[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

A Molecular Orbital Theory of Organic Chemistry. V.[1] Theories of Reactivity and the Relationship between Them

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The relationship between the transition state theory and various alternative treatments of reactivity in mesomeric systems is discussed; the significance of such theoretical quantities as the index of free valency or self-polarizability is indicated. An explanation is given for the empirical success of the electrostatic theory of reactivity. It is concluded that the transition state approach alone is valid.

Reactivities of mesomeric organic compounds have been predicted in three different ways. Two of these relate reactivity to static properties of the reactants, the third to energy differences between the initial and transition states.

The electrostatic theory[3] correlates reactivity with the differential charge densities at various positions in the reactants; these can be estimated qualitatively by resonance theory, or more quantitatively[4] by the MO method. If there are no such differences (*e.g.*, in AH's where the charge distribution is uniform), reactivity is related[4] to the self-polarizabilities, these being measures of the charges that can be induced electrostatically by approaching reagents.

The free valency theory[5] relates reactivity to the *index of free valency*, a quantity defined by

$$f_r = \text{constant} - \sum_s p_{rs} \qquad (1)$$

where f_r is the index of free valency of atom r, p_{rs} the bond order of the bond between atoms r and s calculated by the VB method, and the sum is over atoms s adjacent to atom r. A corresponding *free valency number* can be defined[6] by using MO bond orders in equation (1), and is known to be closely correlated with the index of free valency.[7]

The transition state theory is best exemplified by the work of Wheland[8] on aromatic substitution, where the rate of reaction was related to the loss of π-electron binding energy when the carbon undergoing attack changes its hybridization to sp^3 and is removed from conjugation.

These methods have been applied mainly to aromatic substitution where all three lead to similar conclusions. In this paper the reason for this correlation will be investigated.

Theorem 67. The energy difference R_{RS} between an even hydrocarbon RS, and the odd AH R obtained by removal of one atom S, is numerically less, the greater the free valency number of S in RS. From equation (1)

$$f_s = C - p_{rs} \qquad (3)$$

(as usual, single attachment of S to R is assumed, the extension to multiple attachment being self-evident).

From theorem 12 of Part II[1]

$$R_{RS} = 2\beta p_{rs} \qquad (4)$$

Hence

$$R_{RS} = 2\beta(C - f_s) \qquad (5)$$

which proves the theorem. The result holds equally for fission into ($R^+ + S^-$) or ($R^- + S^+$), since the three sets of products differ only in the distribution of two electrons between the NBMO of R and the AO of S, and the energies of these orbitals are equal.

Note that the theorem holds for non-alternant hydrocarbons RS, provided that R is alternant.

Theorem 68. In the notation of the last section, if R contains heteroatoms, and if $R_{\overset{+}{\mathrm{R}}\overset{-}{\mathrm{S}}}$, $R_{\dot{\mathrm{R}}\dot{\mathrm{S}}}$ and $R_{\overset{-}{\mathrm{R}}\overset{+}{\mathrm{S}}}$ are the energy differences between RS and ($R^+ + S^-$), ($R^{\cdot} + S^{\cdot}$) and ($R^- + S^+$), respectively, then

$$R_{\overset{-}{\mathrm{R}}\overset{+}{\mathrm{S}}} = 2\beta(C - f_s) \qquad (6)$$

$$R_{\dot{\mathrm{R}}\dot{\mathrm{S}}} = R_{\overset{-}{\mathrm{R}}\overset{+}{\mathrm{S}}} - E_o \qquad (7)$$

$$R_{\overset{+}{\mathrm{R}}\overset{-}{\mathrm{S}}} = R_{\overset{-}{\mathrm{R}}\overset{+}{\mathrm{S}}} - 2E_o \qquad (8)$$

where E_o is the energy of the higher occupied MO in R. Equation (4) holds only if the occupied MO's of RS are those obtained by perturbation of the occupied MO's of the dissociation fragments. Now if R is heteroatomic, all the MO's of R^- have negative energies, and so all of them lie below the AO of S. Hence the occupied MO's of RS correspond to the occupied MO's of R^-, and so equation (6) holds. Equations (7) and (8) follow as immediate corollaries, since $(\dot{\mathrm{R}} + \dot{\mathrm{S}})$, $(\overset{+}{\mathrm{R}} + \overset{-}{\mathrm{S}})$ differ by $-E_o$, $-2E_o$, respectively, from $(\overset{-}{\mathrm{R}} + \overset{+}{\mathrm{S}})$.

The theorem will hold whenever all the occupied MO's of R have negative energies; this appears to be so in all cases where R is not an AH.

Theorem 69. Theorem 67 holds if RS is odd, provided that fission gives neutral even R. The proof follows the same lines as that of theorem 67, but using theorem 11 of Part II.[1] It appears that in this case

$$R_{RS} = \beta(C - f_s) \qquad (9)$$

Values of R_{RS} for other modes of fission can be found as in theorem 68.

Theorem 70. In an even alternant compound RS, S being a carbon atom, the energy required to convert RS to ($R^- + S^+$) is approximately proportional to the excess charge density (q_s − 1) at S, and the energy required to convert RS to $R^+ + S^-$ approximately inversely proportional. First consider the case where R contains one heteroatom U; *i.e.*, R ≡ TU, where T is an even AH. Let U be attached to T at atom r, S at atom t. Let the NBMO coefficients of U'T (the AH, corresponding to UT) at atoms U, t be a_u, a_t, respectively, and those of the NBMO of TS at atoms r, S be b_r, b_s, respectively. Let the coulomb term of U be α where α is assumed small as a first approximation.

