PERTURBATION THEORY OF SUBSTITUENT EFFECT. QUANTUM CHEMICAL ESTIMATION OF THE HAMMETT ϱ CONSTANTS

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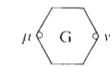
Based upon a simple model describing the substituent effect only by a change in the Coulombic integral $\Delta\alpha_\mu$, a relation is derived which can be viewed as a quantum chemical analogue of the Hammett equation. This relation and knowledge of the reaction constant ϱ for a reaction on a skeleton chosen as a standard make it possible to predict theoretically the magnitude of the ϱ constant for this reaction on an arbitrary conjugated skeleton provided that for the latter the Hammett equation holds.

The Hammett equation represents one of a few successful attempts at predicting reaction rates for a given reaction within a series of substituted compounds. Mechanistically important are particularly the sign and the absolute value of the reaction constant ϱ, both assumed to be in relation to the reaction mechanism and the structure of the transition state[1]. However, difficulties arise when an attempt is made to extend the validity of the Hammett equation to skeletons other than benzene. These difficulties can be resolved essentially by two possible approaches. One approach requires different scales of σ constants to be determined for different skeletons supposing that, similarly as in the series of substituted benzoic acids, the ϱ constant for dissociation is equal to one. On the theoretical level, this approach has been adopted by Dewar in his FM method[2,3]. The second approach starts with the conventional Hammett σ constants even for different skeletons. Different values of ϱ constants reflect, when compared with an analogous ϱ constant for the benzene series, different sensitivities of these skeletons to the transmission of the substituent effect. The latter approach has been accepted in the preliminary communication[4] as well as in the present work. Starting from the second-order perturbation theory on HMO level, an equation has been derived which makes it possible to estimate directly the "intrinsic" sensitivity of different skeletons to the transmission of the substituent effect.

THEORETICAL

Let us consider a simple quantum chemical model of the substituent effect similar to that suggested in the preliminary communication[4]. Let G be a general conjugated

structural unit where μ denotes the site of attachment of a substituent and ν the reaction center (Scheme 1). Introduction of a substituent is modelled by the change

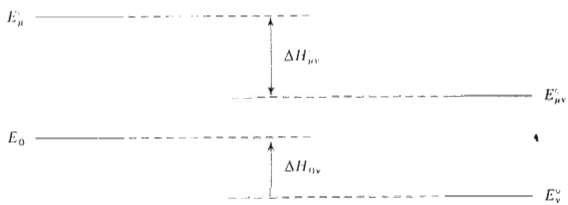


SCHEME 1

$\Delta\alpha_\mu$ in the corresponding Coulombic integral and an equilibrium or a rate process is described by the change $\Delta\alpha_\nu$ at the reaction center. The Eq. (*1*) then holds for the ratio of equilibrium or rate constants for a reaction of an unsubstituted and a substituted molecule.

$$\log k_{\mu\nu}/k_{0\nu} = [(\Delta H^0_{0\nu} - \Delta H^0_{\mu\nu}) - T(\Delta S^0_{0\nu} - \Delta S^0_{\mu\nu})]/2{\cdot}3\boldsymbol{RT}. \qquad (1)$$

Definition of the required ΔH^0 and ΔS^0 quantities is evident from the thermodynamic cycle presented in Scheme 2. The given ratio of the equilibrium constants



SCHEME 2

(Eq. (*1*)) can be expressed for our purposes more conveniently by means of the statistical thermodynamics in terms of the partition functions (Eqs (*2a*)–(*2c*)).

$$A_i \underset{}{\overset{K_{iv}}{\rightleftharpoons}} B_i \qquad (2a)$$

$$K_{iv} = \frac{[q_{rel}, i]_B}{[q_{rel}, i]_A} \exp\left(-\Delta E^0_{iv}/\boldsymbol{RT}\right) \qquad (2b)$$

$$\Delta E^0_{iv} = E^0_{iv} - E^0_0 . \qquad (2c)$$

As only electronic partition functions are influenced by the changes $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$, an important simplification for the calculation of $K_{i\nu}$ results from our model of the substituent effect. Energies $E^0_{\mu\nu}$, E^0_μ and E^0_ν required for the calculation of the electronic partition functions can be expressed on the basis of the second-order perturbation theory. For illustration, the expression for the $E^0_{\mu\nu}$ term is given by the Eq. (*3*)

$$E^0_{\mu\nu} = E^0_0 + q_\mu \Delta\alpha_\mu + q_\nu \Delta\alpha_\nu + \pi_{\mu\mu} \Delta\alpha^2_\mu/2 + \pi_{\nu\nu} \Delta\alpha^2_\nu/2 + \pi_{\mu\nu} \Delta\alpha_\mu \Delta\alpha_\nu , \qquad (3)$$

where q_μ and q_ν are electronic densities on atoms μ and ν and $\pi_{\mu\nu}$, $\pi_{\nu\nu}$, $\pi_{\mu\mu}$ are the corresponding atom–atom polarisabilities[5]. In cases where the inclusion of the electronic repulsion is necessary (*vide infra*), the HMO quantities should be replaced by their equivalents in the Hartree–Fock perturbation theory[6] or SCF-LCI theory[7,8].

