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A VALENCE AND CHARGE CRITERION FOR REACTIVITY OF π ELECTRON SYSTEMS

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A new criterion for the reactivity of π electron systems is proposed. The method incorporates and modifies ideas of Coulson and Fukui *et al.* about free valence. The proposed reactivity index includes covalent and ionic components and is suitable for electrophilic, radical and nucleophilic attack. The method is tested for a few simple π systems and differences from Coulson and Fukui *et al.* are discussed. Finally, it is applied to the electrophilic attack of a series of substituted benzenes and to nucleophilic attack of a series of substituted benzoic acid esters.

INTRODUCTION

The definition and application of reactivity indices has been an important topic in the development of quantum chemistry. In the framework of valence bond (VB) theory, Svartholm[1] calculated electronic charge distributions in condensed unsaturated hydrocarbons. Svartholm recognized two different competing kinds of reactivity, namely reactivity at atoms and reactivity at bonds. The uneven distribution of π electrons in such systems was considered to be the key to reactivity. Daudel and Pullman[2] improved this approach by normalizing the sum of all portions of π electrons in bonds or at atoms to the total number of π electrons. This procedure allowed a comparison between sites in different molecules and predicted trends from benzene to anthracene. It was concluded that the α-position in naphthalene is more reactive than the carbon positions in benzene. This was the intuitive birth of the idea of free valence of atoms in molecules. This expression was actually introduced by Daudel *et al.*[3] several years later.

An alternative concept was created by Coulson[4] in the framework of molecular orbital (MO) theory. Coulson considered the π electron system of a molecule on the Hückel level and defined charge q_A and the bond order P_{AB} between atomic π electron orbitals a and b at different atomic centres A and B as

$$q_A = \sum_i^{\mathrm{occ}} c_{ia}^2 \qquad P_{AB} = \sum_i^{\mathrm{occ}} c_{ia}c_{ib} \tag{1}$$

where the c_{ia} are the expansion coefficients of MOs ψ_i in AOs χ_a:

$$\psi_i = \sum_a c_{ia}\chi_a \tag{2}$$

The σ electrons were considered as a non-polarizable core and neglected in the subsequent discussion. The valence number N_A of an atom was then defined as the sum of all bond orders P_{AB} of neighbour atoms B which were bound to reference atom A:

$$N_A = \sum_B P_{AB} \tag{3}$$

It was then postulated that a maximum valence number could be obtained depending on the nature of the atom and its state of hybridization. Free valence of an atom for a free-radical attack[5] was then introduced as

$$F_A = N_{\max} - N_A \tag{4}$$

$N_{\max} = \sqrt{3}$ was the maximum for tertiary carbon atoms, $N_{\max} = \sqrt{2}$ for secondary carbon atoms and $N_{\max} = 1$ for primary carbon atoms.[6] $N_A = N_{\max} = \sqrt{3}$ is reached in trimethylenemethane. In Coulson's approach, the influence of charge was completely disregarded, but it would be essential for electrophilic and nucleophilic attack. In the following we call F_A the Coulson reactivity index.

Fukui *et al.*[7] recognized the importance of frontier orbitals. The electronic distribution of the highest molecular orbital (HOMO) for an electrophilic reaction and the lowest unoccupied molecular orbital (LUMO) for a nucleophilic reaction.[8] The highest singly occupied molecular orbital (SOMO) was considered most important in a radical reaction. The frontier orbital concept was based on the observation that the valence orbitals

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play the key role in the formation of molecules from atoms. Recently, Fujimoto *et al.*[9] modified this idea by a projection technique with a reference function which is projected on all occupied and unoccupied orbitals. This procedure serves to generate localized orbitals on the specific reactive region of molecules. The idea was applied to substitution reaction in benzenes[9] and addition reactions of the Diels–Alder type.[10]

Reactivity indices of the type introduced by Daudel *et al.*, Coulson and Fukui *et al.* serve to interpret the initiation of the chemical reaction. They are concerned with the pretransition stage, but do not describe the final stage of the reaction, in particular the relative stability of the product. In the following section, we introduce a new reactivity index which combines the covalent and ionic influences of a reactive system. We then demonstrate the similarities and differences with respect to Coulson and Fukui *et al.* Finally, we apply the method to a series of substituted benzenes and benzoic acid esters.

