Semiempirical All-electron Calculations on the Reactivity of Aromatic Molecules

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Calculations by the MINDO/2 method of quantities expected to correlate with the rates of pyrolysis of heterocyclic arylethyl acetates show no improvement over Hückel calculations. There is nothing in these results to encourage the use of all-valence-electron SCF methods in the field of aromatic reactivity.

MOLECULAR orbital theories of π electrons have been used with reasonable success to correlate the reactivities of aromatic molecules. These calculations have for the most part used as a measure of reactivity either the localization energy or the charge on an atom, and calculations have been based on the Hückel method or on the self-consistent-field techniques. The work has been reviewed extensively,[1,2] and we will not refer to it in detail. It would be generally agreed that there is plenty of room for improvements in the theories.

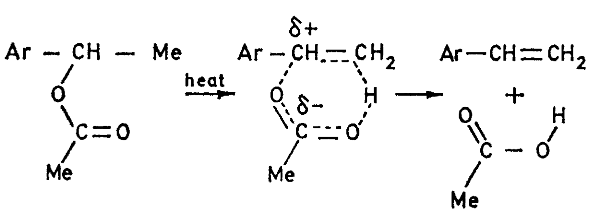
In recent years there have been developments in SCF MO theory and in computer techniques which allow all electrons to be explicitly considered in the calculations, so that there is no need to introduce assumptions about σ–π separability. However, the time taken to do a calculation using one of the approximate SCF MO theories (the so-called zero-differential-overlap theories) is roughly proportional to n^2 where n is the number of valence electrons. For example, an all-valence-electron SCF calculation on naphthalene will take about 25 times longer than a π-SCF calculation, and this is again considerably longer than for a Hückel calculation.

The question we attempt to answer in this paper is whether the all-electron results show a sufficient improvement over the π-electron results to justify this expenditure of time (and money).

The first all-electron calculations on the reactivity of aromatic molecules were made by Streitwieser and his coworkers.[3] They used the CNDO/2 method to calculate localization energies ($L_\mu{}^+$) for aromatic hydrocarbons and their methyl derivatives. The results were found to be much better than those obtained by Hückel theory when tested by the rate of hydrogen exchange. However, the correlation line showing the effect of methyl substitution had a very different slope from that found for the unsubstituted hydrocarbons, and for three compounds (benzocyclobutene, biphenylene, and fluorene) the results were poor. These calculations therefore gave some encouragement for further studies in the field without the certainty of great improvement.

For our investigation we have chosen to look at a series of molecules which includes aza-aromatics. These, having a polar σ-framework, should provide a better criterion for testing all-electron calculations than hydrocarbons alone.

We have also chosen to look at a reaction in the gas-phase, the pyrolysis of 1-arylethyl acetates (Scheme) so that the effects of polarity are not masked by solvation effects. This reaction is known to occur as a unimolecular elimination with a cyclic transition state (see Scheme), in which positive charge develops at the α carbon atom of the side chain.[4] This has been established by the correlation of the rates with Hammett σ^+ values and by the negative ρ factor for the reaction.[5]



SCHEME

Because σ^+ values correlate with the rates of electrophilic substitution reactions, one would expect to relate the rate of the reaction we are considering to calculated properties of the parent aromatic, either charge or localization energy. The latter we calculate as the energy of protonation of the hydrocarbon. If, on the other

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[1] A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, London, 1961.

[2] L. Salem, 'The Molecular Orbital Theory of Conjugated Systems,' Benjamin Inc., New York, Amsterdam, 1966.

[3] A. Streitwieser, jun., P. C. Mowery, R. G. Jesaitis, and A. Lewis, *J. Amer. Chem. Soc.*, 1970, **92**, 6529.

[4] R. Taylor, *J.C.S. Perkin II*, 1972, 165.

[5] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

hand, the C–O bond is substantially broken in the transition state, then the π electrons will be delocalized to the α carbon atom, and the rate should correlate with properties of the arylmethylcarbonium ion. We have therefore calculated the energy required to remove H$^-$ from the methyl-substituted hydrocarbon. All calculations were made with standard parameters. The Hückel parameters are given in ref. 6 and for the MINDO/2 calculations idealized geometries were assumed for the aromatic rings (all bond lengths of 1·40 Å and angles of 120°), and CH bond lengths were taken as 1·084 Å. The topography of the aromatic ring was assumed to be unaffected by protonation, and the two hydrogen atoms at the protonated centre were placed symmetrically above and below the molecular plane (HCH angle of 109·5°). The exocyclic methyl group was taken as tetrahedral with a CC bond length of 1·51 Å and CH bond lengths of 1·093 Å. The exocyclic methylene group was assumed to be coplanar with the ring (CC bond length of 1·40 Å).

