

SCF-CI PERTURBATION THEORY OF SUBSTITUENT EFFECT — A NOTE ON DEWAR F, M METHOD

R. PONEC

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát 2*

Received March 28th, 1975

Assuming that the substituent effect can be simulated by one electron perturbation $\mathbf{P}_{\mu\mu} = \Delta\alpha_{\mu}$, the SCF-CI perturbation theory gives an equation formally corresponding to Hammett equation. Power-series expansion of the equation leads to various approximations for calculation of ρ or σ constants. Of these approximations that which includes the first order repulsive terms formally corresponds to the so-called Dewar F, M method suggested on the basis of empirical considerations. The approach adopted here permits a discussion of the individual mechanisms of substituent effect transmission especially of the so-called "field effect".

The Hammett equation has proved itself to be exceptionally valuable. This is, in large part, due to the mechanistic conclusions that can be derived from the sign of ρ constant. The absolute value of this constant is also useful as it yields information about the nature of the transition state. Difficulties are encountered, however, when interpretation of ρ constants of analogous reactions on different structural skeletons is attempted. These difficulties have been partially overcome by the so-called Dewar F, M method¹ for the calculation of $\sigma_{\mu\nu}$ constants. In addition to this a relation for the ρ constant was recently derived² on the basis of HMO perturbation theory. The relation indicates a dependence of the ρ constant on the type of structural skeleton and on the relative position of the substituent to the reaction center. Validity of the relation was verified on a series of selected reactions. Despite that, in some cases the validity of the relation was limited due to the neglect of electron repulsions by the HMO method. Above all, it was necessary to limit the interpretation to the cases with such relative position of the substituent to the reaction center that permitted their direct resonance interaction on the given skeleton. It appeared interesting to derive analogous relationships also for SCF wave functions. Then, after the electron repulsion is incorporated, one can see whether this model can correctly describe the transmission of the substituent effect.

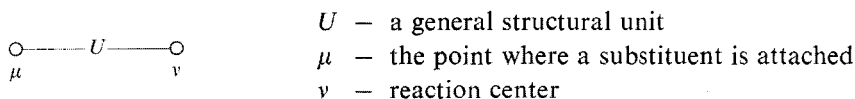
THEORETICAL

The following equation holds for the ratio of equilibrium (or rate) constants of non-substituted and substituted molecules:

$$\ln K_{\mu\nu}/K_0 = (\Delta G_0 - \Delta G_{\mu})/RT. \quad (1)$$

In the subsequent discussion we shall limit ourselves only to the cases when either

$\Delta \Delta S \approx \Delta \Delta H$ or $\Delta \Delta S = 0$. Then the corresponding changes of $\Delta \Delta H$ can be calculated by quantum chemical methods. Let us consider this model: (Scheme 1)



SCHEME 1

If the effect of the substituent can be described by a one-electron perturbation $\mathbf{P}_{\mu\mu} = \Delta\alpha_{\mu}$ only and the equilibrium or the rate process by a change $\Delta\alpha_{\nu}$ at the reaction center, then

$$\Delta H_0 = f(\Delta\alpha_{\nu}), \quad \Delta H_{\mu} = f(\Delta\alpha_{\mu}, \Delta\alpha_{\nu}). \quad (2)$$

The functions ΔH_0 and ΔH_{μ} can be expressed by SCF-CI perturbation theory. If we know the Hartree-Fock solution E_{HF} and $|\psi_0\rangle$ for the unperturbed Hamiltonian

$$E_{\text{HF}} = \langle \psi_0 | \mathbf{H} | \psi_0 \rangle, \quad (3)$$

the solution for the perturbed system can be written in the form

$$(\mathbf{H} + \mathbf{P}) |\psi\rangle = E |\psi\rangle, \quad (4)$$

where

$$E = E_{\text{HF}} + E' + E'' + \dots$$

$$|\psi\rangle = |\psi_0\rangle + |\psi'_0\rangle + |\psi''_0\rangle + \dots$$

($|\psi'_0\rangle$, $|\psi''_0\rangle$... represent contributions of monoexcited, biexcited, etc. configurations). After neglecting the contributions of biexcited configurations we obtain

$$E = E_{\text{HF}} + \langle \psi_0 | \mathbf{P} | \psi_0 \rangle + \sum_i^{\text{occ.}} \sum_k^{\text{unocc.}} b_{ik} \langle \psi_0 | \mathbf{P} | \psi_{i \rightarrow k} \rangle; \quad (5)$$

(the perturbation \mathbf{P} does not mix the states of different multiplicity).

