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Charge Density—Activation Energy Correlations in Electrophilic Aromatic Substitution Reactions

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Charge-density calculations have been made on six aromatic molecules by making use of *Hückel* MO LCAO and *Del Re* methods and correlated with experimental activation energy values to test certain earlier interpretations given.

(Keywords: Activation energy; Aromatic substitution; Charge density; Del Re method; Hückel method)

Korrelation von Ladungsdichte und Aktivierungsenergie für elektrophile aromatische Substitutionsreaktionen

Für sechs aromatische Moleküle wurden mittels *Hückel*rechnung (MO-LCAO) und nach der Methode von *Del Re* die Ladungsdichten errechnet und diese mit experimentellen Aktivierungsenergien korreliert.

The general form of a reaction involving electrophilic attack on aromatics may be written as

$$Ar\mathrm{H} + E^{+} \xrightarrow{\text{Slow}} EAr\mathrm{H}^{+} \xrightarrow{\text{Fast}} \text{Products}$$

Absence of any significant kinetic isotope effect proves that the second step is fast and kinetically insignificant[1]. Suppose that a substituent introduced in benzene increases the electron-density on the different ring carbon atoms. The effect of such a substituent will be an increase in the attraction between E^{+} and the center of a reaction. This in turn should decrease the activation energy (E_a) for the reaction. This has been the point of view taken by *Hinshelwood* and others[2–4]. Further, the activation energy E_a, for a dipole-dipole reaction is generally expressed as

$$E_a = E_n + E_e$$

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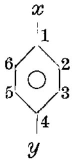
where E_e is an electrostatic component and E_n a nonelectrostatic component[5]. Combining these ideas *Ganesan* has recently shown that for a given reaction in a given solvent the values of E_n may remain constant for benzene and simple derivatives of benzene but E_e may be different for different aromatics[4]. This difference should lead to a variation in E_a. Values of E_e and hence E_a should therefore give an indication about electron-densities at the center of reaction. In an electrophilic aromatic substitution reaction, one may therefore conclude that the lower the activation energy, the greater is the electron-density on the carbon atom where substitution takes place. Such an interpretation was given by *Nanjan* and *Ganesan* recently for the trend observed in the experimentally determined E_a values for the bromination of certain aromatic compounds[6, 7]. In order to test this interpretation, we have now calculated charge-density distribution for six aromatic molecules. Further, we refer to the often discussed question whether groups like OH, OCH_3 and $NHCOCH_3$ are capable of activating the *meta* position. Conflicting results have been given by various workers[8, 9]. Indirect kinetic comparisons do not seem to provide information on the true electronic effect of the substituents. An answer to this question may be obtained by calculation of electron-densities at the various ring carbon atoms of these compounds.

An analysis of the results given in Table 1 leads to the following main conclusions: (1) It supports our earlier approach namely, the lower the activation energy the greater is the electron-density on the center of reaction. (2) It indicates that the electron-density is highest at the second (or the sixth) carbon atom in all the six molecules.



which is in excellent agreement with the actual preferred position of attack by an electrophile and finally. (3) It also indicates that groups like OH, OCH_3 and $NHCOCH_3$ do activate the *meta* position to a considerable extent. For example, the charge-density at the second carbon atom is higher in 1,4-dimethoxy benzene than it is in 4-methylanisole. Further work on the calculation of charge-densities for several homocyclic and heterocyclic systems are in progress to correlate them with experimental activation energies.