COVALENT AND IONIC REACTIVITY

Since Coulson's idea of a reactivity index was superseded by the more specific approach of Fukui *et al.*, we shall address ourselves in detail only to the latter. Fukui *et al.* distinguished between reactions with a nucleophilic, an electrophic and a radical reagent (Figure 1). In a nucleophilic reaction, the reagent furnishes electrons from its HOMO for binding with unoccupied molecular orbitals (UMOs). From perturbation theory, Fukui *et al.* concluded that this transfer of electrons would be inversely proportional to the energy difference between the HOMO of the reagent and the UMO of the reactant and proportional to the magnitude of charge that an UMO can attract at a particular atomic site. On the Hückel level, one can then define the following dimensionless quantity as the reactivity index R_A^n for nucleophilic attack at atom A:

$$R_A^n = 2 \sum_i^{\text{UMOs}} c_{ia}{}^2 \frac{\beta}{\alpha - \varepsilon_i} \tag{5}$$

Here it is assumed that there is only one π orbital a on atom A.

In a similar way, the efficiency of an electrophilic reaction depends on the feasibility of transfer of electrons from all occupied molecular orbitals (OMOs) to the LUMO of the electrophilic reagent. If the reactant is a closed-shell system, the corresponding equation would be

$$R_A^e = 2 \sum_i^{\text{OMOs}} c_{ia}{}^2 \frac{\beta}{\varepsilon_i - \alpha} \tag{6}$$

In a radical reaction two ways of charge transfer are possible. Electrons can be transferred from the OMOs of the reactant to the SOMO of the radical reagent or from the SOMO of the reagent to the UMOs of the reactant. In consequence, a combined equation from nucleophilic and electrophilic attack is obtained for the radical reactivity index:

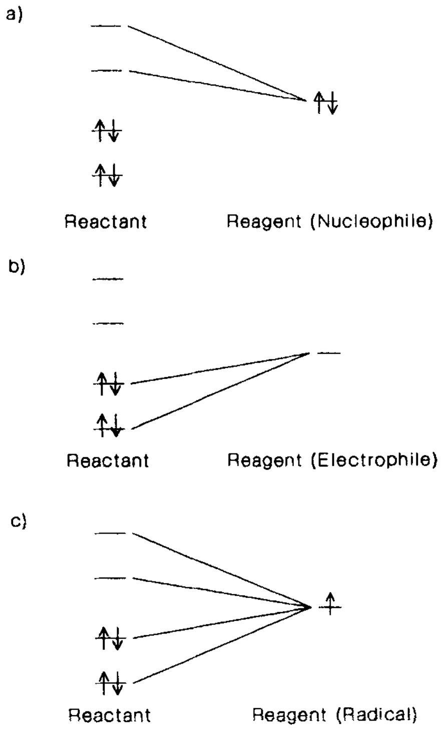

Figure 1. Reactions with (a) nucleophilic, (b) electrophilic and (c) radical reagents

$$R_A^n = \sum_i^{\text{UMOs}} c_{ia}{}^2 \frac{\beta}{\alpha - \varepsilon_i} + \sum_i^{\text{OMOs}} c_{ia}{}^2 \frac{\beta}{\varepsilon_i - \alpha} \tag{7}$$

In all cases α refers to the MO energy of the reagents, i.e. HOMO for nucleophiles, LUMO for electrophiles and SOMO for radicals. We now propose the following alternative procedure. We consider the electron transfer in the light of changes in covalent and ionic bonding in the reactant. The covalent bonding of atom A in the reactant can be described by the atomic valence number V_A.[11] This index was derived from an equation suggested by Wiberg[12] and based on symmetrically orthogonalized atomic orbitals.[13]

The atomic valence number V_A measures the amount of covalent bonding and antibonding extended from atom A to all other atoms in the molecule. We suggest that the reactivity of atom A in the reactant is increased if the covalent bonding in the reactant at the reactive site is reduced by the electron transfer. The lost valence in the reactant can then be used for the new bonding between reactant and reagent. However, there is also an ionic component in the reactivity which is important in nucleophilic and electrophilic attack. We argue similarly to Fukui *et al.* that the reactivity also increases with increasing change in charge at a particular atomic site. Parr and Yang[14] introduced the so-called Fukui function which measures the change in density with respect to change in the number of electrons. The more atom A is able to acquire charge in a nucleophilic attack or lose charge in an electrophilic attack, the more it should react. However, this simple picture has to be modified. Atom A will favour the acquisition of charge in a nucleophilic attack only to the point where it reaches its normal charge, i.e. the charge in the free neutral atom. If its net charge is already negative, it will resist further charge transfer and reduce the reactivity index R^n. In an electrophilic reaction, an atom with a negative net charge will favour charge transfer to the electrophilic reagent, whereas an atom with a positive net charge will resist charge transfer.