As it follows from the Eq. (*2b*), equilibrium constants in our model of the substituent effect are influenced only by values of the electronic energies and the entropic term $(\Delta S^0_{0\nu} - \Delta S^0_{\mu\nu})$ in the Eq. (*1*) is equal to zero. This simplification makes it possible to transform the Eq. (*1*) into the expression (*4*) which is formally equivalent to the Hammett equation.

$$(\log k_{\mu\nu}/k_{0\nu})_A = \varrho_A \sigma^A_{\mu\nu} = -\pi^A_{\mu\nu} \Delta\alpha^A_\nu \Delta\alpha_\mu/2{\cdot}3RT \qquad (4)$$

In the Eq. (*4*), the superscript A stands for the term $\log (k/k_0)$ referring to the skeleton A; because the perturbation $\Delta\alpha_\mu$ characterizes the substituent μ, the superscript A in $\Delta\alpha_\mu$ will be neglected. On the other hand, the magnitude of the perturbation $\Delta\alpha_\nu$ does depend on the type of the skeleton; this is reflected by the superscript A in $\Delta\alpha^A_\nu$. The value of $\Delta\alpha_\nu$ is a significant structural characteristics describing, when applied, *e.g.* to rate processes, the structure of the transition state in terms of the structure of starting molecules. Therefore, it becomes evident that the knowledge of the absolute values of $\Delta\alpha_\nu$ would markedly improve the characterization of the transition state structure. On the basis of Eq. (*4*) and the knowledge of the term $\log (k/k_0)$, it is possible to calculate the magnitude of the product $\Delta\alpha_\mu \Delta\alpha_\nu$. However, as we show later, a calculation of the absolute values of the individual perturbations $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$ is not possible. One of the consequences resulting from this fact is that the Hammett ϱ constants cannot be taken, in contrast to a generally accepted view, as a measure of the transition state structure. This problem will be discussed in detail elsewhere[9].

Let us now return to the question of impossibility to calculate the values of perturbations $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$. For this purpose, let us decompose the right-hand side term in Eq. (*4*) into the terms corresponding to the ϱ and σ constants. In order to ensure ϱ and σ to be dimensionless and, at the same time, to satisfy the generally accepted conditions for these constants that $\varrho = f(1/T)$ and $\sigma \neq f(T)$, the decomposition will

be performed in the following way:

$$\varrho_A = \Delta\alpha_\nu^A / 2{\cdot}3RT \qquad (5a)$$

$$\sigma_{\mu\nu}^A = -\pi_{\mu\nu}^A \Delta\alpha\mu \,. \qquad (5b)$$

The Eq. (*5a*) offers seemingly the possibility of calculating the values of $\Delta\alpha_\nu$. However, the numerical factor 2·3 could be included equally well into the expression for the σ constant and then, depending on the choice between both possibilities, one would obtain different values of $\Delta\alpha_\nu$. In addition to this ambiguity, there is another even more important factor indicating the impossibility of calculating the absolute values of $\Delta\alpha_\nu$: only the experimentally accessible expression $\log (k/k_0)$ has a physical meaning and whatever decomposition into the ϱ and σ terms can only be made on a definitional basis. For instance, a choice of a ϱ value differing from one for the dissociation of benzoic acids should necessarily lead to different values of σ constants and according to the Eq. (*5a*), also to different values of perturbations $\Delta\alpha_\nu$. From this it follows that it is impossible to calculate the really "absolute", *i.e.* upon definition of the magnitude of ϱ independent values of perturbations $\Delta\alpha_\nu$. However, this limitation becomes unimportant if we limit ourselves to a comparison of ϱ constants for a given reaction in a series of structurally similar skeletons provided that all reaction constants ϱ have been obtained using the same set of σ constants. Eqs (*6a*) and (*6b*) will then hold for reactions on the standard skeleton 0 and the given skeleton A, respectively.

