Experimental Section

Calorimeter. The reaction vessel was constructed of glass using a design similar to that of Rossini.[18,19] It permitted a stream of the hydrocarbon, diluted with helium, to be premixed with oxygen prior to burning in an atmosphere of oxygen. The reaction vessel was immersed in water contained in a covered dewar flask which was equipped with a constant-speed stirrer, a thermistor probe, and a heater. The exit gases from the vessel passed through a spiral equilibrating tube also immersed in the calorimeter water. The water and carbon dioxide formed in the combustion were absorbed by Anhydrone and Ascarite, respectively. The water in the dewar was at 25.0° at the beginning of the combustion experiment, and the dewar was immersed in a water bath at 28.000 ± 0.005°.

Combustion. After a 16-min fore period, during which the temperature change was noted, the hydrocarbon mixture was passed into the calorimeter. At 20 min, the combustion was initiated by an electrical spark. The combustion was allowed to proceed until about a 2° temperature rise was noted. During this period, temperature readings were taken periodically, and this was continued until 44 min from the beginning of the experiment. The last 8 min was taken as the after period. The amount of water vapor formed was determined by weighing the Anhydrone tube; the latter was returned to the exit line, and the calorimeter was swept out with oxygen. The Ascarite tube was weighed after 0.5 hr, but the system was swept overnight in order to collect all of the water. The weights of water and carbon dioxide agreed within 0.7% of the theoretical ratio, and the weight of hydrocarbon used was based on the carbon dioxide since it should be the more accurate of the two.

The electrical calibration was performed immediately after each combustion experiment in order to minimize errors. The temperature data were collected in a fashion similar to that of the combustion, with a fore period, a heating period, and an after period. During the heating period, the voltage across and the current through the heater were determined using a precision potentiometer. The time of heating was determined using an electronic clock with a precision of better than 0.01%.

The heat equivalent of the calorimeter and the heat of combustion were determined using a computer program which calculated the stirring and conduction energies from the fore and after periods and corrected the combustion or heating periods by integrating the stirring and conduction energies over the period. Corrections were made for the spark energy, the heat of vaporization of the water which appeared as water vapor at the end of the combustion, and the heat capacity of the gases which flowed through the calorimeter.

Since the hydrocarbon entering the calorimeter was at the water bath temperature, 28°, a small correction was necessary to obtain the heat of combustion at 25°. This correction was calculated to be 0.1 kcal/mol, and the values in Tables I and II have been corrected in this way. The complete experimental data and detailed calculation are given in the thesis of R. A. F. which is available through University Microfilms.

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(18) F. D. Rossini, *J. Res. Natl. Bur. Std.*, 6, 1 (1931).

(19) The calorimeter is described in detail in the thesis of R. A. F., which is available from University Microfilms, Ann Arbor, Mich.

Factors Influencing the Rates of Reaction at Arylmethyl Carbon Atoms. An Evaluation of the Importance of Steric Effects within the SCF–LCAO Approach

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Abstract: The relationships obtained by correlating the relative rates of arylmethyl ion formation with the corresponding changes in calculated π energies have been reexamined. Inclusion of nonbonded interactions does not favorably affect the HMO results; however, in many cases the use of these interactions with the SCF results improves the precision of the correlation. For nonalternant molecules the change in angle strain upon reaction may also introduce a pronounced effect.

The Hückel molecular orbital (HMO) approach provides a satisfactory treatment for alternate hydrocarbons; however, because of neglect of electronic interactions, calculations on nonalternants, ions, and heterocycles often prove less reliable.[1] For these latter systems the use of some self-consistent field (SCF) method can usually ameliorate the results. A comparison of attempts to correlate the rates of formation of arylmethyl ions, (shown in eq 1 and 2) by the two treatments illustrates this variance.

$$ArCH_3 + B^- \longrightarrow ArCH_2^- + BH \qquad (1)$$

$$ArCH_2X \longrightarrow ArCH_2^+ + X^- \qquad (2)$$

Streitwieser and Langworthy have examined the rates of formation of arylmethyl anions.[2] Correlations with HMO calculations were successful only if the compounds were divided into two sets. One, noted as the phenyl or β'-naphthyl type, was considered to involve no essential change in steric factors upon undergoing reaction. The second class of molecules was composed of compounds similar to α-methylnaphthalene, where upon going to the transition state (here taken as being equivalent to the planar ion) severe nonbonded interactions might occur between a hydrogen atom on the exocyclic carbon atom and one in a *peri* site such as the 8 position in naphthalene. When this dichotomy was employed, a fair correlation of the data was obtained, although certain compounds showed an unexpectedly large deviation from the relationship. When the same experimental data were utilized in an SCF approach, however, a single excellent correlation was observed.[3]

This study was undertaken to test the question of whether the steric factor predicted by HMO results is truly present. The possibility of such *peri* interactions is intuitively attractive despite the fact that SCF results

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(1) M. J. S. Dewar, *Rev. Mod. Phys.*, 35, 586 (1963).

