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ORIENTATION IN THE MECHANISM OF THE BIRCH REDUCTION OF ANISOLE

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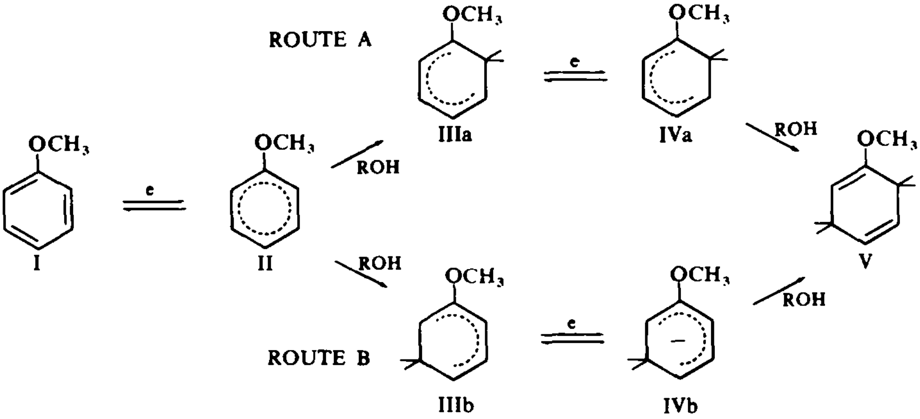
Abstract—The Birch reduction of anisole is thought to proceed by the formation of the radical anion which is protonated to give a cyclohexadienyl radical. The observed product, 2,5 dihydroanisole, can be formed from two possible cyclohexadienyls, one arising by *ortho* protonation of the anisole anion and the other by *meta* attack. This protonation step is considered in terms of both a polarized state model of the transition state and the energies of the resulting cyclohexadienyls. The energies of possible transition state configurations are also considered. It is concluded that protonation is unlikely to occur predominantly at the *ortho* position.

There is general agreement that the Birch reduction of monobenzenoid aromatics has one of the mechanisms shown in Scheme 1 for anisole.[1-5]

Scheme 1



The existence of radical anions like II has been demonstrated by ESR studies of the alkali metal reduction of alkyl[6-7] and alkoxybenzenes[4,8,9] in ethereal solvents. However it has not been possible to obtain further information about the mechanism using this technique.[10] Kinetic studies of the liquid ammonia reduction of benzene[3] have shown the reaction to be first order in alkali metal, aromatic and added alcohol and are consistent with this mechanism provided that the rate determining step is the irreversible protonation of the anion II to give a cyclohexadienyl, III. The product, V, can arise from either IIIa or IIIb (routes A and B) and the question of which one of these operates (or if both do) is the subject of the present paper.

Route B has been supported by Birch[1] and others[2,3] on the grounds that the substituent opposes the accumulation of charge in the *ortho* and *para* positions and so causes a high unpaired electron density in the *meta* positions. Indeed, the largest spin density has been shown by ESR to occur at the *meta* position of the toluene[6] and anisole[4,8] radical anions. Route A has been supported by Zimmerman[5] on the basis of some Hückel (HMO) calculations which predict a larger *ortho* charge density. It is difficult to assess this result as HMO estimates of the unpaired electron densities fail to account for the observed difference between the *ortho* and *meta* splitting constants of anisole radical anion. A recent Unrestricted Hartree–Fock (UHF) calculation[8] which gives an adequate account of the spin distribution in this species also gives a larger *ortho* charge density. Nonetheless it is not obvious that protonation will occur at the site with the highest charge density and for this reason several models for the transition state have been investigated.

THE TRANSITION STATE

Polarized state model

The protonation of the radical anion II appears to be kinetically controlled, so it is necessary to estimate the relative energies of each of the possible transition states. Zimmerman[5] has suggested that this protonation step is governed by the charge distribution and not by localization energies. This means that the transition state occurs near the beginning of the reaction and it is a reasonable approximation to consider the reacting species as distinct entities. Under these conditions the polarized state model[11] may be used and the interaction energy of the proton and radical anion is given to first order by

$$\Delta E = \sum_{r}^{\text{all atoms}} q_r \Delta\alpha_r + E_{\text{rep}}^{\text{core}} \tag{1}$$

where q_r is the total π-charge on atom r, $\Delta\alpha_r$ is the change in the coulomb integral of atom r, and $E_{\text{rep}}^{\text{core}}$ represents the repulsion between the positively charged core stripped of its π-electrons and the proton.