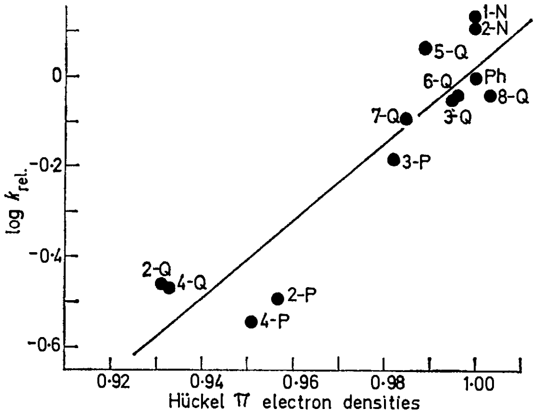

FIGURE 1 Plot of log $k_{\text{rel.}}$ values for pyrolysis of 1-arylethyl acetates against Hückel π-electron densities

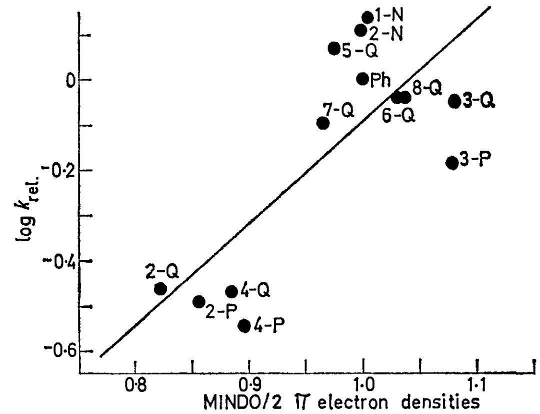

FIGURE 2 Plot of log $k_{\text{rel.}}$ values for pyrolysis of 1-arylethyl acetates against MINDO/2 π-electron densities

The correlations between log $k_{\text{rel.}}$ and the calculated quantities are shown in the Figures 1—7 where $k_{\text{rel.}}$ is defined as the ratio of the first-order rate constant for the reaction of the molecule under consideration to that of 1-phenylethyl acetate; data are available on the naphthalene, pyridine, and quinoline series.[5,6] The least-square lines are shown on each Figure.

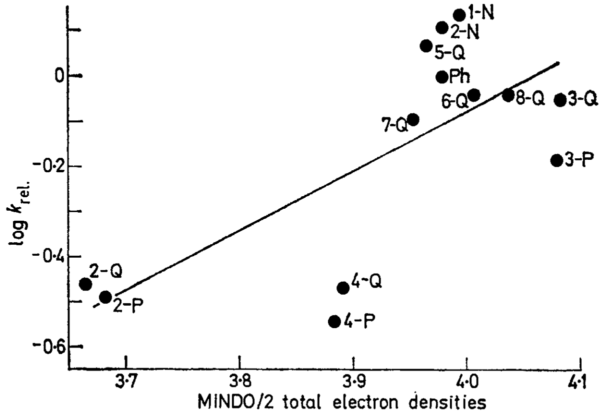

FIGURE 3 Plot of log $k_{\text{rel.}}$ values for pyrolysis of 1-arylethyl acetates against MINDO/2 total electron densities

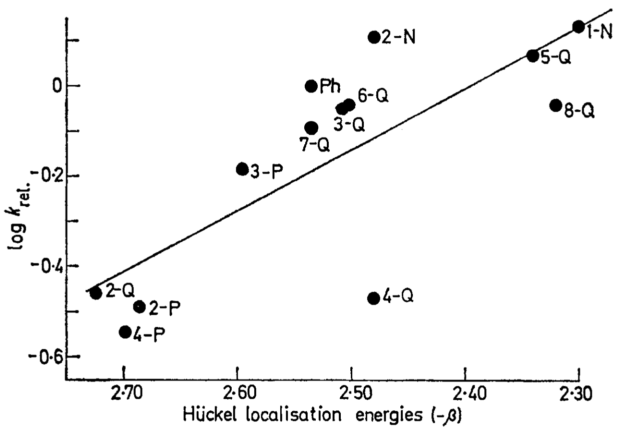

FIGURE 4 Plot of log $k_{\text{rel.}}$ values for pyrolysis of 1-arylethyl acetates against Hückel localization energies

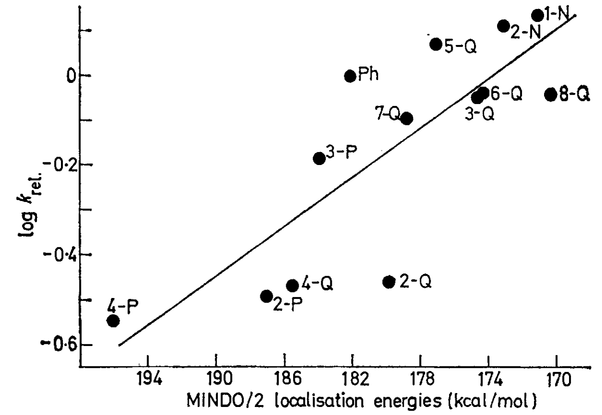

FIGURE 5 Plot of log $k_{\text{rel.}}$ values for pyrolysis of 1-arylethyl acetates against MINDO/2 localization energies

Figures 1—3 show the correlations with Hückel π, MINDO π, and MINDO total charges. Figures 4 and 5 show the localization energies calculated by the two methods, and Figures 6 and 7 show the delocalization energies.

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[6] R. Taylor, *J. Chem. Soc.* (*B*), 1962, 4881; 1971, 2382.

