the quasi-double bond and in view of the crudity of the model detailed calculations along these lines did not seem worthwhile. Instead we returned to the Wheland–Gold model, in which hyperconjugation is neglected, and used Hückel orbitals corrected for electron interaction. Brickstock and Pople [12] have made calculations for a number of carbonium ions by this method, including the diphenylmethyl ion which is equivalent in this approximation to the σ-complex from 9,10-dihydroanthracene. We have extended the calculations to the *S-cis*-conformations of the *cis*-pentadienyl and 1-phenylallyl ions. The figures for comparison in Table 1 were obtained by subtracting the experimental values for hyperconjugative coupling (p. 3110) in the hydroaromatic compound from the difference between the vertical resonance energies of the hydroaromatic system and of the corresponding σ-complex. The observed order is

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[6] Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, p. 280.

[7] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[8] Heilbronner and Simonetta, *Helv. Chim. Acta*, 1952, **35**, 1049.

[9] Gold and Tye, *J.*, 1952, 2184.

[10] Muller, Pickett, and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 4771.

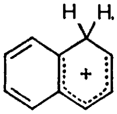
[11] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

[12] Brickstock and Pople, *Trans. Faraday Soc.*, 1954, **50**, 901.

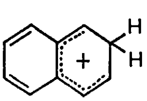
the same as for the other approximations although in this case the numerical differences are so small as to be insignificant. Judged from the magnitude of the hyperconjugation energies of these ions calculated from the Mulliken model (see below) these differences would be increased somewhat if this hyperconjugation had been taken into account in the Pople approximation.

The values in Table 1 all indicate that the increase in stability of the intermediate ion over that of the hydroaromatic system decreases as one ascends the polyacene series and thus the relative rate sequence observed in Part III is consistent with a two-step ionic mechanism. These findings do not, of course, rule out the possibility that subsequent removal of the proton has to some extent begun in the rate-controlling step. It is hoped that a study of isotope effects may allow a more precise formulation of the intermediate. The calculated energy differences, have, of course, little quantitative significance although it appears that, when electron interaction is included, the differences are very small and indeed the observed rate constants suggest that this is so.

Calculations for the 1- and 2-naphthalenium ion [(III) and (IV)] reveal the former as having the higher resonance energy, the difference being significant in all approximations used (Table 2). This suggests that the 2-position is the preferred point of attack in the dehydrogenation of 1,2-dihydronaphthalene. This is supported by the observation [13] that the reactions of 1,2-dihydronaphthalene and several 1,1-dialkyl-1,2-dihydronaphthalenes with tetrachloro-*o*-benzoquinone have nearly the same energies of activation.



(III)



(IV)

TABLE 1. *Resonance energy gains (kcal. mole^{-1}) for σ-complex formation from hydroaromatic hydrocarbons.*

Method	1,4-Dihydrobenzene	1,4-Dihydronaphthalene	9,10-Dihydroanthracene [a]
Gold and Tye [9]	6·4	3·0	0·0
Mulliken model [b]	8·9	5·1	0·0
[c]	27·3	23·1	0·0
[d]	29·9	24·5	0·0
Pople method	0·3	0·2	0·0

[a] The resonance energy gain for 9,10-dihydroanthracene has been taken as an arbitrary zero of energy. [b] Uncorrected for overlap and compression. [c] Corrected for compression only. [d] Corrected for compression and overlap.

TABLE 2. *Resonance energies (kcal. mole^{-1}) of* 1- *and* 2-*naphthalenium ions.*

Method	(III)	(IV)	Difference
Gold and Tye [9]	60·8	57·3	3·5
Mulliken model [b]	73·7	71·5	2·1
[c]	83·0	81·0	2·0
[d]	77·1	72·2	4·9
Pople method [a]	199·4	186·3	13·1

[a] These values are vertical resonance energies obtained with $\beta = 55{\cdot}1$ kcal. mole^{-1}. [b, c, d] See corresponding footnotes to Table 1.