(2) A. Streitwieser, Jr., and W. C. Langworthy, *J. Am. Chem. Soc.*, 85, 1757, 1761 (1963).

(3) M. J. S. Dewar and C. C. Thompson, Jr., *ibid.*, 87, 4414 (1965).

are more reliable for conjugated systems.[4] It was decided to calculate directly the change in strain energy (enthalpy) between the ground and transition states for the reacting systems. By comparing this energy change with that of the π system it is possible to assess the relative importance of the two effects and to observe whether inclusion of this strain factor can improve results. The suggested combination of factors can approximately be considered as a total energy change incorporating changes in both the π and σ portions of the molecules.[5]

Within the framework of σ–π separability the approach which has been adopted for this study combines the usual SCF–LCAO type calculation of the energy of the π system[4] with an evaluation of the strain energy in the aromatic σ system as determined *via* classical considerations.[9] These energies were obtained for both the arylmethanes and the corresponding anions. The change in total energies was expressed relative to the toluene–benzyl anion system taken as zero. In accord with previous studies a negative energy change implies a system which reacts faster than the toluene–benzyl anion standard.[3] Calculations were carried out employing three models of increasing complexity. Initially, all systems were treated as having constant bond lengths (CBL) in a rigid geometry. The lengths assigned were sp^2–sp^2 carbon–carbon (1.400 Å), sp^3–sp^2 carbon–carbon (1.515 Å), sp^3 carbon–hydrogen (1.108 Å), and sp^2 carbon–hydrogen (1.075 Å). In essence such an approach leaves the geometry of the aryl portion of the molecule unmodified upon the formation of the ion. The sole change in the σ strain energy upon reaction may, therefore, be associated with changes involving nonbonded interactions of the exocyclic unit with the remainder of the molecule. In the second approach, the SCF calculation on the π system was used to determine self-consistent values for the lengths of the sp^2–sp^2 carbon–carbon bonds (VBL). This was done by employing the following relationship between bond order and bond length.[10]

$$r_{ij} = 1.515 - 0.177p_{ij} \qquad (3)$$

These values were used in combination with single bonds given above to construct the appropriate geometries. As it is usually possible to construct angle-strain-free geometries, the net effect is to again consider the σ strain energy as primarily arising from nonbonded interactions. Now, however, these interactions have also changed within the aryl portion of the molecules upon undergoing reaction as well as between the aryl and exocyclic moieties of the systems. The third approach was closely related to the second. The calculated bond lengths were again used to construct geometries; however, these geometries were now varied until an energy minimum for strain in the σ system was obtained (VBL$_{\text{min}}$). The change in the σ strain energy is now not only due to changes in the nonbonded interactions present but include contributions due to deviations from the equilibrium bond length and bond angle values. The latter two methods yield almost identical results when applied to benzenoid systems. This is due to the ease with which the calculated bond lengths may be incorporated into six-membered rings with almost no angle strain. When applied to nonalternant systems, however, these two approaches may yield quite different results as regards equilibrium structure and the amount of σ strain energy present.

The use of machine calculations to evaluate the strain energy present in molecules and its effect in determining the equilibrium structure of aliphatic systems has become increasingly more fruitful.[11–13] Work has also appeared which has combined such calculations with various molecular orbital techniques to arrive at conclusions regarding the geometries of conjugated systems, particularly any possible deviation from expected planarity.[9,14] Such calculations have also been extended to problems in chemical kinetics. With a judicious choice of parameters, calculations have been carried out to determine the differences in strain energy between the ground states and transition states for a series of bridgehead halides undergoing solvolysis. An excellent agreement was obtained between the calculated energy differences and the relative rates of reaction.[15]

The choice of the parameters employed is a matter of paramount concern. The carbon–carbon, carbon–hydrogen, and hydrogen–hydrogennon bonded interaction functions used in this study are identical with those previously described.[15] These are based on the experimental findings of Bartell and may be regarded as representing the nonbonded interactions of atoms in molecules rather than in free atoms.[16] The same functions are used irrespective of the hybridization state of any particular carbon atom. While this can in no way be theoretically justified, experimentally no large uncertainty will thus be introduced, especially if the discussion is limited to energy differences. This latter factor assumes an even greater significance considering the problem of equating an absolute nonbonded interaction with a physical property,[15] *e.g.*, even benzene is calculated to possess over 3 kcal/mol of nonbonded interaction strain.[9] Both bond and angle deformation may be treated by simple harmonic potentials of the form

$$E = k(\tau - f)^2 \qquad (4)$$

where τ and f are the equilibrium and true values, respectively, of some bond length or valence angle and

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(4) M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 459 (1966), and references cited therein.