Comparison with the SCF Hamiltonian in the Zero Differential Overlap approximation[11–13] suggests that

$$\Delta\alpha_r = -\gamma_{r,H^+} \tag{2}$$

where γ_{r,H^+} is analogous to the two centre electron repulsion integrals of the π-system. Naively this may be considered to vary as $1/r$ and, with a similar dependence for the core repulsion term, Eq. (1) simplifies to

$$\Delta E = -\sum_{r}^{\text{all atoms}} (q_r - Z_r)/r_{r,H^+} \tag{3}$$

where Z_r is the number of electrons donated to the π-system. A better formulation of the electron repulsion type term, γ_{r,H^+}, is one similar to that proposed by Mataga[14]

$$\gamma_{r,H^+} = \frac{1}{(a_r + r_{r,H^+})} \tag{4}$$

where the constant a_r can be determined when r_{r,H^+} is zero as $\Delta\alpha_r$ is equal to the difference in the valence state ionization potentials

$$\Delta\alpha_r = I_C - I_{N^+} = -\frac{1}{a_r} \tag{5}$$

The repulsion between the proton and the core nuclei can be expressed as the Coulomb repulsion of point charges[15] so that

$$E_{\rm rep}^{\rm core} = \sum_r Z_r/r_{r,H^+} \tag{6}$$

However Del Re and Parr[16] have suggested that the repulsion between the positively charged atoms of the core of an aromatic compound is not between point charges but between orbital-like positive lobes in neutral charge clouds. The coulomb repulsion term is then given by

$$E_{\rm rep}^{\rm core} = \sum_r Z_r \gamma_{r,H^+} \tag{7}$$

Both expressions (6) and (7) have been considered in this work. Substitution of (7), (4) and (2) into (1) gives

$$\Delta E = -\sum_r \frac{(q_r - Z_r)}{(a_r + r_{r,H^+})} \tag{8}$$

The interaction energy between a proton and the anisole radical anion has been calculated using Zimmerman's Hückel charge densities[5] as well as those obtained from the UHF calculation (Table 1).[8] In these calculations the proton is situated 1·6 Å above the plane of the ring but over the hydrogen adjacent to the site of protonation, i.e. a deformed cyclohexadienyl geometry. In addition the effect of the ethoxide gegenion has been considered.

TABLE 1.
THE CHARGE DENSITIES IN ANISOLE RADICAL ANION FROM THE UHF CALCULATION[8]

Position*	Oxygen	1	2	3	4
π-charge	1·892	0·979	1·287	1·245	1·007

* Substituent carrying position numbered 1.

π-energy approach. It can be argued that the transition state occurs at a point well along the reaction co-ordinate and that the differences in the activation energies are more closely represented by the differences in the energies of the product cyclohexadienyls. These energies have been calculated by the HMO[17] and UHF[15] methods using hyperconjugative models for the methyl and methylene groups.[18,19] The parameters used in the HMO calculations were[4,17,18]

$$h_{\rm H_3,\,H_2} = -0{\cdot}5 \qquad k_{\rm C—H_2} = 2{\cdot}5 \qquad k_{\rm C—H_3} = 2{\cdot}0$$

$$h_{\rm C_{CH_3,CH_2}} = -0{\cdot}1 \qquad k_{\rm C—CH_2} = 0{\cdot}8 \qquad k_{\rm \ddot{O}—CH_3} = 0{\cdot}5$$

$$h_{\rm \ddot{O}} = 2{\cdot}0 \qquad k_{\rm \ddot{O}—C} = 0{\cdot}8$$

The semi-empirical UHF parameters have been transferred, where applicable, from previous calculations[8,19] and the additional ones obtained by conventional methods.[12,13]

The total energy, E, of the radical has been taken as

$$E = E_\pi + E_{\rm rep}^{\rm core}$$

where E_{π} is the π-electron energy and $E_{\text{rep}}^{\text{core}}$ is a term representing the repulsion between the core charges. The use of this expression implies that the sigma energies, etc, are assumed to be the same for each radical. In the HMO calculations, where the total π-energy includes the electron repulsion integrals summed twice, the core repulsion term has been neglected in the hope that the two terms compensate for each other.