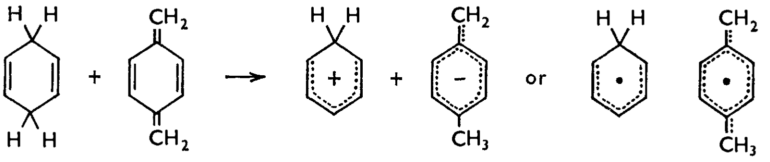
The activation energy for the dehydrogenation of 1,2-dihydronaphthalene by tetrachloro-*o*-benzoquinone has been shown by Braude, Jackman, Linstead, and Shannon [14] to exceed that of the corresponding reaction of the 1,4-isomer by 3·0 kcal. mole^{-1}. From the above argument it is apparent that the ionic intermediate is the same for both isomers. This energy difference must therefore arise from the difference in resonance energies of the two isomeric hydrocarbons and is hence in excellent agreement with the observed difference

[13] Braude, Jackman, Linstead, and Lowe, *J.*, 1960, 837.

[14] Braude, Jackman, Linstead, and Shannon, following paper.

(3·0 kcal. mole^{-1}) in the heats of hydrogenation of the two hydrocarbons although it should be noted that the transition states of the two reactions are not identical.

Most of the foregoing arguments for a two-step ionic mechanism apply equally to a two-step free-radical mechanism. However, the evidence presented in Parts II and III favoured an ionic process. Further, the observation [15] that dehydrogenation of " blocked " hydroaromatic compounds, such as 1,1-dimethyltetralin, is accompanied by a ready rearrangement of the Wagner–Meerwein type whereas radical dehydrogenation with dipicrylhydrazyl is not [13] offers strong support for this view since it is only in the carbonium ion that a low-lying π-orbital can be used for the formation of the non-classical intermediate involved in re-arrangement.[16] On the other hand, the radical mechanism seems at first sight more likely, particularly for reactions in non-polar solvents, since the energy required for the separation of the ionic intermediates would be appreciable unless reduced by solvation. The explanation for the preference for the ionic mechanism must therefore lie in the relative stabilities of the intermediates involved in the two mechanisms. In this connection it is instructive to consider the hypothetical reaction between 1,4-dihydrobenzene (V) and *p*-quinodimethane (VI). In the simple M.O. method the odd electron in both the radical intermediates, (IX) and (X), occupies a non-bonding molecular orbital and no difference between the resonance stabilisation of these intermediates and their ionic counterparts, (VII) and (VIII), is predicted. However the inclusion of electron interaction terms profoundly alters this conclusion and substantial differences in favour of the ionic process appear. An estimate of the overall energy difference between the two pairs of intermediates has been made on the assumption that the resonance energies of the 4-methylbenzyl anion (VIII) and of the radical (X), which would arise from the *p*-quinodimethane, are roughly the same as for the benzyl anion and radical, respectively. The values of the resonance energy differences between ion and radical are 40·2 and 39·6 kcal./mole for the benzenium and 4-methylbenzyl [11] system respectively.* It thus appears that in terms of vertical resonance energies the ionic mechanism is favoured to the extent of 80 kcal. mole^{-1}.



(V) (VI) (VII) (VIII) (IX) (X)

This difference will be even larger for quinone itself, for owing to the higher electronegativity of oxygen the non-bonding molecular orbital of the quinodimethane becomes bonding and the resonance energy of the anion will be greater than that of the radical by an amount equal to the energy of this orbital. Perturbation theory using $\alpha_O + \beta$ as the value of the coulomb integral of oxygen gives 10 kcal. mole^{-1} as a rough estimate of this additional stabilisation. The ionic mechanism for the reaction of 1,4-dihydrobenzene with *p*-benzoquinone may therefore be expected to have a vertical resonance stabilisation of 90 kcal. mole^{-1} above that of the radical process, of which 40 and 50 kcal. mole^{-1} arise from the cation and the anion respectively.