(5) It must be admitted that there exists a better, alternative approach to the problem which does not involve the arbitrary division of some molecule into π and σ components. This would necessitate either a single SCF calculation of the entire system or, at least, the treatment of the σ system *via* quantum mechanical rather than classical terms as will be utilized here. Although the former type of calculations are becoming more common in the literature,[6–8] the relatively large size of the systems considered in this study would seem to preclude their utilization. It should be pointed out, however, that it will ultimately be such an approach which will yield the final word on the problem.

(6) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); **44**, 3289 (1966).

(7) G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964); **87**, 3300 (1965).

(8) M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967); N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967).

(9) G. J. Gleicher, *Tetrahedron*, **23**, 4257 (1967).

(10) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(11) J. B. Hendrikson, *ibid.*, **86**, 4854 (1964), and references cited therein.

(12) K. B. Wigerg, *ibid.*, **87**, 1070 (1965).

(13) N. L. Allinger, M. A. Miller, F. A. Van Cutledge, and J. A. Hirsch, *ibid.*, **89**, 4345 (1967).

(14) N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *ibid.*, **87**, 3430 (1965); N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966).

(15) G. J. Gleicher and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582 (1967).

(16) L. S. Bartell, *J. Chem. Soc.*, **32**, 827 (1960).

k is the appropriate force constant. Most of the force constants for carbon–hydrogen stretching and the various in-plane bending motions can be found in the literature.[15,17] A compilation of these force constants, along with the corresponding equilibrium values, is given in Table I.

Table I. Force Constants and Equilibrium Values

Interaction	τ	k
C_{sp^3}–H stretch	1.108 Å	360.0 kcal/mol A [a]
C_{sp^2}–H stretch	1.075 Å	360.0 kcal/mol Å [b]
C–C_{sp^2}–C in-plane bend	120°	104.1 kcal/mol radian^2 [b]
C–C_{sp^2}–H in-plane bend	120°	94.8 kcal/mol radian^2 [a]
C–C_{sp^3}–H	109.5°	39.6 kcal/mol radian^2 [a]
H–C_{sp^3}–H	109.5°	23.0 kcal/mol radian^2 [a]
H–C_{sp^2}–H	120°	92.0 kcal/mol radian^2 [c]

[a] Reference 15. [b] Reference 17. [c] Estimated value.

Table II. Proton Abstractions from Arylmethanes

Aryl group	Rel rate[a]	ΔE_π[b] CBL	ΔE_π[b] VBL	ΔE_σ CBL	ΔE_σ VBL	ΔE_σ VBL_{min}	ΔE_{total} CBL	ΔE_{total} VBL	ΔE_{total} VBL_{min}
Phenyl	1.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Naphthyl	7.4	−0.298	−0.315	0.028	0.002	0.007	−0.287	−0.313	−0.308
1-Naphthyl	10.3	−0.522	−0.429	0.177	0.087	0.098	−0.345	−0.342	−0.331
3-Phenanthryl	14	−0.479	−0.483	0.000	0.004	0.007	−0.479	−0.479	−0.476
8-Fluoranthyl	14	−0.529	−0.537	0.009	0.010	0.042	−0.520	−0.527	−0.495
2-Pyrenyl	15	−0.400	−0.460	0.000	0.006	0.004	−0.400	−0.454	−0.456
9-Phenanthryl	19	−0.647	−0.558	0.182	0.145	0.107	−0.465	−0.413	−0.451
2-Anthracyl	30	−0.507	−0.547	0.004	0.000	0.003	−0.503	−0.547	−0.544
4-Pyrenyl	40	−0.764	−0.666	0.178	0.123	0.129	−0.586	−0.543	−0.537
1-Pyrenyl	190	−1.013	−0.940	0.176	0.131	0.126	−0.837	−0.809	−0.814
3-Fluoranthyl	*Ca.* 200	−1.113	−1.164	0.175	0.190	0.216	−0.958	−0.974	−0.948

[a] Reference 2. [b] All energies given in electron volts.