Table 1. *π-charges, σ-charges and total charge-densities for the six ring carbon atoms and activation energies for the bromination of various molecules in acetic acid*

No.	Molecule	Position	Charge densities			E_a
			π	σ	Total	kcal mol^{-1}
1.	$X = NHCOCH_3$	C_1	+0.0655	+0.0505	+0.1160	13.1 ± 0.15
	$Y = CH_3$	C_2, C_6	−0.0684	−0.0260	−0.0944	
		C_3, C_5	+0.0004	−0.0560	−0.0556	
		C_4	−0.0016	+0.0220	+0.0204	
2.	$X = OCH_3$	C_1	+0.0725	+0.2045	+0.2770	10.2 ± 0.25
	$Y = CH_3$	C_2, C_6	−0.0730	−0.0250	−0.0980	
		C_3, C_5	−0.0055	−0.0465	−0.0520	
		C_4	−0.0015	+0.0223	+0.0208	
3.	$X = NHCOCH_3$	C_1	+0.0669	+0.0505	+0.1174	8.9 ± 0.22
	$Y = NHCOCH_3$	C_2, C_6	−0.0734	−0.0260	−0.0994	
		C_3, C_5	−0.0734	−0.0260	−0.0994	
		C_4	+0.0669	+0.0505	+0.1174	
4.	$X = OCH_3$	C_1	+0.0719	+0.2045	+0.2764	7.6 ± 0.14
	$Y = OCH_3$	C_2, C_6	−0.0765	−0.0250	−0.1015	
		C_3, C_5	−0.0765	−0.0250	−0.1015	
		C_4	+0.0719	+0.2045	+0.2764	
5.	$X = OH$	C_1	+0.0780	+0.1305	+0.2085	6.3 ± 0.16
	$Y = CH_3$	C_2, C_6	−0.0830	−0.0320	−0.1150	
		C_3, C_5	−0.0055	−0.0485	−0.0540	
		C_4	−0.0017	+0.0010	−0.0007	
6.	$X = OH$	C_1	+0.0771	+0.1305	+0.2076	E_a could not be determined because of its high reactivity
	$Y = OH$	C_2, C_6	−0.0840	−0.0320	−0.1160	
		C_3, C_5	−0.0840	−0.0320	−0.1160	
		C_4	+0.0771	+0.1305	+0.2076	

The calculation of π-charges was done by the *Hückel* MO LCAO method, a standard technique in quantum chemistry[10]. It is generally agreed that with the correct choice of parameters the HMO method gives fairly good charge-density distributions which are comparable with SCF calculations[11]. σ-charges were calculated by the method of *Del Re*[12]. These methods are not described here as they have been dealt with extensively by several authors[12–14]. Values of the coefficients of h_X and k_{X-Y} used for calculating π-charges are given in Table 2. The values of parameters used for calculating σ-charges are given in Table 3. These values are taken from literature[12–16]. The calculations of π- and σ-charges were performed on an IBM 1130 computer. π- and σ-charges were calculated for the six molecules given in Table 1. The total charge-

Table 2. *The parameters used in the π-charge calculations*

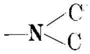
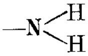
Atom	h_X	Ref.	Bond (X—Y)	k_{X-Y}	Ref.
$C_{\text{aliphatic}}$	—0.20	11	$=C{-}CH_3$	0.10	14
$=\mathbf{C}{-}CH_3$	—0.10	11	$C_{(\text{aliph.})}{-}O$	0.40	15
C_{aromatic}	0.00	11	C—N	0.90	11
=O	1.20	11	C—O	0.90	11
	1.60	12	C=C	1.00	11
	1.80	12	C=O	1.50	11
O	2.00	11			

Table 3. *The parameters used in the σ-charge calculations*

Atom	$\delta^\circ X$	Ref.	Bond	ε_{X-Y}	ν_{XY}	ν_{YX}	Ref.
H	0.00	17	N—H O—H	0.45	0.30	0.40	17
C_{sp^3}	0.07	17	C = O C = N	0.70	0.10	0.10	12
C_{sp^2}	0.12	12	C—O	0.95	0.10	0.10	17
N	0.24	17	C=C C—C C—N	1.00	0.10	0.10	17
=O	0.28	12	C—H	1.00	0.30	0.40	17
—O—	0.40	17					

density of the atoms is obtained by adding π- and σ-charges[17–20]. The E_a values and the method applied for their accurate determination have been reported already[6, 7].

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