Although this estimated difference in resonance stabilisation is certainly larger than the actual value, it may nevertheless be concluded that this factor is important and, when added to the expected stabilisation of the ionic intermediates by weak solvation,

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* That these figures are also a reasonable approximation to the difference in experimental resonance energies is, in part, justified by the satisfactory agreement between the calculated and the observed difference for the benzyl system.[11]

[15] Linstead, Braude, Jackman, and Beames, *Chem. and Ind.*, 1954, 1174.

[16] Dewar, Tilden Lecture delivered before the Chemical Society, 1953.

ion-pair formation, and charge transfer forces, may account for the ionic nature of the reaction.

The calculated values of the vertical resonance energy differences between the 1-naphthalenium and the 9-anthracenium ions and the corresponding radicals are 46·4 and 54·2 kcal. mole^{-1}, respectively. Thus the two-step radical mechanism should exhibit the same qualitative rate sequence as the analogous ionic mechanism for the three hydrocarbons under consideration. It is interesting that, as the stabilisation of the radical relative to the carbonium ion decrease along the series, benzenium, 1-naphthalenium, 9-anthracenium, radical aromatic substitution should be *less* sensitive than electrophilic aromatic substitution to annelation. The observations of Dewar and his co-workers [17] suggest that this is so. These authors have attributed the varying sensitivities of aromatic substitution reactions towards structural changes to differing degrees of hybridisation in the transition states of the substitution processes. However, the above calculations indicate that it is probably not legitimate to compare ionic with free-radical reactions in this way.

As pointed out in Part III [2] a mechanism involving the concerted removal of two hydrogen atoms should also give rise to the observed reactivity sequence for the three hydroaromatic hydrocarbons.

The conclusions which can be drawn from the above considerations are that: (i) the argument advanced in Part III against the simple two-step ionic process is invalid and this mechanism must again be considered as a possibility; (ii) the qualitative order of hydrogen-donor reactivity in the series, 1,4-dihydrobenzene, 1,4-dihydronaphthalene, and 9,10-dihydroanthracene, is likely to be the same for all three mechanisms considered; and (iii) the greater vertical resonance energy of an aromatic carbonium ion than of the corresponding radical would favour, but not necessitate, an ionic mechanism.

CALCULATIONS

The Mulliken Model.—(a) *Direct M.O. calculations.* These calculations were performed in the usual manner, with the assumptions adopted by Muller, Pickett, and Mulliken.[10] The hyperconjugative contribution of the methylene group is calculated as indicated above.

The compression energies, *i.e.*, the energy required to deform the formal bonds of a localised model, were computed from the bond-order–energy relations given by Muller *et al.* Because of the large variations in bond orders found for some of the ions (see Table 3) the values so obtained are far from satisfactory.

TABLE 3. *Bond orders of aromatic ions.*

Bond *	Benzenium	1-Naphthalenium	2-Naphthalenium	9-Anthracenium	Bond *	1-Naphthalenium	2-Naphthalenium	9-Anthracenium
1,2	0·849	0·872	0·854	0·894	8,9	0·636	0·718	0·548
2,3	0·364	0·360	0·341	0·306	9,10	0·664	0·528	
3,4	0·743	0·722	0·819	0·988	10,11	0·649	0·629	
4,5	0·606	0·629	0·487	0·493	11,6	0·544		
5,6		0·528	0·603	0·468	11,2	0·310	0·375	
6,7		0·562	0·685	1·033	10,5		0·483	
7,8		0·699	0·610	0·388	3,8			0·367

* The H_2 quasi-atom is numbered 1, the methylene carbon atom 2, and the remaining atoms clockwise around the molecule.

The orbital energies were obtained in terms of $\beta = -18$ kcal. in calculations which did not take into account overlap or compression, and in terms of $\beta = -31 \cdot 5$ kcal. when compression was included. Energies corrected for both overlap and compression were in terms of $\gamma = -60$ kcal.

Values for vertical hyperconjugation energies [10] (H.C.J.E.) were computed by subtracting the π-electron energies obtained by neglecting hyperconjugation from the values for which it was included. Values uncorrected for overlap are given in Table 4.

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[17] Dewar, Mole, and Warford, *J.*, 1956, 3581; 1957, 342.