The following set of non-homogeneous linear equations holds for the coefficients b_{ik} :

$$\sum_i^{\text{occ.}} \sum_k^{\text{unocc.}} b_{ik} \langle {}^1\psi_{i \rightarrow k} | \mathbf{H} | {}^1\psi_{j \rightarrow l} \rangle + \langle \psi_0 | \mathbf{P} | {}^1\psi_{j \rightarrow l} \rangle = E_{\text{HF}} b_{jl}. \quad (6)$$

If we consider only the term with $i = j$ and $k = l$ in the sum of Eq. (6), which is

equivalent to the assumption that the configuration $|\psi_{j \rightarrow i}\rangle$ is an eigenfunction of the Hamiltonian, the coefficient b_{j1} can be expressed analytically

$$b_{j1} = \langle \psi_0 | \mathbf{P} | \psi_{j \rightarrow i} \rangle / {}^1\Delta_{j \rightarrow i}, \quad (7)$$

where

$${}^1\Delta_{j \rightarrow i} = \varepsilon_j^0 - \varepsilon_i^0 + J_{j1} - 2K_{j1}.$$

After the substitution into Eq. (5) we obtain the expression

$$E = E_{\text{HF}} + 2 \sum_i^{\text{occ.}} \langle i | \mathbf{P} | i \rangle + 2 \sum_i^{\text{occ.}} \sum_k^{\text{unocc.}} \langle i | \mathbf{P} | k \rangle^2 / {}^1\Delta_{i \rightarrow k}, \quad (8)$$

which is equivalent to Pople expression for perturbation energy³. According to Eq. (8) the difference $\Delta \Delta H$ can be expressed as:

$$\Delta H_0 - \Delta H_\mu = -4 \sum_i^{\text{occ.}} \sum_k^{\text{unocc.}} c_{i\mu} c_{i\nu} c_{k\mu} c_{k\nu} \Delta\alpha_\mu \Delta\alpha_\nu / {}^1\Delta_{i \rightarrow k}. \quad (9)$$

After introducing this expression into Eq. (1) we obtain

$$\ln K_{\mu\nu}/K_0 = -\Pi_{\mu\nu}^{\text{LCI}} \Delta\alpha_\mu \Delta\alpha_\nu / RT, \quad (10)$$

where the terms $\Pi_{\mu\nu}^{\text{LCI}}$ represent the "generalized" polarizabilities atom-atom³.

This equation formally corresponds to the Hammett equation but, of course, the division into the parts corresponding to the constants ρ and σ can be achieved in two equivalent ways

$$\ln K_{\mu\nu}/K_0 = (-\Pi_{\nu\mu}^{\text{LCI}} \Delta\alpha_\nu / RT) \cdot \Delta\alpha_\mu, \quad (11a)$$

$$\ln K_{\mu\nu}/K_0 = (\Pi_{\mu\nu}^{\text{LCI}} \Delta\alpha_\mu) \cdot (-\Delta\alpha_\nu / RT) \quad (11b)$$

of which the latter is equivalent to the so-called Dewar F, M method¹. Introducing LCAO approximation into the expression for J_{ik} and K_{ik} and neglecting the differential overlap we obtain:

$$\ln K_{\mu\nu}/K_0 = -\frac{4}{RT} \sum_i^{\text{occ.}} \sum_k^{\text{unocc.}} \frac{c_{i\mu} c_{i\nu} c_{k\mu} c_{k\nu} \Delta\alpha_\mu \Delta\alpha_\nu}{\varepsilon_i^0 - \varepsilon_k^0 - \sum_{\alpha,\beta} (2c_{i\alpha} c_{i\beta} c_{k\alpha} c_{k\beta} - c_{i\alpha}^2 c_{k\beta}^2) \gamma_{\alpha\beta}}. \quad (12)$$