No single value was employed for the force constant required to deform a carbon–carbon bond. Instead, it was decided to treat the force constant as a function of the equilibrium value of the corresponding bond length. The empirical relationship developed by Dewar and Schmeising was utilized.[18]

$$k = -46.978/\tau^2 + 194.813/\tau^4 - 136.486/\tau^6 \quad (5)$$

In eq 5, k is given in terms of dynes × 10^5/Å. The values of τ employed above correspond to the equilibrium values of the bond lengths as determined *via* an SCF calculation in accord with eq 3. By evaluating the force constants in accord with the above relationship, it is found that the weaker force constants will be associated with the longer bonds, *i.e.*, lower bond order, more single-bond character.

The above calculation of the σ strain energy was somewhat simplified by considering all of the systems studied to be essentially planar, thus precluding the need to consider out-of-plane bending motions. Torsional interactions were also neglected in the above treatment. Since all aromatic systems are considered as planar, the change in such interactions becomes a constant. It may also be argued that torsional interactions are implicitly included in the determination of the π energy of the system.[9]

The π energies in this study were calculated in the usual manner using the semiempirical resonance integral which has appeared in previous papers.[4] One additional factor, however, was introduced. Rather than considering the simple arene as the model for the determination of the π energy of the ground state, as was previously done,[3] an attempt was made to include the effect of the methyl substituent. A simple inductive model was employed which had proven effective in treating the polarographic oxidation potentials of alkylaromatics.[19] The effect of this model is to modify one of the diagonal terms in the SCF matrix by lowering the valence-state ionization potential of the sp^2-hybridized carbon atom to which the methyl group is attached. As might be expected, such an approach changes the π energy only negligibly from that of the parent arene.[20] There are, however, slightly larger changes in the bond orders of the linkages to the substituent bearing carbon atom. The equilibrium geometries will, therefore, be somewhat changed.

Table III. Data on Linear Correlations for Rates of Proton Removal from Arylmethanes

System	Slope	Intercept	Av dev	Correl coeff
HMO[a]	−3.544	0.741	0.268	−0.823
HMO with strain[a]	−5.654	0.884	0.298	−0.770
SCF-CBL	−1.910	0.197	0.129	−0.966
SCF-VBL	−2.010	0.176	0.097	−0.976
SCF-CBL with strain	−2.384	0.122	0.106	−0.980
SCF-VBL with strain	−2.256	0.167	0.112	−0.969
SCF-VBL_{min}	−2.469	0.082	0.082	−0.987

[a] Based on a single correlation using $\beta = -49$ kcal/mol for all bonds in accord with ref 2.

Table II presents the composite energy changes between the arylmethanes and the corresponding arylmethyl anions and the relative rates of the anion-forming reaction.[2] Table III presents a summary of the various correlations obtained by plotting the logs of the relative rate constants against the calculated energy differences taken relative to the toluene–benzyl anion system. The reported values were derived *via* a least-squares approach in accordance with the equation for a straight line.

In examining these data it must first be noted that inclusion of σ strain energy (nonbonded interactions) within the framework of the simple HMO approach does not improve the correlation but actually worsens

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(17) S. Cyvin, *Acta Chem. Scand.*, **11**, 1499 (1957).

(18) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(19) G. J. Gleicher and M. K. Gleicher, *J. Phys. Chem.*, 71, 3693 (1967).

(20) M. J. S. Dewar, *Tetrahedron*, **19**, 89 (1963).

it. It is possible that this is due to a poor choice of parameters. However, in order to remedy the discrepancy in results merely by changing parameters, it would be necessary to either increase the value of the HMO resonance integral threefold or to drastically reduce the nonbonded interaction repulsion potentials. Even if this were done, two points, 2-pyrenyl and 3-fluoranthyl, would still show significant deviation. It would appear that the poor correlations obtained using the HMO approach are not the result of neglected steric interactions, but represent, in the main, deficiencies inherent in the technique. Streitwieser and Langworthy have suggested that systems of the 1-methylnaphthalene type may, upon going to the ion, assume a structure in which the exocyclic group is rotated approximately 17° out of the plane of the aryl group. It would appear from this study that the unfavorable interactions could be more easily remedied *via* in-plane bending deformations at both the exocyclic carbon and the carbon to which it is attached along with an out-of-plane deformation of one hydrogen at the exocyclic site and an opposite such deformation at the *peri* position.