$$(\log k_{\mu\nu}/k_{0\nu})_0 = \varrho_0\sigma_{\mu\nu}^0 = -\pi_{\mu\nu}^0 \Delta\alpha_\nu^0 \Delta\alpha_\mu / 2{\cdot}3\boldsymbol{RT} \qquad (6a)$$

$$(\log k_{\mu\nu}/k_{0\nu})_A = \varrho_A\sigma_{\mu\nu}^A = -\pi_{\mu\nu}^A \Delta\alpha_\nu^A \Delta\alpha_\mu / 2{\cdot}3\boldsymbol{RT} = \varrho_A^{\mathrm{eff}}\sigma_{\nu\mu}^0 \qquad (6b)$$

On the basis of Eq. (*5b*), the constants $\sigma_{\mu\nu}^A$ for the skeleton A can be expressed by means of the standard constants $\sigma_{\mu\nu}^0$ (Eq. (*7*)).

$$\sigma_{\mu\nu}^A = -\pi_{\nu\mu}^A \Delta\alpha_\mu = -\frac{\pi_{\mu\nu}^A}{\pi_{\mu\nu}^0} \pi_{\mu\nu}^0 \Delta\alpha_\mu = \frac{\pi_{\mu\nu}^A}{\pi_{\mu\nu}^0} \sigma_{\mu\nu}^0 \qquad (7)$$

The effective constant ϱ_A^{eff}, which has been derived from the correlation $\log (k/k_0)_A \sim \sim \sigma_{\mu\nu}^0$, can be described by the Eq. (*8*).

$$\varrho_A^{\mathrm{eff}} = \frac{\pi_{\mu\nu}^A}{\pi_{\mu\nu}^0} \frac{\Delta\alpha_\nu^A}{2{\cdot}3RT} \qquad (8)$$

If the values of $\Delta\alpha_\nu^A$ in the given reaction series are supposed to remain roughly constant for all the skeletons under study, there a correlation should exist between the Hammett

ϱ constants and the corresponding atom-atom polarisabilities. The regression line should pass through the origin and its slope should be equal to $\varrho_0/\pi^0_{\mu\nu}$. The existence of a linear relationship between the experimental ϱ constants and the calculated polarisabilities thus makes it possible to predict theoretically the values of ϱ constants for a given reaction on arbitrary structural skeletons.

RESULTS AND DISCUSSION

The expected linear correlation of the Hammett ϱ constants with the polarisabilities $\pi_{\mu\nu}$ was tested on several examples for which ϱ constants determined under compa-

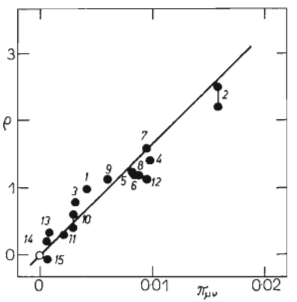


FIG. 1

Dependence of the Experimental Values of ϱ Constants for the Dissociation of Substituted Carboxylic Acids upon the Corresponding Atom–Atom Polarisabilities

1 Benzoic acid, *2* *cis*- and *trans*-acrylic acids, *3* 9,10-anthraquinone-1-carboxylic acid, *4* furan-2-carboxylic acid, *5* thiophene-2-carboxylic acid, *6* selenophene-2-carboxylic acid, *7* pyrrole-2-carboxylic acid, *8* tellurophene-2-carboxylic acid, *9* 1-naphthoic acid, *10* *cis*- and *trans*-cinnamic acids, *11* 4-phenyl-1,3-butadienecarboxylic acid, *12* 9-anthroic acid, *13* diphenyl-4-carboxylic acid, *14* p-(phenyliminomethyl)benzoic acid, *15* 2-oxo-4-phenyl-3-butenecarboxylic acid.

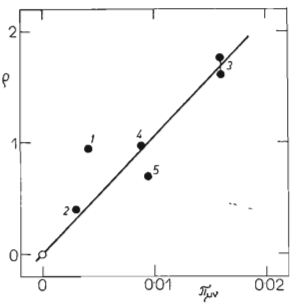
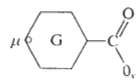


FIG. 2

Dependence of the Experimental Values of ϱ Constants for the Reaction of Carboxylic Acids with Diphenyldiazomethane upon the Corresponding Atom–Atom Polarisabilities

1 Benzoic acid, *2* *trans*-cinnamic acid, *3* *cis*- and *trans*-acrylic acids, *4* furan-2-carboxylic acid, *5* 9-anthroic acid.

