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A MATHEMATICAL MODEL FOR THE DIRECT FIELD ELECTROSTATIC EFFECT IN ELECTROPHILIC AROMATIC SUBSTITUTION

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As part of a general investigation of various semi empirical methods for correlating substituent effects upon electrophilic aromatic substitution reaction rates,[1] we have developed a new model for the polar direct field effect[2] of a substituent upon the π electron systems in such reactions. This is an electrostatic interaction potential E_i defined as:-

$$E_i = \tfrac{1}{2}\sum_i \sum_{j\neq i} \zeta_i \zeta_j / r_{ij} \qquad \text{- - - (1)}$$

where ζ_i is the π charge density on the i^{th} atom, and r_{ij} is the distance between atom i and atom j.

In the case of hydrocarbons without substituents this is of course a rough approximation to an SCF calculation, E being some measure of electron-electron repulsion. In such systems differential σ bond energies between ground and transition states should be negligible, and we have therefore investigated the use of equation (1) for protodetritiation rate data for unsubstituted hydrocarbons.[3,4,5] Defining $E_i^+ = E_{i\,\text{WHELAND INTERMEDIATE}} - E_{i\,\text{GROUND STATE}}$, table I lists values of E_i^+ for various positions in these hydrocarbons calculated by Hückel[6] and Omega[7] techniques.

Correlations of experimental data (a) with π electron localisation energies[7] L^+ and (b) with L^+ and E^+ values were examined using functions (2) and (3) respectively.

$$\text{Log } k = A + BL^+ \qquad \text{- - - (2)}$$

$$\text{Log } k = A + BL^+ + CE^+ \qquad \text{- - - (3)}$$

The data was examined in two groups: (i) all available data for alternant hydrocarbons[3,4] and (ii) our data for all five positions in the non-alternant fluoranthene system.[5] The ratios of the standard error of estimate[8] for functions (2) and (3) are listed in table II.

TABLE I

Electrostatic potentials as calculated by H.M.O. and Omega Theory

Hydrocarbon	Position	$E^{+}_{\text{H.M.O.}}$	E^{+}_{Omega}
Benzene	-	0.013	0.024
Naphthalene	1	0.000	0.000
	2	-0.005	0.001
Phenanthrene	1	-0.002	-0.012
	2	0.001	0.006
	3	0.000	-0.010
	4	.002	-0.009
	9	-0.017	-0.012
Triphenylene	1	0.005	-0.015
	2	0.003	-0.054
Chrysene	6	-0.012	-0.023
Pyrene	1	-0.006	-0.025
	2	0.006	-0.013
	4	-0.017	-0.015
Perylene	3	-0.014	-0.035
Fluoranthene	1	-0.031	-0.035
	2	-0.017	-0.012
	3	-0.022	-0.031
	7	-0.045	-0.039
	8	-0.027	-0.030

TABLE II

Ratio of standard errors of estimate using functions (2) and (3) respectively

Hydrocarbon	Ratio H.M.O.	Ratio Omega
All protodetritiation data *	1.02	1.03
Fluoranthene data +	1.00	0.86

* ref. 3,4 and references therein. + ref. 5

The results for the alternant hydrocarbons show little difference on including E^+ values, as do the Hückel results for the non-alternant fluoranthene. However use of the more sophisticated Omega technique in conjunction with E^+ values for fluoranthene gives a significant improvement in the correlation by some 14%.

Hückel calculations in non-alternant systems are particularly prone to error,[9] and it is for such systems as these that calculations of the Omega type, and those inherent in equation (1) may be expected to give improved results. Hetero-atom substituted hydrocarbons are of course also non-alternant. Subsequently we hope to examine the application of equation (1) (in conjunction with various mathematical models for σ bond electrostatic interaction) to substituent effects in such systems.

References

(1) K.C.C. Bancroft and G.R. Howe, Tetrahedron Letters, 1967, 4207.

(2) J.G. Kirkwood and F.H. Westheimer, J. Chem. Phys., 1938, 6,506; F.H. Westheimer and J.G. Kirkwood, ibid., 1938, 6,513.

(3) K.C.C. Bancroft, R.W. Bott, and C. Eaborn, Chem. and Ind., 1965, 1951.

(4) A. Lewis, Ph.D. Thesis, University of California, 1967.

(5) G.R. Howe, Ph.D. Thesis, University of Leicester, 1969.

(6) A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists', Wiley, New York and London, 1961, Chap. 11.

(7) A. Streitwieser, J.I. Brauman, and J.B. Bush, Tetrahedron, 1963, 19, Sup.2., 379.

(8) K.W. Smillie, 'An Introduction to Regression and Correlation,' Academic Press, London, 1966.

(9) M.J.S. Dewar, International Symposium on Aromaticity, 1966, Sheffield. (Chemical Society. Special Publication - No. 21).