

Parametric Variation and Chemical Effects: SCF Treatment of Arylmethyl Cations

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The solvolytic reactivity of arylmethyl tosylates can be well correlated by simple full-overlap treatments of the SCF Mulliken type. These types of theories balance more adequately the energetic contribution due to effects which can be classified as 'charge-dipole' and 'delocalization' derived, than the corresponding zero-differential overlap theory, CNDO/2. The sensitivity of the predictions to the parameters used in the theories gives indications of the nature of the qualitative interactions present in the arylmethyl systems.

MOLECULAR orbital methods are commonly used as an aid in the prediction and rationalization of chemical behaviour.¹ Because of the approximations in the methods and their applications, it is not certain that the behaviour predicted for the process calculated by the theory will agree with that observed in practice.² Two limiting possibilities may be expected if there is disagreement. In one extreme case, the variations of the predictions with respect to the observed behaviour will take an appearance of randomness, or scatter. In the other, the deviations will appear to be systematic. If the source of the variation can be derived, this information can be of chemical significance. We have been engaged in an effort to determine the 'chemical consequences' of parametric variation.

These general considerations are demonstrated

¹ For a review see, 'Sigma Molecular Orbital Theory,' eds. O. Sinanoglu and K. B. Wiberg, Yale University Press, 1970.

² Two of the most often applied semiempirical techniques CNDO/2 and MINDO differ markedly in the rationale for the types of approximations in the parameters, *cf.* (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S136; (b) N. Boder, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 3854.

by the example of arylmethyl cations. The solvolytic reactivity of arylmethyl tosylates can be postulated to be modelled by the energy charge for the system.



Several previous attempts at the elucidation of the chemical behaviour of these molecules have been of the correlative type.^{3,4} The attempts to correlate the reactivity with quantum methods have been shown to be deficient in various ways. Pure π methods, of course, cannot simply treat benzyl systems which have been modified with substituents. All electron methods tend to be extremely slow if full *ab-initio* techniques are used. On the other hand, the commonly used CNDO/2 method correlates data only within limited subsets of the full

³ M. J. S. Dewar and C. C. Thompson, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 4414.

⁴ A. Streitwieser, jun., H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5141, and references therein.

range.⁵ That is, the substituted benzyl systems and the polynuclear aromatic arylmethyl systems are each well correlated but the correlations are different for each of the series. Perturbative methods have had a measure of success equal to the SCF methods.⁶

The fact that all the methods are as successful as they are indicates that the linear free energy relation between the equilibrium reaction in the gas phase (calculated) and the kinetic reaction in solution (observed) holds very well. At least part of the random variation in the correlations can be ascribed to the impossibility of solvation energy being absolutely linearly correlated with reaction energy. Similarly, the enhancement small in correlative ability added by geometry optimization⁴ can be considered to be simply due to the addition of one additional parametric relaxation and not to any conceptually useful variation.

We have postulated that for the purpose of energy evaluation CNDO/2 weights 'charge-charge' types of interaction terms considerably more lightly than 'bond-delocalization' types.^{7,8} The former might be expected to be of greater importance in the substituted benzyl systems and the latter in the polynuclear aromatics. A verification of the rationale for the dispersion of the CNDO data into two sets could be obtained by the use of a method which balances more exactly the treatment of the two types of terms.

Thus we used the Mulliken full-overlap treatment based on the CNDO parametrization, previously reported, to calculate the energy change for the reaction.⁷ The terms used for the secular determinant are shown in equation (1).^{*} The latter exchange integrals were also calculated by the Mulliken approximation.⁹

$$F_{\mu\nu} = (\varepsilon_{\mu} + \varepsilon_{\nu})S_{\mu\nu}/2 - D_{\mu\nu} + \frac{1}{2}S_{\mu\nu}\sum_{\sigma} [Q_{\sigma}(\gamma_{AC} + \gamma_{BC}) - Z_{\sigma}(V_{AC} + V_{BC})] + \frac{1}{4}S_{\mu\nu}(\gamma_{AA} + \gamma_{BB}) - \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\sigma/\nu\lambda) \quad (1)$$

Table 1 and Figure 1 summarize the data. The benzyl compounds are well correlated by the method. For the purposes of testing whether the polynuclear aromatics were correlated by the same line, we used as a representative set the 1-naphthyl and the 2-naphthyl systems together with the parent benzyl system. These compounds represent most of the range of rate behaviour observed. The behaviour is related by the same correlation line. The change of net charge on the CH_3 group on being converted to the CH_2 group is similarly not as clearly resolvable into a delocalization effect and a charge-dipole effect as in the CNDO approach.

Consequently, this verifies the postulated reason for the dispersion. However, more exciting is the observa-

tion that the artificial increment in the bond energy term in the CNDO approach can be thought of as an aid in separating the two interaction mechanisms. Although

TABLE 1

Substituent	Calculated reaction values			
	$\Delta E/\text{eV}$	q-Me ^a	Δq^b	$-\log k^c$
	30.54	+0.0677	+0.4214	4.77
<i>p</i> -F	30.73	+0.0515	+0.4606	4.38
<i>m</i> -F	31.50	+0.0976	+0.4172	6.78
<i>p</i> -Me	29.12	+0.0451	+0.4223	3.02
<i>m</i> -Me	30.61	+0.0615	+0.4139	4.35
<i>p</i> -CF ₃	31.78	+0.1167	+0.3939	8.27
<i>p</i> -Me	29.17	+0.0477	+0.4294	0.34
<i>m</i> -OMe	30.97	+0.0694	+0.4086	5.04
<i>p</i> -NO ₂	31.66	+0.1158	+0.3994	9.29
1-C ₁₀ H ₇	30.05	+0.0770	+0.3842	2.80
2-C ₁₀ H ₇	30.36	+0.0706	+0.3989	3.67

