Tetrahedron Vol 33, pp 1921 to 1923 Pergamon Press 1977 Printed in Great Britain

A CORRELATION OF THE RELATIVE RATES OF HETEROARYLMETHYL CATION FORMATION BY SCF MOLECULAR ORBITAL THEORY

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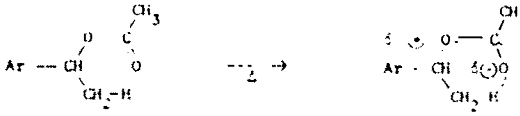
(Received in USA 30 August 1976; Received in the UK for publication 16 February 1977)

Abstract—Recent experimental findings have made it possible to extend molecular orbital correlations for the generation of arylmethyl systems to heteroaromatic species. In the present paper an SCF pi electron approach has been used to correlate the relative rates of pyrolysis of 1-pyridyl-, 1-quinolyl and 1-isoquinolylethyl acetates. Although far from good, it was found that calculated total energy differences yielded a correlation superior to that obtained from charge densities. The latter parameter, however, may have utility within the framework of a four parameter equation.

Attempts to correlate the chemical reactivity of conjugated systems with molecular orbital parameters have been common for over 20 years.[1] Particularly well studied have been those reactions which lead to arylmethyl species, $ArCH_2$. Carbonium ions,[2] carbanions[3] and finally free radicals[4] of this type have been investigated. The general treatment has usually involved consideration of relative rates of reaction versus a "delocalization energy". This term is a calculated pi energy difference between the transition state, taken as an arylmethyl species, and the starting material which is frequently assumed to be the unperturbed parent arene, ArH. This definition has been used in both HMO and more advanced SCF approaches.

Although less common in application to arylmethyl systems, an alternate approach for the correlation of reactions of conjugated systems exists. The methodology of this approach has been reviewed by Greenwood and McWeeny.[5] It is a "ground state" or "isolated molecule" technique wherein the pi electron distribution or some derivative of the same in the initial arene is used to predict the extent of reaction. This technique has found its principal application in the treatment of heteroaromatic and non-alternant homoaromatic species. These systems, of course, all show a non-uniform pi electron distribution in the ground state. The vast majority of arylmethyl systems which have been studied, however, have been derived from alternant moieties which, by definition possess a pi electron distribution of unity at all conjugated positions.[6] Simple ground state charge correlations are, therefore, inoperable.

A potentially great advance in the field may be based on the work of Taylor who initially studied the pyrolyses of 1-pyridylethyl acetates and 1-quinolylethyl acetates.[7] These substrates apparently react through a transition state in which appreciable charge is developed at the benzylic like position. In both the calculations which accompanied the original report and in a subsequent theoretical paper[8] it is stated that optimum correlation is with ground state charge densities as calculated by simple Hückel calculations. Both Hückel localization and delocalization models and all-electron MINDO/2 calculations yielded poorer correlations. More recently Glyde and Taylor extended these studies to the pyrolyses of 1-isoquinolylethyl acetates.[9] Although an experimental uncertainty of only one percent was associated with all data, the inclusion of these results noticeably worsened an already marginal correlation. Table 1 indicates the results of linear least square correlations of the original data. Although the correlation with Hückel charge density is still reported to be the optimum one, it was felt desirable to re-examine the problem using a more advanced approach.



The method utilized in the present calculations was developed by Dewar *et al.*[10] It is a self-consistant field, pi electron technique during the course of which the sigma energy of the underlying aromatic carbon–carbon (or carbon–nitrogen) bonds is obtained from the thermocycle used to evaluate resonance integrals. Two treatments of pyridine like molecules have appeared.[11,12] The more recent of the two allows for the possible electron polarization through the sigma system if several additional one center parameters are introduced for both the nitrogen and the adjacent carbon atoms.[11] It was the author's intent to minimize the number of parameters used and, therefore, the formalism of the earlier approach[12] was followed. The newer empirical data for the thermocycle, however, were utilized.[11]

It was felt that the optimum correlation should be with a delocalization energy as only this term is mechanistically meaningful in the light of what is known about the pyrolysis reaction. Ideally this should be a difference in heats of formation rather than a difference of pi energies only. The former definition has been partially adhered to in the present work by considering energy changes of the total aromatic system, i.e. the pi energies and the sigma bond energies of the conjugated systems. The neglected terms should be same for both starting heterocycle and derived ions, such as the energy of aromatic carbon–hydrogen bonds, or at least common to all systems considered, such as that of the CH_3CHOAc group. This approach has recently been successfully used to correlate the rates of arylethyl radical formation.[13] The calculated energies and experimental rate data are given in Table 2 which also lists the SCF charge densities

Table 1. Summary of correlations of relative rate data against calculated molecular orbital parameters

Parameter	Remarks	Correlation Coefficient	Average Deviation of log of Relative Rates
Hückel charge densities	pyridines and quinolines only	0.918	0.081
Hückel charge densities	pyridines, quinolines and isoquinolines	0.863	0.081
SCF charge densities	"	0.761	0.095
SCF delocalization energies	"	0.900	0.069
SCF delocalization energies and charge densities	"	0.938	0.049