Assuming that $|(2K_{ik} - J_{ik})/(\varepsilon_i^0 - \varepsilon_k^0)| < 1$ which holds practically always, the expression (12) can be taken for a sum of infinite geometrical series. Therefore it can

be rewritten

$$\ln K_{\mu\nu}/K_0 = - \frac{4 \Delta\alpha_\mu \Delta\alpha_\nu}{RT} \sum_i^{\text{occ.}} \sum_k^{\text{unocc.}} \frac{c_{i\mu} c_{i\nu} c_{k\mu} c_{k\nu}}{\epsilon_i^0 - \epsilon_k^0} \left(1 + \frac{\Gamma_{ik}}{\epsilon_i^0 - \epsilon_k^0} + \frac{\Gamma_{ik}^2}{(\epsilon_i^0 - \epsilon_k^0)^2} + \dots \right), \quad (13)$$

where

$$\Gamma_{ik} = \sum_\alpha \sum_\beta (2c_{i\alpha} c_{i\beta} c_{i\alpha} c_{k\beta} - c_{i\alpha}^2 c_{k\beta}^2) \gamma_{\alpha\beta}.$$

If we consider only the first term in the expansion (13) we obtain an expression equivalent to Dalgarno expression⁴ of "uncoupled" Hartree-Fock perturbation theory:

$$\ln K_{\mu\nu}/K_0 = (-\pi_{\mu\nu} \Delta\alpha_\mu \Delta\alpha_\nu)/RT. \quad (14)$$

The other approximation includes the second term in the expansion (13), it is essentially equivalent to the F, M method suggested by Dewar¹ for a calculation of $\sigma_{\mu\nu}$ constants:

$$\sigma_{\mu\nu} = M \cdot \pi_{\mu\nu} + F/r_{\mu\nu}. \quad (15)$$

Dewar $\sigma_{\mu\nu}$ constants are always determined for a certain skeleton on the assumption that ρ constants of dissociation of the corresponding substituted acids are, similarly as in the case of substituted benzoic acids, equal to 1 and that Γ_{ik} are always the same for a given skeleton. In addition to this, it holds that

$$\gamma_{\alpha\beta} \approx \gamma_{\mu\nu} \approx r_{\mu\nu}^{-1}. \quad (16)$$

Equation (13) can be rewritten

$$\ln K_{\mu\nu}/K_0 = (\pi_{\mu\nu} \Delta\alpha_\mu + k_{\mu\nu} \Delta\alpha_\mu/r_{\mu\nu})(\Delta\alpha_\nu/RT). \quad (17)$$

The origin and the role of the field effect in the whole substituent effect are apparent from the form of Eq. (17).

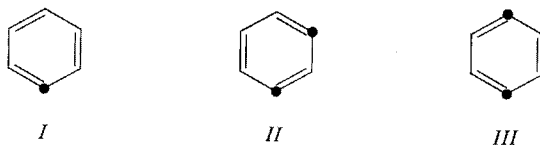
The total field effect corresponds to the difference between the expressions (13) and (14), the term proportional to $r_{\mu\nu}^{-1}$ is only its most rough approximation. With the respect to the fact that the contributions from higher order terms of expansion (13) decrease ($\Gamma_{ik}^n \sim r_{\mu\nu}^{-n}$) the net contribution corresponding to the field effect can be described by an expression formally analogous to Eq. (17) but with a different "effective" value of $k_{\mu\nu}$. It must be realised, however, that such an expression does not necessarily correctly describe the dependence of the potential on $r_{\mu\nu}$. This fact has been

already pointed out in a connection with the F, M method⁵. For practical purposes of organic chemistry this approximation will be apparently sufficient.