The somewhat unrealistic assumption that the transition state has the same geometry as the product radical can be avoided. The most marked change in geometry will be in the C—H bonds of the methylene group, so the energies of the cyclohexadienyls have been calculated by both HMO and UHF methods with the assumption that $r_{C—H_2}$ = 1·34 Å instead of Morita's[19] value of 1·10 Å. In addition, an attempt to include the effect of the ethoxide ion has been made by allowing the interaction of the $\ddot{O}$ of the ethoxide with the π-systems through the $C—H_2$ bond. The $\ddot{O}—H_2$ "bond"length was taken to be 1·70 Å.

RESULTS AND DISCUSSION

Polarized state model

As expected, the polarized state models (Table 2) predict that *ortho* and *meta* protonation are considerably favoured over *para* protonation. In the absence of an ethoxide ion, the approach of a proton to the *meta* position results in an energy 3 kcal/mole lower than that for the *ortho* in spite of a higher charge density on the latter site. This is a consequence of the net positive charge on the ether oxygen.

TABLE 2. INTERACTION ENERGIES CALCULATED USING POLARIZED-STATE MODEL

Site of protonation		Calculated Energies in kcal/mole					
		From Eq. (3)			From Eq. (8)		
		Proton	Ethoxide	Total	Proton	Ethoxide	Total
ortho	UHF*	−113	80	−33	−86	62	−24
	HMO†	−119	85	−34	−91	66	−25
meta	UHF	−116	82	−34	−89	63	−25
	HMO	−121	86	−35	−93	66	−26
para	UHF	−107	80	−27	−84	63	−21
	HMO	−112	84	−28	−88	66	−23

* Calculated from UHF charge densities.
† Calculated from HMO charge densities.

However if the interaction of the ethoxide ion is also considered, the energy difference becomes smaller and is clearly dependent on the arbitrarily chosen geometry of the transition state. These results suggest that the site of protonation may depend on whether the reaction involves a proton or an ethanol molecule. Attack by ethanol seems probable since it reacts more slowly with solvated electrons than radical anions, whereas for proton sources such as the ammonium cation, the reverse is true.[2, 3] It should be pointed out that the $C_2H_5O^-$ . . . H^+ interactions will be the same in each case and need not be considered. Further, incomplete separation of the charges in this species would simply reduce the two contributing terms proportionally.

It is satisfying that the polarized state model in the simple form described by Eq. (3) and the somewhat more sophisticated form described by Eq. (8) give essentially similar results for both HMO and UHF charge densities. However if Eq. (6) is used to evaluate $E_{\text{rep}}^{\text{core}}$ the activation energy for the reaction of anisole anion with a proton is of the order of 100 kcal/mole! Clearly this result is not meaningful and it appears that the same approximation must be used for both the core–electron attraction and the core–core repulsion terms.

It is interesting to assess the accuracy of Eq. (1). UHF calculations have been performed for the anisole radical anion in which the core terms have been modified by the field of the additional proton, assumed for comparative purposes to vary as $1/r$. These calculations give energies 129·7 kcal/mole and 133·3 kcal/mole lower than the parent radical anion for *ortho* and *meta* attack respectively. The agreement with the corresponding values in Table 2 is fair and this result suggests that the estimate of the differences in energy between *ortho* and *meta* protonation obtained from Eqs (3) and (8) using the UHF charge densities are reasonable for the values of $\Delta\alpha$ chosen.

The polarized state approach gives some support to the route B, although this cannot be regarded as unequivocal. However it does show that the *meta* site becomes more strongly preferred as the $C_2H_5O^- \ldots H^+$ distance increases. Moreover it does not support the view put forward by Birch,[1] Zimmerman[5] and others[2,3] that protonation occurs at the site of highest charge density. The breakdown of the correlation between charge density and reactivity, which is frequently observed for ionic reactions, arises from the asymmetric nature of the charge distribution in anisole anion radical. Polarization of the σ core by the π-electrons is considered unlikely to affect the general conclusions. In addition, it should be noted that for the protonation of toluene radical anion there is no centre of positive charge like that on the ether oxygen of anisole, so protonation at the *ortho* position becomes more probable.