The most striking feature of Figures 1—3 is that both MINDO charges give a less satisfactory correlation than the Hückel charges, the MINDO total charges showing a particularly poor correlation with the relative rates. However, this is entirely due to the two molecules in which the substituent is *ortho* to the nitrogen atom. Whether or not the MINDO charges for these positions are a good representation of the true charges, we can certainly say that MINDO total charges are an unsatisfactory basis for interpreting the relative rate constants of our reaction.

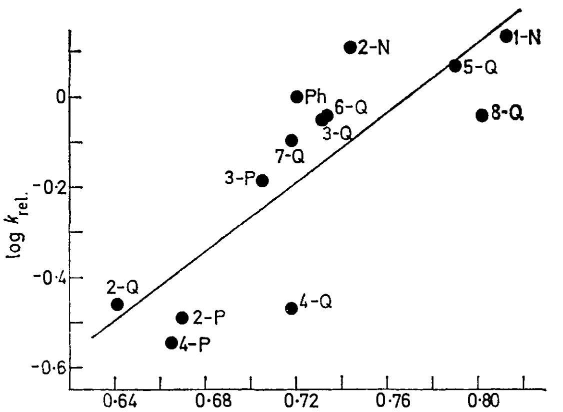

FIGURE 6 Plot of log $k_{rel.}$ values for pyrolysis of 1-arylethyl acetates against Hückel delocalization energies

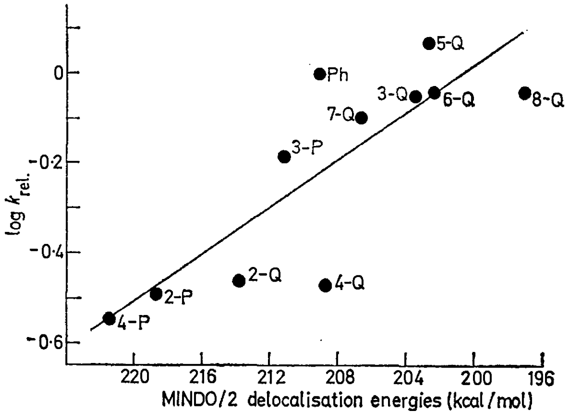

FIGURE 7 Plot of log $k_{rel.}$ values for pyrolysis of 1-arylethyl acetates against MINDO/2 delocalization energies

From Figures 4 and 5 it can be seen that there is little correlation between the MINDO energy of protonation and the Hückel π localization energy, but they are both rather poor in their correlation with the relative rate constants. The Hückel results appear to fall into two classes, the α-positions of naphthalene and quinoline on the one hand, and the β-positions and pyridine on the other. This division does not appear in the MINDO results, primarily because the relative reactivities of the 2- and 4-positions in both pyridine and quinoline are predicted to be quite different.

Finally we turn to the two calculations of delocalization energies. These again show little improvement over the localization energies, although it is again noticeable that the Hückel and MINDO results are appreciably different in their predicted order of reactivity.

None of the Figures we have shown can be said to form the basis of a satisfactory interpretation of the relative rates of the reaction we have considered. However, it is noticeable that the compounds showing most deviation from the best correlation line are different in almost all cases. This suggests that some interpretation based on a mixture of charge density and localization or delocalization energy might show a significant improvement, and we would justify this mixture on the grounds that in the transition state there is only partial development of charge on the α-carbon atom. In this respect we note that the best of the correlation lines is that based on the Hückel π-electron densities, and of the points above the line three are of the α-naphthalene type for which any measure of localization or delocalization will move closer to the line. The 8-quinoline is the most striking failure to fit into Hückel theory as its predicted reactivity is too high on either charge, localization, or delocalization model. The MINDO results cannot be adjusted so readily because the charges, either π or total, show a rather poor correlation with the rates.

Because the MINDO method makes no assumptions about σ–π separability, it is possible to perform calculations on structures in which bonds are partially broken, and, in principle, to find the structure and energy of the transition state for each species. We note from Figure 7 that the energy required to remove H^- from an alkyl group is of the order of 200 kcal mol^{-1}, which is greatly in excess of the observed activation energy for the reaction (*ca.* 40 kcal mol^{-1}). To see if an improved correlation is found for a transition state in which the CH bond is only partially broken, we have calculated the activation energy with the H^- located 1·8 Å directly above the carbon atom of the methyl group. The resulting activation energies were reduced to the order of 60 kcal mol^{-1}, but the correlation was found to be substantially poorer than for the fully broken CH bond.

Our conclusion from this study is that the all-valence-electron SCF theories, as typified by MINDO/2, do not necessarily lead to improved correlation with chemical reactivity (*cf.* ref. 7). The greater cost in computer time of such calculations has not been justified by our results. The only apparent advantage of the all-electron methods lies in their applicability to any assumed structure of the transition state, but even if the structure of the transition state were calculated for each molecule, we doubt whether improved results would be obtained, and the cost of such calculations would be considerable.

[2/2137 *Received*, 13*th September*, 1972]

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[7] J. T. Gleghorn, *J.C.S. Perkin II*, 1972, 479.