rable conditions could be found in the literature. The first typical example examined was the dissociation of substituted carboxylic acids where experimental data are most abundant; 15 sets of substituted carboxylic acids were found covering the most different structural types[10–21]. The ϱ constants determined under nonstandard conditions (nonaqueous solutions, temperature ≠ 25°C) were normalised by dividing the corresponding ϱ value with that of the ϱ constant for dissociation of benzoic acids in this medium. For the calculation of polarisabilities $\pi_{\mu\nu}$, molecules of parent unsubstituted carboxylic acids (Scheme 3) with standard HMO parameters given by Streitwieser[22] were used as the pertinent quantum chemical model. As the reaction



SCHEME 3

center and its neighbourhood are the same throughout the whole series, the presumption on the constancy of $\Delta\alpha_\nu$ appears to be quite acceptable; a condition for the existence of the above correlation is thus fulfilled. The resulting regression line is shown in Fig. 1. Since the correlation encompasses not only aromatic but also heteroaromatic carboxylic acids, there is a very satisfactory accordance between the theory and experiment.

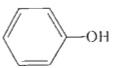
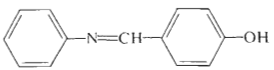
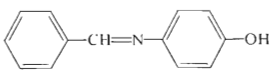
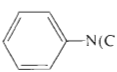
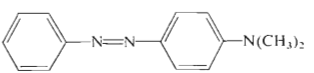
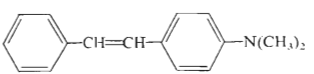
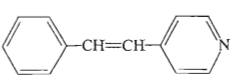
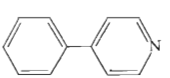
TABLE I
HMO Parameters Used for Calculations of Polarisabilities[a]

X	h_X, β	k_{CX}, β
—N—	−1·5	−0·8
—N=	−0·5	−0·8[b]
—O—	−2·0	−0·8
O=	−1·0	−1·0
—S—	−1·0[c]	−0·7[c]
—Se—	−0·8[d]	−0·6[d]
—Te—	−0·6[d]	−0·5[d]

[a] $\alpha_X = \alpha_C + h_X\beta$; $\beta_{CX} = k_{CX}\beta$; [b] $\beta_{N=N} = -0{\cdot}8$. [c] values taken from the ref.[34]; [d] revised values from the ref.[4].

TABLE II

Experimental (ϱ_{exp}) and Calculated (ϱ_{calc}) Values of the Hammett Constants for Several Reactions on Various Structural Skeletons

Compound[a]	ϱ_{exp}	ϱ_{calc}	$\pi_{\mu v}$
	2·01	2·01	0·0121
	0·29	0·27	0·0016
	0·37	0·25	0·0015
	4·2	4·2	0·0183
	0·53	0·68	0·0300
	0·65	0·64	0·0028
	5·71	5·71	0·1275
	0·85	0·72	0·0160
	0·97	0·94	0·0210

[a] Substituents at the 4 or 4′ position.

In the series of substituted acrylic and cinnamic acids and 4-phenyl-1,3-butadiene-carboxylic acid, small differences are encountered in the values of ϱ constants for the dissociation of the *cis* and *trans* isomers; although it was suggested to neglect these differences as statistically insignificant[23], they are believed to reflect the real changes in the electronic structure of the *cis* and *trans* isomers. However, treatment on the level of the HMO method presented above does not allow to account for this subtle difference. A proper description would require inclusion of electronic repulsion either on the level of the Hartree–Fock perturbation theory[6] or of the more general SCF-LCI theory[7,8]. These calculations are in progress in our laboratory and will be published elsewhere[24].

The proposed relationship between the Hammett ϱ constants and polarisabilities $\pi_{\mu\nu}$ was further tested on several examples including dissociation of substituted phenols[25], basicities of substituted dimethylanilines[26,27] and pyridines[28–30] as well as reactions of carboxylic acids with diphenyldiazomethane[31–33]. Molecules of the corresponding unsubstituted phenols, dimethylanilines, pyridines and carboxylic acids were taken as the pertinent quantum chemical models. Values of the HMO parameters used for calculations are summarized in Table I. The experimental data are much more scarce in these cases. Examination of Table II shows again a very satisfactory agreement between the experimental and calculated ϱ constants. Larger deviations were found only for reactions of substituted carboxylic acids with diazo-methane (Fig. 2); these deviations are presumably due to steric requirements of the bulky diphenyldiazomethane.