π-Energy approach. In the second approach, the energies of the product cyclohexadienyl radicals IIIa and IIIb have been calculated. The Hückel energies increase in the order *ortho* < *para* < *meta* and the sense of this result appears to be independent of the parameters chosen. This can be seen from a comparison of the results in the columns (1) of Table 3 with those in the columns (2) where the oxygen coulomb

TABLE 3. π-ENERGIES OF CYCLOHEXADIENYLS CALCULATED BY THE HÜCKEL METHOD

Site of protonation	π-Energy in eV*				Relative π-energies in kcal/mole			
	(1)†	(2)	(3)	(4)	(1)	(2)	(3)	(4)
ortho	−43·16	−38·72	−38·90	−49·00	−2·2	−5·0	−1·4	−1·1
meta	−43·06	−38·50	−38·81	−48·96	0·0	0·0	0·0	−0·1
para	−43·10	−38·62	−38·85	−48·95	−1·0	−2·7	−0·3	0·0

* $\beta = -2{\cdot}395$ eV.

† (1) Parameters given in text; (2) Parameters given in text except $\alpha_O = \alpha_C + 1{\cdot}0\,\beta_{CC}$; (3) Parameters given in text except $\beta_{C—H_2} = 1{\cdot}5\,\beta_{C—C}$; (4) As (3) but including alcohol oxygen $\beta_{O—H_2} = 0{\cdot}8\,\beta_{CC}$, $\alpha_O = \alpha_{CC} + 2{\cdot}0\,\beta_{CC}$.

integral has been altered and with columns (3) where an attempt is made to represent more nearly the transition state by reducing β_{C-H_2}. The inclusion of the alcohol oxygen into the π-system at the transition state, columns (4) in Table 3, reverses the order in energy of the *meta* and *para* cyclohexadienyls but the *ortho* isomer is still preferred. However the energy differences are extremely small and should be treated with caution in view of the many approximations in the Hückel method.

When the UHF method is applied to the cyclohexadienyls, the calculated π-energies increase in the order *ortho* < *meta* < *para*. (Table 4). To obtain the total energy of a radical, the core repulsion must be added to the π-energy and, as with the polarized-state model, this may be evaluated either as point charges (cf. Eq. 6) or as positive "orbital-like" lobes (cf. Eq. 7). Both methods are used but the point charge model has the disadvantage of giving a positive total energy so that the net effect of the π-system is repulsive! The total energies show that *meta* protonation of the anisole anion leads to the most stable cyclohexadienyl. Increasing the CH_2 bond length from 1·10 Å to 1·34 Å alters the total energy of each radical but has no effect on their relative positions. Similarly, the inclusion of the alcohol oxygen in the π-system has little effect on the relative energies.

It is unsatisfactory that the HMO and UHF methods give different results for the relative stabilities of the cyclohexadienyls. However, as the sums of the one-electron energies from the UHF calculations incorrectly suggest that the *ortho* isomer has the lowest energy, the Hückel energies cannot be regarded as reliable. Clearly *meta* protonation is strongly supported by the MO calculations on the products III but only slightly favoured by the charge distribution in the anion. Thus the reaction most probably occurs at the *meta* position but may occur at both sites at similar rates.

Spin density. An estimate of the accuracy of the UHF wavefunction can be obtained from a comparison of the calculated spin distributions of the cyclohexadienyls with the ESR hyperfine splitting constants found experimentally for similar radicals.[20–22] Unfortunately the UHF wave function is not an eigenfunction of S^2 and, while the π-energy is not strongly influenced by this, the spin densities are. Annihilation of the quartet part of the wavefunction by the method of Amos and Snyder[15] improves the expectation value of S^2 (Table 4) and the resulting spin densities are in good agree-

TABLE 4. TOTAL AND π-ENERGIES OF CYCLOHEXADIENYLS BY UHF METHOD

Site of protonation		E^π eV	Core repulsion energy in eV		Total energy eV		$\langle S^2 \rangle_{SD}$	$\langle S^2 \rangle_{AA}$
			(1)*	(2)	(1)	(2)		
ortho	(A)†	−310·4	320·6	272·8	10·2	−37·6	0·8862	0·7592
	(B)	−306·5	316·3	270·8	9·8	−35·7	0·8823	0·7603
	(C)	−404·0	400·2	350·3	−3·8	−53·7	0·8796	0·7602
meta	(A)	−306·9	312·9	266·1	6·0	−40·8	0·8907	0·7600
	(B)	−302·8	308·5	263·9	5·7	−38·9	0·8850	0·7609
	(C)	−389·8	381·4	332·8	−8·4	−57·0	0·8807	0·7604
para	(A)	−301·8	311·4	264·4	9·6	−37·4	0·8817	0·7593

* (1) Point Charge model; (2) Using electron repulsion integrals.