Table 2. Calculated molecular orbital parameters

System		Aromatic			Arylmethyl Cation					
		E_π[a]	E_σ[b]	E_T	E_π	E_σ	E_T	ΔE_T	$\log k_{rel}$[c]	q[d]
Pyridine	2	9.698	21.167	30.685	11.912	24.858	36.770	6.085	-0.490	0.829
	3				12.349	24.839	37.188	6.503	-0.185	1.061
	4				11.652	24.904	36.556	5.871	-0.545	0.921
Quinoline	2	15.797	39.632	55.429	18.134	43.497	61.631	6.202	-0.460	0.800
	3				18.708	43.454	62.182	6.733	-0.050	1.060
	4				18.166	43.545	61.711	6.282	-0.470	0.916
	5				18.678	43.505	62.183	6.754	+0.068	0.993
	6				18.797	43.460	62.257	6.828	-0.040	1.015
	7				18.574	43.484	62.058	6.629	-0.096	0.984
	8				18.932	43.516	62.448	7.020	-0.040	1.009
Isoquinoline	1	15.357	39.655	55.012	18.183	43.475	61.658	6.646	0.320	0.792
	3				17.996	43.558	61.554	6.542	-0.260	0.844
	4				18.638	43.530	62.168	7.156	+0.015	1.069
	5				18.421	43.539	61.960	6.948	-0.045	1.015
	6				19.895	43.551	61.446	6.434	-0.195	0.976
	7				17.993	43.898	61.891	6.879	-0.045	1.015
	8				17.879	43.955	61.834	6.822	-0.160	0.983

a) All energies in electron volts.

b) Carbon - carbon and carbon - nitrogen bonds.

c) From references 7 and 9

d) Charge densities.

determined for the various positions of interest in the heterocycles. Table 1 contains the result of fitting the data to least squares analyses.

The correlation with SCF charge densities is poor. That based on the delocalization model, however, is appreciably better than either of those utilizing charge densities. The correlation coefficient of 0.900, while not good, is appreciably better than the value of 0.863 found using Hückel charge densities. A graphical representation of the present correlation is found in Fig. 1.

In their paper Murrell, Schmidt and Taylor also suggested that some approach based on a combination of charge density and delocalization energies might lead to a significant improvement in the correlation.[9] The rationale for this is that only incomplete charge may be developed in the transition state. This suggestion has been taken and the available SCF charge densities and delocalization energy differences used to empirically evaluate the following relationship:

$$\log k_{rel} = 0.3917(\Delta E_T) + 0.7653(q) - 3.5096.$$

The calculated logs of the relative rates are given in Table 3. A plot of the calculated vs the experimental energy terms is given in Fig. 2. The correlation while still not good, is the best to date with a coefficient of 0.938 and an average deviation thirty percent better than its nearest competitor. Caution, of course, must still be exhibited. The inclusion of additional variable parameters should always improve a correlation of this type without being mechanistically meaningful.

It is felt that the present correlations are more in line

Table 3. Calculated logs of relative rates from the four parameter equation

System		calc. log k_{rel}	exp. log k_{rel}
Pyridine	2	-0.492	-0.490
	3	-0.150	-0.185
	4	-0.505	-0.545
Quinoline	2	-0.468	-0.460
	3	-0.061	-0.050
	4	-0.348	-0.470
	5	-0.104	+0.068
	6	-0.058	-0.040
	7	-0.160	-0.096
	8	+0.012	-0.040
Isoquinoline	1	-0.300	-0.320
	3	-0.301	-0.260
	4	+0.112	+0.015
	5	-0.011	-0.045
	6	-0.242	-0.195
	7	-0.038	-0.045
	8	-0.085	-0.160

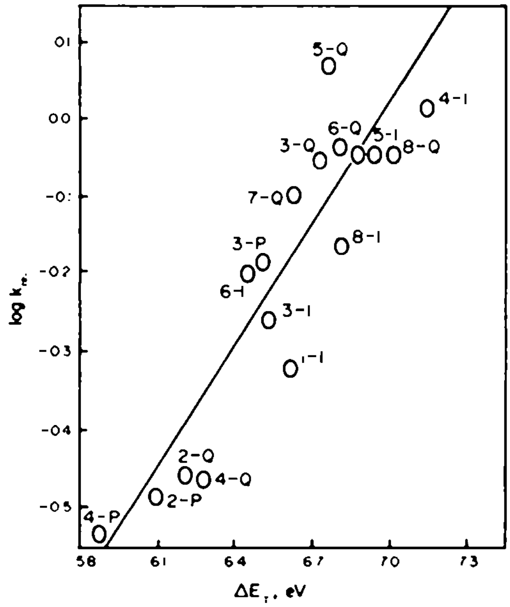


Fig. 1. Logs of relative rates of reaction vs energy differences calculated by an SCF approach.

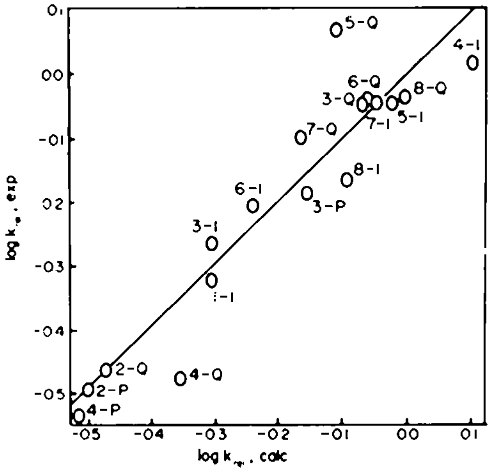


Fig. 2. Logs of experimental relative rates of reaction vs their calculated counterparts.

with what is mechanistically known about the reaction. The use of charge densities alone to correlate these pyrolyses is misleading when the endothermicity of the reaction and the degree of probable charge development are considered. As complete charge formation has not occurred, however, inclusion of charge densities within a multi-parameter equation may indicate the role of ground state electronic distribution on the overall reaction.

Acknowledgement—The Computer Center of Oregon State University is thanked for generously donating the funds required for these calculations.

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