In general, all deviations from the correlation $\varrho - \pi_{\mu\nu}$ may be explained by the nonconstancy of the $\Delta\alpha_\nu$ value in the studied series. This nonconstancy may be due to several reasons. The first and most important reason can lie in the quantum chemical model for the calculation of $\pi_{\mu\nu}$, which presumably neglects an important structural factor applying specifically to some members of the series under study. Inclusion of this factor then necessitates an attempt to be made at modification of the original unsatisfactory Hamiltonian. Physical interpretation of changes required to improve the original Hamiltonian could markedly contribute to the elucidation of factors affecting the transmission of the substituent effect (*cf.*, for instance, the positive bridging effect[4]).

Another reason for the nonconstancy of $\Delta\alpha_\nu$ values may be, as already suggested above, the steric effects, *i.e.* the fact that the standard entropy $\Delta\,\Delta S^0$ changes substantially within the series of compounds under study. Nevertheless, also in this case it is possible to interpret mechanistically the changes in the $\Delta\alpha_\nu$ values. This question will be resolved elsewhere[9].

REFERENCES

1. Stock L. M., Brown H. C.: Advan. Phys. Org. Chem. *1*, 35 (1963).
2. Dewar M. J. S., Grisdale P. J.: J. Amer. Chem. Soc. *84*, 3539 (1962).
3. Dewar M. J. S., Dougherty R.: PMO *Theory of Organic Chemistry*, Chapter 4. Plenum Press, New York 1975.
4. Ponec R., Chvalovský V.: This Journal *39*, 3091 (1974).
5. Longuet-Higgins H. C., Coulson C. A.: Proc. Roy. Soc. A *191*, 39 (1947).
6. Ponec R.: This Journal *41*, 1105 (1976).
7. Ponec R., Málek J.: This Journal *41*, 3027 (1976).
8. Ponec R.: This Journal *42*, 2772 (1977).
9. Ponec R.: Chem. Scr., in press.
10. Zhdanovich V. J., Parnes Z. N., Kryptanov D. N.: Dokl. Akad. Nauk SSSR *165*, 566 (1965).
11. Jaffé H. H.: Chem. Rev. *53*, 191 (1953).
12. Bowden K.: Can. J. Chem. *43*, 3354 (1965).
13. Ritcher J. D. S., Miller S. I.: J. Amer. Chem. Soc. *86*, 1507 (1964).
14. Molho D., Giraud M.: Bull. Soc. Chim. Fr. *1969*, 4447.
15. Berliner E., Bloomers E.: J. Amer. Chem. Soc. *73*, 2479 (1951).
16. Zhdanov Yu., Minkin V. I., Medyayeva E. A.: Zh. Obshch. Khim. *35*, 1280 (1965).
17. Kalfus K., Šlosar J., Štěrba V., Večeřa M.: This Journal *34*, 2083 (1969).
18. Fringuelli F., Marino G., Savelli G.: Tetrahedron *25*, 5815 (1969).
19. Dewar M. J. S., Grisdale P. J.: J. Amer. Chem. Soc. *84*, 3548 (1962).
20. Marino G.: J. Chem. Soc., Perkin Trans. 2, 1783 (1972).
21. Bowden K.: Can. J. Chem. *41*, 2781 (1963).
22. Streitwieser A.: *Molecular Orbital Theory*, Chapter 5. Wiley, New York 1963.
23. Exner O. in the book: *Advances in Linear Free Energy Relationships* (J. Shorter, N. B. Chapman, Eds), p. 20. Plenum Press, New York 1972.
24. Ponec R.: This Journal *45*, 1655 (1980).
25. Minkin V. I., Zhdanov Yu., Medyayeva E. A.: Dokl. Akad. Nauk SSSR *159*, 1370 (1964).
26. Jerumanis S., Bruylants A.: Bull. Soc. Chim. Belg. *72*, 69 (1963).
27. Feytmans de Medicis, Bruylants A.: Bull. Soc. Chim. Belg. *72*, 603 (1963).
28. Katritzky A. R., Short J. D., Boulton A. J.: J. Chem. Soc. *1960*, 1516.
29. Jaffé H. H., Doak G. O.: J. Amer. Chem. Soc. *77*, 4441 (1955).
30. Katritzky A. R., Simmons M.: J. Chem. Soc. *1960*, 1508.
31. Bowden K.: Can. J. Chem. *43*, 3354 (1965).
32. Bowden K., Chapman N. B., Shorter J.: Can J. Chem. *42*, 1979 (1964).
33. Kwork K. W., O'Ferrall M. R. A., Miller S. I.: Tetrahedron *20*, 1913 (1964).
34. Zahradník R., Parkanyi C., Horák V., Koutecký J.: This Journal *28*, 776 (1963).

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