We therefore suggest the following reactivity index R^n for a nucleophilic reaction at the site of atom A of the reactant:

$$R^n_A = \sum_{i}^{\text{UMOs}} (-\Delta V_{Ai} + K_A\,\Delta q_{Ai})\,\frac{\varepsilon^{\text{LUMO}}_{\text{ethylene}}}{\varepsilon_i} \qquad (8)$$

with $\Delta V_{Ai} = V_{Ai} - V_{A0}$, $\Delta q_{Ai} = q_{Ai} - q_{A0}$ and $K_A = Q_A$. Here V_{A0} and q_{A0} are valence number and electronic charge of atom A in the ground state of the reactant, respectively, and V_{Ai} and q_{Ai} are the valence number and charge of the dianion of the reactant where UMO i is doubly occupied. Similarly to Coulson, the valence numbers V_{A0} and V_{Ai} are calculated with the inclusion of nearest neighbours only. This approach differs from our previous papers where all other atoms were included. Q_A is the net charge on atom A. Nalewajski and Koninski[15] extended the discussion of Parr and Yang by inclusion of the perturbing electrostatic potential produced by a point charge reagent. Lee *et al.*[16] concentrated on the charge transfer by using the condensed Fukui function, which corresponds to the Δq of the second term in equation (8). However, there is an additional covalent contribution contained in the first term. This contribution is not present in Lee *et al.*'s theory.

In a similar way, R^e_A for an electrophilic attack can be defined as

$$R^e_A = \sum_{i}^{\text{OMOs}} (-\Delta V_{Ai} + K_A\,\Delta q_{Ai})\,\frac{\varepsilon^{\text{HOMO}}_{\text{ethylene}}}{\varepsilon_i} \qquad (9)$$

Finally, the radical attack is expressed by a combination of the two previous equations:

$$R^r_A = \sum_{i}^{\text{UMOs}} (-\Delta V_{Ai} + K_A\,\Delta q_{Ai})\,\frac{\varepsilon^{\text{LUMO}}_{\text{ethylene}}}{\varepsilon_i} + \sum_{i}^{\text{OMOs}} (-\Delta V_{Ai} + K_A\,\Delta q_{Ai})\,\frac{\varepsilon^{\text{HOMO}}_{\text{ethylene}}}{\varepsilon_i} \qquad (10)$$

It is now necessary to observe that

$$\sum_A \Delta q_{Ai} = \begin{cases} 2 & \text{nucleophilic UMO} \\ 1 & \text{radical UMO} \\ -1 & \text{radical OMO} \\ -2 & \text{electrophilic OMO} \end{cases} \quad \text{for}$$

The reactivity index R^r_A for radical attack is not the average of the indices for nucleophilic and electrophilic attack, because the covalent term is quadratic and the ionic term linear in density matrix elements. In summary, we can say that each covalent term depends on a sum of interactions between the reference atom and its neighbour atoms and each ionic term on the reference atom. It is not possible to reduce the covalent term to charge contributions only. In the following section we give details and discuss the significance of this approach.

COMPARISON OF DIFFERENT METHODS FOR SIMPLE π ELECTRON SYSTEMS

Let us start with the simplest case of a reaction with ethylene. For nucleophilic, electrophilic and radical attack of a reagent, we calculate the reactivity indices R^n, R^e and R^r. In Coulson's approach, these three reactivity indices are all equal and represented by the free valence index F_{C}. Since the π bond order P_{CC} between the two carbon atoms is 1, $F_{\mathrm{C}} = 0{\cdot}73$ according to equation 4 and $N_{\max} = \sqrt{3}$.

In Fukui *et al.*'s approach we can use $\varepsilon = \alpha - \beta$ for the single UMO, $\varepsilon = \alpha + \beta$ for the single OMO and $c_a^{\,2} = 0{\cdot}5$ for both UMO and OMO. In consequence, we obtain $R = 1$ for nucleophilic, electrophilic and radical attack according to equations 5–7.