From the definition[4] of mutual polarizability, the charge density q_s at S in RS is given approximately by

$$q_s = 1 + \pi_{u,s}\alpha \qquad (10)$$

From theorem 2 of Part II,[1] the energy difference E between UTS (≡RS) and $(UT)^-$ (≡R^-) is given approximately by

$$E = E_o + a_u^2\alpha \qquad (11)$$

where E_o is the corresponding energy difference between U'TS and $(U'T)^-$.

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(1) For Parts I-IV see THIS JOURNAL, **74**, 3341 ff. (1952).

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(3) *Cf.* C. C. Price, *Chem. Revs.*, **29**, 37 (1941).

(4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947).

(5) *Cf.* R. Daudel, A. Pullman and B. Pullman, *J. chim. phys.*, **43**, 77 (1946).

(6) C. A. Coulson, *ibid.*, **45**, 243 (1948).

(7) C. A. Coulson, P. Daudel and R. Daudel, *Rev. Scientifique*, **85**, 29 (1947); *Bull. soc. chim.*, **15**, 1181 (1948).

(8) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).

From theorem 12 of Part II[1]

$$E = 2\beta a_t \qquad (12)$$

Hence the change ΔE in E due to changing U to the heteroatom U, is given approximately by

$$\frac{\Delta E}{E_o} = \frac{E - E_o}{E_o} = \frac{a_u^2}{2\beta a_t}\,\alpha \qquad (13)$$

Hence from theorem 35 of Part III[1]

$$\Delta E/E_o = \pi_{s.u}\,\alpha \qquad (14)$$

But from theorem 35

$$\pi_{s.u} = \pi_{u.s} \qquad (15)$$

Hence from equations (10), (14) and (15)

$$\Delta E/E_o = -(q_s - 1) \qquad (16)$$

which is the first result required. The extension to cases where R contains more than one heteroatom follows immediately, since the result was obtained by first order perturbation theory, and first order perturbations are additive. And the second part of the theorem can be proved in an exactly similar manner, the sign in equation (11) being reversed.

Theorem 71. If RS is an odd alternant anion, S being a carbon atom, the energy difference between RS and $(R + S^-)$ *is greater, the less the charge density at S in RS.* The energy difference R_{RS} between RS and $(R + S^-)$ is given approximately by

$$R_{RS} = 2\sum_m^{\text{unocc}} \frac{a_{mr}^2\beta^2}{E_m} \qquad (17)$$

The charge density q_s at S is given likewise by

$$q_s = 2 - 2\sum_m^{\text{unocc}} \frac{a_{mr}^2\beta^2}{E_m^2} \qquad (18)$$

As a first approximation, replace the sums in equations (17), (18) by means $\overline{E_m}$, etc.; then

$$R_{RS} \simeq (2 - q_s)\overline{E_m} \qquad (19)$$

which establishes the theorem. Also since $\overline{E_m}$ is much the same for different compounds, the relation between R_{RS} and q_s should be similar in different compounds.

Theorem 72. The self-polarizability $\pi_{s,s}$ *of atom S in an even AH RS is given approximately by* $-(2a_{or}\beta)^{-1}$. From the definitions[4] of mutual polarizabilities

$$\begin{aligned}\pi_{s,s} &= -\sum_{n\neq s}\pi_{s,n}\\ &= -\sum_{n\neq r}\frac{a_{on}^2}{2a_{or}^2\beta} \qquad (20)\end{aligned}$$

from theorem 35 of Part III,[1] where the a_{on} are NBMO coefficients of R. But this MO is normalized; hence

$$\pi_{s,s} \simeq -\frac{1 - a_{or}^2}{2a_{or}\beta} \simeq -(2a_{or}\beta)^{-1} \qquad (21)$$

to a first approximation.

Theorem 73. The energy difference R_{RS} ***between*** *RS* ***and*** $(R + S)$ *(notation of theorem 72) is approximately* $-(\pi_{s,s})^{-1}$. From theorem 13 of Part II[1]

$$\begin{aligned}R_{RS} &= 2a_{or}\beta\\ &= (\pi_{s.s})^{-1} \qquad (22)\end{aligned}$$

from equation (21).

Theorem 74. The FVN in an even AH varies in qualitatively the same way as the self-polarizability. From equations (9) and (22)

$$(\pi_{s.s})^{-1} = \beta(C - f_s) \qquad (23)$$

Therefore the smaller f_s, the smaller $\pi_{s.s}$.

Discussion

Theorem 67 shows that the energy required to remove one atom in an even AH from conjugation with the rest of the molecule is greater, the less its free valency number. The correlation of reactivities predicted by the free valency and transition state theories follows directly.

From theorems 72–74 a similar correlation must exist in the case of AH's with reactivities predicted from self-polarizabilities.

Theorems 70, 71 show that in heterocyclic systems a correlation must in general exist between reactivities predicted from charge distributions by the electrostatic theory, and reactivities predicted from the resonance energies of transition states (see also Theorem 48 of Part III[1]).

The remaining theorems indicate that in all systems other than AH's, the reactivity depends not only on the free valency number but also on the type of reagent. This well-known phenomenon has been interpreted similarly by Burkitt, Coulson and Longuet-Higgins.[9]

The success of the electrostatic and free valency theories is probably due entirely to these correlations, and provides no evidence for the correctness of their basic premises. Since there is little theoretical justification for these premises, it seems clear that reliance should rather be placed on the transition state approach which is well founded.

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[9] F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).