Contrasted with this behavior, it may be observed that in two of the three cases studied, in which SCF calculations were employed, inclusion of σ strain energies led to a small but real improvement of results. As might be expected, the greatest improvement is noted in the case where a constant bond length approach was employed. Such a representation must strongly emphasize possible nonbonded interactions. When the change in π energy was calculated using a variable bond length technique a slightly better correlation is obtained over the constant bond length method. However, inclusion of σ strain energy now leads to a worsening of results. It can be argued that in this model the importance of nonbonded interactions should be minimized. Possible *peri* effects are decreased relative to the constant bond length model. The ions are calculated to possess a high degree of bond alternation. The bond orders for bonds attached to the carbon bonded to the exocyclic position have particularly low values. The corresponding bonds should be rather long. Thus, in the 1-naphthylmethyl anion the internuclear separation between the two hydrogen atoms causing the unfavorable *peri* interaction is 1.720 Å in the constant bond length approach but only 1.862 Å in the variable bond length method. The fact that inclusion of only nonbonded interactions in the above case leads to a less satisfactory correlation is strongly suggestive that some other factor, which might have previously been overshadowed in its relative importance, is now playing a dominant role. A perusal of the data showed that it was primarily the deviation of two points from the calculated relationship which caused the poorer correlation. These delinquent points are the two nonalternant fluoranthene derivatives. When a full minimization of the σ strain energies was carried out, these two points no longer represent exceptional results. Unlike the case for the benzenoid compounds where the calculated geometries can be used to construct systems which are essentially devoid of angle strain, the presence of the odd-membered ring in the methylfluoranthenes would yield structures calculated to possess appreciable angle strain. The changes in the calculated values of the bond lengths can substantially affect the degree of angle strain in the odd-membered ring. The correlation obtained using the results of a full energy minimization on the σ system show a significant improvement over all other treatments.

An interesting corollary may be developed from the above findings. For nonalternant systems such as fluoranthene (I) which contain a potential source of strain, the true structure should involve an accommodation between σ and π energy factors. This rather obvious conclusion may be illustrated by the results in Table IV which show the calculated structural factors for fluoranthene as obtained *via* an SCF determination of the π system both alone and in combination with a minimized strain energy approach. There are sufficiently large differences between the two sets of results so that an actual structure determination of the molecule could decide the validity of this treatment.

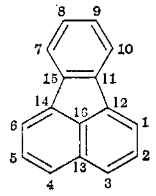

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Table IV. Calculated Structural Factors in Fluoranthene

Bond length[a]	π	$\pi-\sigma$	Internal bond angles[b]	π	$\pi-\sigma$
1–2	1.419	1.440	2–1–12	120	118.7
2–3	1.378	1.389	1–2–2	120	123.2
3–13	1.427	1.410	2–3–13	120	117.9
7–8	1.395	1.408	13–16–12	120	125.0
8–9	1.401	1.406	16–12–1	120	117.3
10–11	1.403	1.407	12–16–14	120	109.8
11–12	1.467	1.490	16–12–11	98.7	107.9
11–15	1.405	1.404	12–11–15	111.3	107.5
12–16	1.429	1.397	8–7–15	120	119.0
13–16	1.409	1.400	10–11–15	120	120.6
1–12	1.383	1.381	7–8–9	120	120.5
			3–13–16	120	117.8

[a] In angstrom units. [b] In degrees.

This over-all approach should in theory be equally applicable to all reactions which generate trivalent species at benzylic sites. The extension to the formation of arylmethyl cations, eq 2, however, leads to certain fundamental problems. Several of these center about the identity of the exocyclic moiety. The presence of a $-CH_2X$ function rather than a methyl group should necessitate the use of different inductive and steric parameters in the ground state. The difference in inductive effect seems to be of only secondary importance as can be shown by a comparison of the calculated π energies of the arenes and their monomethyl derivatives. It may also be argued that the methyl group will be an adequate model for $-CH_2X$ if X is a monoatomic function such as halogen.[15] There exists in the literature a wealth of information on the solvolyses of arylmethyl halides.[21,22] Unfortunately,

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(21) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p 370.

(22) L. Verbit and E. Berliner, *J. Am. Chem. Soc.*, **86**, 3307 (1964).