RESULTS AND DISCUSSION

In order to verify the suggested perturbation theory only the following fundamental question has to be answered: does the theory describe adequately the transmission of the substituent effect into *m*-position or, anotherwords, does it describe correctly the relative importance of π inductive and field effects for the *m*-position? This problem has been tested on model calculations of benzene perturbed in positions 1,3 and 1,4 by one-electron perturbations $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$. The calculations were carried out by Pople version of SCF (ref.⁶) in π electron approximation, gamma integrals were approximated according to Mataga⁷ ($\gamma_{11} = 10.84$ eV, $\beta = -2.318$ eV, IP = 11.42 eV).

The results of the calculations are given in Table I where are also shown, for the purpose of comparison, the results of the exact SCF calculations of perturbed molecules, HMO perturbation theory, and "uncoupled" Hartree-Fock perturbation theory⁴.



SCHEME 2

TABLE I

The Total Energy and Atom-Atom Polarizability of Substituted Benzenes Calculated by Various Perturbation Methods

Compound ^a	E_{tot}^b , eV	E_{tot}^c , eV	E_{tot}^d , eV	$\Pi_{\mu\nu}$, $\beta^{-1}\text{HMO}$	$\Pi_{\mu\nu}$, eV^{-1c}	$\Pi_{\mu\nu}^{\text{LCI}}$, eV^{-1d}
I	-144.0832	-144.0815	-144.0865	-0.398	-0.0914	-0.1317
II	-144.5978	-144.5931	-144.6032	-0.0093	-0.0011	-0.0008
III	-144.5908	-144.5882	-144.5961	+0.1019	+0.0187	+0.0276

^a See Scheme 2, perturbation $\Delta\alpha_\mu = \Delta\alpha_\nu = -0.5$ eV in the positions marked by ●; ^b exact SCF calculation; ^c "uncoupled" HF perturbation theory⁴; ^d SCF-CI perturbation theory, energy of "unperturbed" benzene = -143.5700 eV.

The following identity can be used in the verification of the quantum chemical calculations, according to Eq. (1) and (10):

$$(\text{p}K_0 - \text{p}K_\mu^m)/(\text{p}K_0 - \text{p}K_\mu^p) = \Pi_{13}^{\text{LCI}}/\Pi_{14}^{\text{LCI}} = \sigma_m/\sigma_p. \quad (18)$$

Indeed, with the exception of the substituent with a strong M effect, the ratio σ_m/σ_p is roughly constant (8). Of course, the polarizability values indicate that non of the perturbation theories shown gives satisfactory results for the *meta* position.

The main deficiency lies in the opposite sign of the resulting values of Π_{13}^{LCI} . It should be noticed, however, that the incorporated electronic repulsions bring about a gradual improvement of the results. It can be assumed that the SCF-CI theory, naturally without the simplifications introduced by Pople³, will be even capable of quantitative description of the transmission of the substituent effect into the *meta* position. These calculations and the exact calculations with a complete configurational interaction using the basis of monoexcited singlet states are being carried out in this laboratory now.

REFERENCES

1. Dewar M. J. S., Grisdale P. D.: *J. Amer. Chem. Soc.* **84**, 3539 (1962).
2. Ponec R., Chvalovský V.: *This Journal* **39**, 3091 (1974).
3. Pople J. A.: *Proc. Roy. Soc. A* **233**, 233 (1955).
4. Dalgarno A.: *Advan. Phys.* **11**, 281 (1962).
5. Exner O. in book: *Advances in LFER* (J. Shorter, N. B. Chapman, Eds). Plenum Press, New York 1972.
6. Pople J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953).
7. Mataga N., Nishimoto K.: *Z. Phys. Chem. (Leipzig)* **13**, 140 (1957).
8. Dewar M. J. S.: *Hyperconjugation*, Chapter 6. The Ronald Press Company, New York 1962.

Translated by J. Schraml.