In our new approach we need the following three density matrices for the calculation of the reactivity indices:

$$P^o = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \qquad P^n = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}, \qquad P^e = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

Here P^o is the π orbital density matrix of the ground state of ethylene, P^n the corresponding matrix of the dianion and P^e the matrix of the dication. For nucleophilic attack we obtain $\Delta V_{\mathrm{C}} = -1$, $\Delta q_{\mathrm{C}} = 1$ and $K_{\mathrm{C}} = 0$, hence $R^n_{\mathrm{C}} = 1$. For electrophilic attack we obtain $\Delta V_{\mathrm{C}} = -1$, $\Delta q_{\mathrm{C}} = -1$ and $K_{\mathrm{C}} = 0$, hence $R^e_{\mathrm{C}} = 1$. In a similar way one can derive $R^r_{\mathrm{C}} = 1{\cdot}5$. This means that there is no qualitative difference between Coulson's, Fukui *et al.*'s and our new approach with respect the three types of reactivity in ethylene.

To understand more generally the similarities and differences between the three methods, we have calculated reactivity indices for several simple π electron systems. The results for nucleophilic reactivity indices R^n are given in Table 1, for electrophilic reactivity indices R^e in Table 2 and for radical reactivity indices R^r in Table 3. Here we have used Hückel calculations throughout for uniform comparison and in particular since Fukui *et al.*'s method was formulated on this level.

From Table 1, it is obvious that Coulson's approach is in general unqualified for the description of nucleophilic reactivity. It reproduces the trends correctly only for ethylene and butadiene, but cannot identify the most reactive centre in the other molecules. The trends of Fukui *et al.*'s and our approach are very similar and even the numbers are very close in most cases. The sequences of reactive centres are the same for all molecules with these two methods. The correct prediction is particularly striking in the case of acrolein, where the most reactive centre is indeed the carbon atom C-1. This is supported by the fact that a Michael addition of acrolein occurs via a 1,4-nucleophilic attack.[17] However, if we compare the relative reactivities of different molecules, Fukui *et al.*'s method would predict that acrolein is more reactive than formaldehyde, whereas this work suggests the opposite trend. From the literature,[17] we would expect formaldehyde to be more reactive, since the equilibrium constant $K = k_1/k_{-1}$ for the reaction

$$\mathrm{CH_2O} + H_2\mathrm{O} \overset{K}{\rightleftharpoons} \mathrm{HOCH_2OH} \qquad (11)$$

Table 1. Reactivity index R^n for nucleophilic reactions of selected molecules with different methods

Molecule	Reactive centre	$R^{n\,a}$ A	B	C	D	E
$H_2C{=}CH_2$	C	0·73	1·00	1·00	1·00	0·00
$H_2C{=}CHCH{=}CH_2$	C-1	0·84	1·34	1·34	1·34	0·00
	C-2	0·39	0·90	0·90	0·90	0·00
$H_2C{=}CHCH{=}O$	C-1	0·87	2·72	2·28	1·65	0·63
	C-2	0·37	0·86	0·79	0·82	−0·03
	C-3	0·48	2·35	1·62	0·83	0·79
	O	0·98	1·12	1·07	1·67	−0·60
$H_2C{=}O$	C	0·84	2·34	2·34	1·29	1·05
	O	0·84	0·89	0·89	1·29	−0·40
HCOOH	C	0·53	1·82	1·81	1·01	0·80
	O-1	0·93	0·56	0·49	0·81	−0·32
	O-2	1·33	0·15	0·07	0·21	−0·14
$O{=}C{=}O$	C	0·39	1·33	1·33	0·89	0·44
	O	1·06	0·33	0·22	0·45	−0·23

[a] A, Coulson (Hückel); B, Fukui *et al.* (Hückel); C, this work (Hückel); D, this work (Hückel, covalent part); E, this work (Hückel, ionic part).

Table 2. Reactivity index R^e for electrophilic reactions of selected molecules with different methods

Molecule	Reactive centre	$R^{e\,a}$ A	B	C	D	E
$H_2C{=}CH_2$	C	0·73	1·00	1·00	1·00	0·00
$H_2C{=}CHCH{=}CH_2$	C-1	0·84	1·34	1·34	1·34	0·00
	C-2	0·39	0·90	0·90	0·90	0·00
$H_2C{=}CHCH{=}O$	C-1	0·87	0·72	0·69	0·86	−0·17
	C-2	0·37	0·86	1·02	0·99	0·03
	C-3	0·48	0·18	0·32	0·33	−0·01
	O	0·98	1·12	0·89	0·30	0·59
$H_2C{=}O$	C	0·84	0·34	0·34	0·49	−0·15
	O	0·84	0·89	0·89	0·49	0·40
HCOOH	C	0·53	0·30	0·21	0·34	−0·13
	O-1	0·93	1·05	1·13	0·55	0·58
	O-2	1·33	0·91	0·60	−0·21	0·81
$O{=}C{=}O$	C	0·39	0·33	0·34	0·44	−0·10
	O	1·06	1·33	1·11	0·22	0·89

[a] As in Table 1.