Table V. Solvolysis of Arylmethyl Chlorides

Aryl group	Rel rate[a]	E_π[b] CBL	VBL	ΔE_σ CBL	VBL	ΔE_{total} CBL	VBL
Phenyl	1.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Naphthyl	2.36×10^1	−0.295	−0.305	0.028	0.002	−0.267	−0.303
2-Phenanthryl	2.44×10^1	−0.384	−0.433	0.000	0.030	−0.384	−0.403
2-Triphenylyl	3.22×10^1	−0.498	−0.535	0.000	0.008	−0.498	−0.527
3-Phenanthryl	1.39×10^2	−0.483	−0.471	0.000	0.004	−0.483	−0.467
1-Phenanthryl	2.62×10^2	−0.625	−0.522	0.176	0.107	−0.449	−0.415
1-Naphthyl	3.83×10^2	−0.520	−0.455	0.177	0.087	−0.343	−0.358
9-Phenanthryl	4.26×10^2	−0.644	−0.560	0.182	0.145	−0.462	−0.415
6-Chrysenyl	1.13×10^4	−0.886	−0.747	0.176	0.080	−0.720	−0.667

[a] Reference 23. [b] All energies given in electron volts.

Dewar and Sampson have shown that a pluralism of mechanism may exist for these reactions which runs from SN1 to SN2 in character depending upon reaction conditions.[23] The dependence of reaction rate on the nature of the aryl group should be most pronounced in the reaction in which a full unit of charge is generated at the exocyclic position. Those data were chosen, therefore, which showed such a large dependence.[23]

Table V presents the calculated energy changes for the solvolyses of a set of arylmethyl chlorides. Table VI offers a compilation of the relationships obtained for least-square correlations of the logs of the rates of relative reaction against the calculated energy differences.

Table VI. Data on Linear Correlations for Rates of Solvolysis of Arylmethyl Chlorides

System	Slope	Intercept	Av dev	Correl coeff
SCF-CBL	−4.374	−0.050	0.223	−0.970
SCF-VBL	−5.181	−0.188	0.286	−0.943
SCF-CBL with strain	−5.344	−0.034	0.313	−0.930
SCF-VBL with strain	−5.822	−0.168	0.374	−0.920

As may be observed, the correlations in Table VI are far less precise than those presented in Table III. This is probably due both to the assumptions made in this approach and the experimental uncertainties present. In regard to the latter, it was deemed necessary to omit the datum on the solvolysis rate of 2-triphenylmethyl chloride from all of the above correlations. Inclusion of σ strain energies led to a disconcerting lessening of reliability. It is possible that the steric requirements of the chlorine atom in the ground-state system must be introduced to provide a sound description of that molecule. It is also possible that in the highly polar medium in which this reaction was studied (a mixed solvent of 6.1% water, 54.1% formic acid, and 39.8% dioxane was employed) specific solvation of the ions may drastically affect reaction rates. No correlation utilizing VBL$_{\text{min}}$ was attempted. For the alternant systems considered in this study the VBL$_{\text{min}}$ values are almost identical with the VBL values. This may be seen in Table II. The added computational expense was, therefore, avoided.

The anions and cations derived from alternant systems differ in having a full and empty nonbonding orbital. Because of this the calculated geometries are the same, thus greatly simplifying the ease of correlation. The SCF π energy of the corresponding radicals can only be obtained by an open-shell calculation.[10] In such cases different geometries might be determined which would require the evaluation of new σ strain energies. Work is now in progress to study the relative rates of hydrogen abstraction from a series of arylmethanes.[24] Correlation is hoped for. This is expected as the steric strain requirements of the ground state can be accurately determined and differential solvation of the arylmethyl radicals formed should be of minimal importance.

Despite the indecisive results obtained for the arylmethyl cations, certain general conclusions can be drawn from this study. The effects of simple nonbonded interactions by themselves do not supply a sufficient explanation for the inability of HMO calculations to provide an adequate single correlation for the rates of formation of arylmethyl ions. In light of this it must be assumed that the use of the SCF method provides a more suitable approach to this type of problem. At the same time, inclusion of σ strain energy within this latter framework can sometimes lead to an improvement of results. This seems particularly true as regards nonalternant molecules where factors other than nonbonded interactions may play a pronounced role. It is possible that future theoretical approaches may be judged by their ability to treat this type of system without invoking exceptional factors.

Acknowledgments. Thanks are extended to the Computer Center of Oregon State University for generously supplying the facilities necessary for carrying out these calculations and to the General Research Fund of the Graduate School of Oregon State University for furnishing additionally needed funds to complete this project.

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(23) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946 (1957).

(24) J. D. Unruh and G. J. Gleicher, work in progress.