† (A) Normal cyclohexadienyl geometry (r_{C-H_2} = 1·10 Å); (B) "Transition state" geometry (r_{C-H_2} = 1·34 Å); (C) As (B) but including alcohol oxygen with r_{O-H_2} = 1·70 Å.

ment with experiment. They are given, together with some previous calculations, in Table 5. In common with many of the earlier results the most marked deviation from experiment is in the position *para* to the CH_2. The agreement is improved by the use of a variable β approximation[23] but this is insufficient to give an adequate description of the spin distribution. Indeed, only the SCF CI calculation on pentadienyl by Hinchliffe[24] gives good agreement with observed ratio of *ortho* and *para* splittings.

TABLE 5. CALCULATED AND EXPERIMENTAL SPLITTING CONSTANTS FOR CYCLOHEXADIENYL AND RELATED RADICALS

Radical	Source	Splitting constants[a] (*gauss*)				Ref
		ortho[b]	*meta*[b]	*para*	CH_2	
Cyclohexadienyl						
o-methoxy-	UHF	7·73	1·80	7·81	51·0[c]	
	UHFVB[d]	8·49	2·03	9·28	49·7[c]	Present
m-methoxy-	UHF	7·97	1·82	8·03	55·8[c]	work
	UHFVB[d]	8·77	2·03	9·54	54·4[c]	
Cyclohexadienyl	SCF CI	9·97	2·77	10·53	42·9	*e*
	VB	11·57	6·58	14·04	—	*f*
Pentadienyl	HMO CI	10·25	2·83	12·16	—	*g*
	SCF CI	8·91	2·47	14·13	—	24
Cyclohexadienyl	Expt	8·99	2·65	13·40	47·71	20
Hydroxycyclohexadienyl[*]	Expt	9·2	2·8	13·4	36·0[h]	21
o-hydroxy-	Expt	8·3	2·4	12·7	27·5[h]	22

[a] Splittings calculated using $a_i^H = Q\rho_i^C$ with $|Q| = 27$ *gauss* unless stated otherwise.

[b] Mean of two sites where there is inequivalence.

[c] Evaluated using the formula of D. H. Levy, *Mol. Phys.* **10**, 233 (1966).

[d] Variable β approximation.

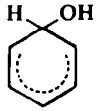
[e] P. Nordio, M. V. Pavan and G. Giacometti, *Theoret. Chim. Acta* **1**, 302 (1963). $|Q| = 27{\cdot}7$ *gauss.*

[f] H. Fischer, *J. Chem. Phys.* **37**, 1094 (1962); **38**, 1023 (1963). $|Q| = 24$ *gauss.*

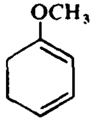
[g] A. Hinchliffe, *Theoret. Chim. Acta* **7**, 25 (1967).

[h] Proton splitting from $>CHOH$.

[*] Radical structure



The second protonation. The protonation of the cyclohexadienyl anion, IV a or b, results in the product V which is less stable than its isomer VI. Consequently the



VI

reaction must be kinetically controlled and the transition state most nearly described by a polarized state model. The charge density distributions of the anions IV are largely governed by the additional electron in the nearly non-bonding orbital of the cyclohexadienyl radicals. The failure of the UHF method, in predicting the ratio of the *ortho* and *para* splittings in these radicals, casts doubt on the ability of the SCF method to give an accurate description of the charge density in the anions. The observed splittings in the cyclohexadienyl radical suggest that the π-charge in the anion is markedly greater *para* to the methylene than *ortho* to it. SCF calculations confirm this but the difference is rather small. In addition, since there is a high unpaired electron density on the methylene protons of the radical, a negatively charged centre at this position of the anion cannot be ruled out. The calculated charge density is strongly dependent on the parameters chosen for the methylene group and such a variation has a profound effect on the site of protonation. A further complication is provided by a comparison of the calculated charge densities with the observed chemical shifts in the related benzenium ions[25] which shows that polarization of the sigma electrons is important in this type of ion. Clearly no positive conclusion on the site of the second protonation can be drawn without a charge distribution more reliable than that presently available.

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