TABLE 4. *Vertical H.C.J.E.'s of some aromatic ions.*

Ion:	Benzenium	1-Naphthalenium	2-Naphthalenium	9-Anthracenium
Vert. H.C.J.E.: $\times \beta (= -18$ kcal.).	0·79	0·71	0·79	0·64

(b) *Perturbation calculations.* In addition to the direct molecular-orbital method we have investigated Dewar and Pettit's perturbation method [18] in which polycyclic systems are regarded as derived from cyclopolyenes and the introduction of the appropriate transannular linkages is treated as a series of perturbations. The method has the advantage that a number of aromatic systems can be derived from one cyclopolyene. In this work the initial problem consisted of finding the orbital energies and coefficients of the appropriate cyclopolyenium ions including the quasi-double bond. The C_{2v} symmetry of these systems permitted partial factorisation of the secular determinants. The introduction of transannular linkages between atoms μ and ν were then considered as perturbations $H\mu\nu$.[1] Where more than one transannular linkage was introduced it was assumed that the perturbations were additive. The various aromatic ions listed in Table 5 were derived from the cyclodecapentaenium and cyclotetradecaheptaenium ions.

TABLE 5. *Perturbation and M.O. vertical resonance energies of aromatic cations.*

Cation	Perturbation energy, $\times \beta$ $(= -18$ kcal.)	M.O. energy, $\times \beta$	Cation	Perturbation energy, $\times \beta$ $(= -18$ cals.)	M.O. energy, $\times \beta$
1-Naphthalenium (III)	3·677	4·094	1-Anthracenium	4·922	—
2-Naphthalenium (IV)	3·573	3·971	2-Anthracenium	4·808	5·645
1-Azulenium	3·683	—	9-Anthracenium	5·158	5·943
2-Azulenium	3·349	3·737	1-Phenanthrenium	4·864	—
4-Azulenium	3·016	—	2-Phenanthrenium	4·808	—
5-Azulenium	3·349	—	3-Phenanthrenium	4·787	—
6-Azulenium	3·016	3·442	4-Phenanthrenium	4·613	—
			9-Phenanthrenium	4·578	5·861

Where known the results of the direct molecular-orbital method have been included for comparison. In agreement with Dewar and Pettit's observations the perturbation method yields values which are consistently lower than those of the direct M.O. method. Further, the relation between the results of the two methods are best represented by the linear equation $E_{\text{M.O.}} = 1{\cdot}37E_{\text{Pert.}} - 0{\cdot}80$, in which the parameters compare favourably with those (1·35 and −0·70 respectively) derived by Dewar and Pettit for the polycyclic aromatic systems.

The Pople Method.—The value for the 9-anthracenium ion was taken as equal to that calculated by Brickstock and Pople [12] for the diphenylmethyl cation, and the remaining examples were calculated by the same method with values of the electron interaction integrals, $\gamma_{\mu\nu}$, computed by Pople's inverse-distance approximation.[11]

Relative Stabilities of Ions and Radicals.—The differences in vertical resonance energies for the various pairs of ions and radicals were calculated by the equation: [12]

$$E_{\text{R}}(\text{ion}) - E_{\text{R}}(\text{radical}) = \sum_{\mu<\nu} C_{0\mu}{}^2\, C_{0\nu}{}^2\, (\gamma_{11} - \gamma_{\mu\nu})$$

where $C_{0\mu}$ and $C_{0\nu}$ are the atomic coefficients for the non-bonding molecular orbital.

The correction for the replacement of the two terminal carbon atoms of *p*-quinodimethane was based on the equation: [19]

$$\delta_{\epsilon_0} = \sum_{\mu} C^2{}_{0\mu}\, \delta\alpha_{\mu}$$

where $C_{0\mu}$'s are the coefficients for the non-bonding molecular orbital of the atomic centres which are being replaced and $\delta\alpha_{\mu} = \beta$ is the difference in the coulomb integrals of oxygen and carbon.

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[18] Dewar and Pettit, *J.*, 1954, 1617.

[19] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.