^a Charge on methyl group. ^b Charge change on going to cation. ^c Observed rate constant (*cf.* ref. 5).

the same physical laws, at a coulombic quantum level of analysis, cause the two effects, it is the parametric factoring which allows us to perceive a useful pattern.¹⁰

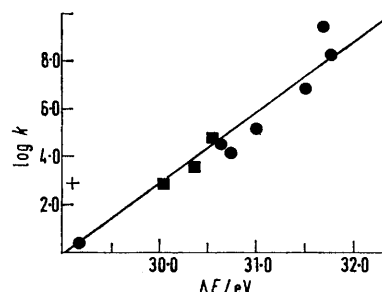


FIGURE 1 Correlation of ΔE with $\log k$. ●, Substituted benzyl systems (see Table 1); ■, unsubstituted systems; and +, *p*-methylbenzyl (because of the marked deviation this point was not included for purposes of determining the best line. The deviation indicates an effect not properly accounted for and should be investigated)

This is of interest since the resolution into two mechanisms, within a delocalized theory, is not an intuitively obvious possibility.

The last two sets of terms in equation (1) nearly cancel. These include the large number of exchange terms which are tedious to calculate, and are also not properly handled by the Mulliken approximation. Since the argument relating to the conclusions of the interaction mechanisms do not depend directly on the form of these exchange terms, we also performed a set of calculations using equation (2) where these two sets of terms were neglected. This corresponds to an extended Hückel

$$F_{\mu\nu} = (\varepsilon_{\mu} + \varepsilon_{\nu})S_{\mu\nu}/2 - D_{\mu\nu} + \frac{1}{2}S_{\mu\nu}\sum_{\sigma} [Q_{\sigma}(\gamma_{AC} + \gamma_{BC}) - Z_{\sigma}(V_{AC} + V_{BC})] \quad (2)$$

* ε_{μ} = Electronegativity of orbital μ , $S_{\mu\nu}$ = overlap of orbitals μ and ν , Q_{σ} = valence electron charge on atom C, γ_{AC} = the repulsion integral of an electron in an S orbital on atom A for one on atom C, Z_{σ} = the core charge of atom C, V_{AC} = the attraction of an electron on A for core C, and $D_{\mu\nu}$ = a correction for the inapplicability of the Mulliken approximation for kinetic energy, *cf.* ref. 7.

⁵ A. Streitwieser, jun., and R. G. Jesaitis, ref. 1, p. 197.

⁶ W. C. Herndon, *Tetrahedron*, 1972, **28**, 3675.

⁷ R. G. Jesaitis, *J. Amer. Chem. Soc.*, 1971, **93**, 3849.

⁸ B. J. Nicholson, *Adv. Chem. Phys.*, 1970, **18**, 249.

⁹ R. S. Mulliken, *J. Chim. Phys.*, 1949, **46**, 497.

¹⁰ S. Watanabe, *Methodologies of Pattern Recognition*, Academic Press, New York, 1970.

treatment¹¹ with a correction to the electronegativity being determined by the charge distribution. This approach is quite satisfactory for rapid indications of the modification of Hückel considerations for molecules with charge separations.¹²

Table 2 and Figure 2 summarize the results of this set of calculations. The scatter of the points is increased

TABLE 2
Mulliken (simplified)

Substituent	E_{ArMe}/eV	E_{ArCH_3}/eV	$\Delta E/eV$	$-\log k$
	1394.145	1360.731	33.414	4.77
<i>p</i> -F	2127.830	2094.573	33.257	4.38
<i>m</i> -F	2127.862	2094.214	33.648	6.78
<i>p</i> -Me	1610.603	1577.709	32.894	3.02
<i>m</i> -Me	1610.615	1577.490	33.125	4.35
<i>p</i> -CF ₃	3808.891	3775.282	33.609	8.27
<i>p</i> -OMe	2109.085	2076.855	32.230	0.34
<i>m</i> -OMe	2108.475	2075.575	32.900	5.04
<i>p</i> -NO ₂	2680.766	2646.895	33.871	9.29
1-C ₁₀ H ₇	2139.511	2106.608	32.903	2.80
2-C ₁₀ H ₇	2139.628	2106.705	32.923	3.67

somewhat, but not greatly, and the same general conclusions hold. As noted above, scatter can be considered to be due to neglect of effects which do not vary systematically, for the type of parametric variation imposed and the type of system chosen.

Overall features of the two approaches are similar to

¹¹ R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

¹² R. Jesaitis, unpublished results.

each other and to other related semiempirical theories. For example, the charge behaviour resembles that of other approaches in that a measure of charge alternation is observed.

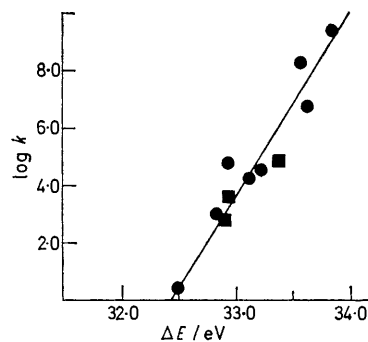


FIGURE 2 Correlation of ΔE with $\log k$ for the simplified approach. For symbols see caption to Figure 1

The results indicate that the systematic variation of parameters upon well defined systems should give insight into the nature of chemical effects as well as the methods themselves.

Acknowledgement is made to the Research Foundation of the State University of New York, the Stony Brook Computer Center, and the Petroleum Research Fund for partial support of this work.

[2/2343 Received, 16th October, 1972]