Table 3. Reactivity index R^r for radical reactions of selected molecules with different methods

Molecule	Reactive centre	$R^{r\,a}$ A	B	C	D	E
$H_2C{=}CH_2$	C	0·73	1·00	1·50	0·75	0·75
$H_2C{=}CHCH{=}CH_2$	C-1	0·84	1·34	1·57	0·78	0·78
	C-2	0·39	0·90	1·34	0·67	0·67
$H_2C{=}CHCH{=}O$	C-1	0·87	1·72	1·72	0·46	1·26
	C-2	0·37	0·86	1·31	0·66	0·65
	C-3	0·48	1·26	1·41	0·27	1·14
	O	0·98	1·12	1·25	0·53	0·72
$H_2C{=}O$	C	0·84	1·34	1·79	0·29	1·50
	O	0·84	0·89	1·33	0·57	0·76
HCOOH	C	0·53	1·06	1·40	0·24	1·16
	O-1	0·93	0·80	1·08	0·45	0·63
	O-2	1·33	0·53	0·46	0·37	0·09
$O{=}C{=}O$	C	0·39	0·83	1·17	0·28	0·89
	O	1·06	0·83	0·84	0·61	0·23

[a] As in Table 1, except D, this work (Hückel, electrophilic part); E, this work (Hückel, nucleophilic part).

is much larger for formaldehyde than for other aldehydes. This is conclusive under the assumption that the rate constant k_{-1} for the back-reaction is independent of the particular aldehyde.

Table 2 for electrophilic reactions shows again the lack of suitability of Coulson's method and the results are rather erratic. Again, Fukui *et al.*'s and this method show similar trends for all cases except acrolein. Fukui *et al.*'s method would predict the oxygen atom to be the most reactive centre, whereas we predict the second carbon atom to be most reactive. In the case of an electrophilic attack of Br_2 on unsaturated carbonyl compounds, our prediction seems to be supported.[18] For formaldehyde Lee *et al.*[16] predicted the same reactive centres for nucleophilic and electrophilic attack as we do.

In the two cases of nucleophilic and electrophilic attack, our equations allow a convenient decomposition of the reactivity index into covalent and ionic contributions. From Table 1 it can be seen that for the nucleophilic attack of the six molecules the covalent contribution is always positive and dominant. The ionic contribution can enhance or diminish the covalent influence. In the case of the electrophilic attack there is a similar picture but with two exceptions. In HCOOH and CO_2 the ionic contribution dominates. For the O-2 atom of the former molecule the covalent contribution is even negative.

Table 3 presents the reactivity indices for radical reactions. Again the Coulson index fails for molecules with heteroatoms. There is again parallelism between Fukui *et al.*'s and our proposed method. The only exception is CO_2, where Fukui *et al.*'s method predict equal reactivity for the C and O atoms. We predict more reactivity at the carbon centre. This seems more plausible since the nucleophilic power of the carbon atom was more pronounced that the electrophilic power of oxygen. From the last two columns it appears that the nucleophilic contribution dominates in the most cases. For HCOOH Lee *et al.*[16] predicted that the oxygen atom is the reactive centre. This is due to the fact that their criterion includes only the second term of our approach in equation (8), namely the charge-transfer contribution.

ELECTROPHILIC ATTACK ON SUBSTITUTED BENZENES

To extend these ideas to relevant reactivity problems, we chose as a first example the electrophilic attack on the π electron systems of substituted benzenes.

Many years ago, Jaffé[19] correlated Hammett's σ values[20] with electron densities calculated by molecular orbital theory. The σ values are defined as

$$\sigma = \rho^{-1} \log(k/k_0) \tag{12}$$

where k_0 and k are the rate (or equilibrium) constants for the unsubstituted and substituted aromatic compound and ρ is a constant characteristic of the reaction and the conditions which it occurs; σ depends only on the substituent group and its position. Jaffé used experimental σ values to define Hückel parameters for heteroatoms. Our approach is different. We used Hückel parameters for heteroatoms from Heilbronner and Bock[21] and applied equation 9 in Hückel calculations on substituted benzenes. The scheme is depicted in Figure 2. We also calculated these systems by the SINDO1 method for first-[22] and second-row[23] elements. The accuracy of this method for geometries and energies of the elemens involved is comprehensively documented.[24,25] We have selected six systems with

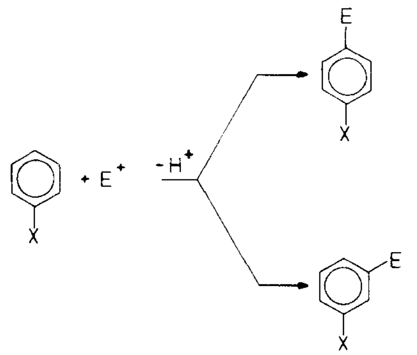

Figure 2. Electrophilic reaction of substituted benzenes

Table 4. Carbon reactivity index R^e for substituted benzenes in *meta* (R^e_m) and *para* (R^e_p) positions

	Hückel			SINDO1		
Substituent	R_m	R_p	R_p/R_m	R_m	R_p	R_p/R_m
H	0·883	0·883	1	1·154	1·154	1
CH_3	0·863	1·076	1·246	1·134	1·355	1·194
NH_2	0·874	1·140	1·304	1·235	1·556	1·259
OH	0·905	1·080	1·193	1·145	1·451	1·267
F	0·828	1·076	1·299	1·083	1·370	1·265
Cl	0·906	1·059	1·168	1·112	1·397	1·256

substituents CH_3, NH_2, OH, F, Cl and the unsubstituted benzene. The results for rate constants R^e_m for the *meta* position and R^e_p for the *para* position are given in Table 4.

The remarkable fact is that the *para* position is favoured over the *meta* position throughout. The Hückel and SINDO1 calculations differ in the positioning of chlorine in the sequence of R^e_p. One would expect from Hammett equations that the reactivity of chlorine would be lower than that of fluorine in solution. It is not clear whether the Hückel parameters of Heilbronner and Bock[21] account for such a solution effect. At any rate, SINDO1 calculations refer to gas-phase reactions and cannot be directly compared with data from solution.

Bader and Chang[26] recently studied the electrophilic attack on substituted benzenes using their derivative of density distribution method. They used as an index the secondary charge concentrations as sites of electrophilic attack. They calculated the second derivative of the electronic density distribution $\nabla^2\rho$ at the out-of-plane saddle points relative to the values in benzene. In Bader and Chang's terminology, these are the greatest concentrations of electronic charge not involved in the bonding. They predicted that *ortho* and *para* positions will be favoured over the *meta* positions in electrophilic attack. This is in line with our conclusions from the reactivity index R^e.

NUCLEOPHILIC ATTACK ON SUBSTITUTED BENZOIC ACID ESTERS

As a second example we chose as π electron systems substituted benzoic acid esters which obey the Hammett equation. The reaction scheme is depicted in Figure 2. From the results a linear relationship of the following form can be established:

$$\log k_X = a \log K_X + b \tag{13}$$

where k_X is the rate constant and K_X the equilibrium constant for the system with substituent X. We have denoted the substituent in the *meta* position by X and in the *para* position by Y. Sykes[27] presented a series of substituted systems which can be ordered in a sequence of increasing rate constants. We selected the following six of these systems which show an increase in rate constant in the following order of substituents: p-CH_3 < H < p-Cl < m-Cl < m-NO_2 < p-NO_2. For these systems we calculated the carbonyl carbon nucleophilic reactivity index R^n_C with the SINDO1 method. The results in Table 5 show that this sequence is reproduced with the exception of the unsubstituted compound by the reactivity index defined in equation 8 in comparison with the Hammett σ value of equation 12.

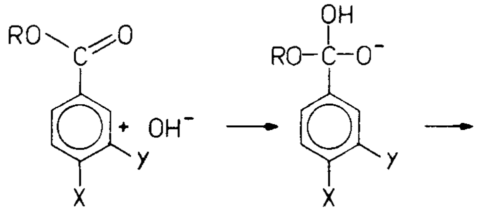

Figure 3. Nucleophilic reaction of substituted benzoic acid esters

Table 5. Carbonyl carbon reactivity index R^n for hydrolysis of substituted benzoic acid esters with *para* (X) or *meta* (Y) substitution

Substituent			
X	Y	R^n_C, SINDO1	σ, exp.[a]
H	CH_3	1·620	−0·17
H	H	1·603	0
H	Cl	1·640	0·23
Cl	H	1·670	0·37
NO_2	H	1·820	0·71
H	NO_2	1·824	0·78

[a] Ref. 28.

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