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SEMI-EMPIRICAL CALCULATIONS ON CARBINOL–CARBONIUM ION EQUILIBRIA

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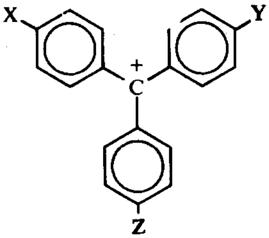
Abstract—Extended Hückel MO (EHMO) calculations have been carried out on the reactants and products in the ionization reaction of *meta*- and *para*-substituted aryl carbinols to the corresponding carbonium ions. The calculated energy differences between the carbinols and the corresponding carbonium ions have been compared with σ^+ values and the charge on the exocyclic C atom (c_7) for the benzyl ions, and with σ^+, σ and the experimental ΔG values for the triarylmethyl carbonium ions. The calculated charge on the exocyclic C atom has been found to give a good correlation with the experimental pK_R+ values. All simple protonation reactions are predicted to be exothermic, as in the gas phase, and are found to be almost independent of the substituents.

INTRODUCTION

THE triarylmethyl carbonium ions (I) are remarkably stable, being formed easily from the corresponding carbinols or chlorides.[1-5]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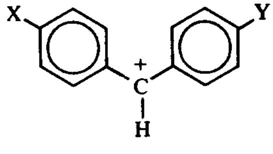
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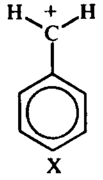

III

Studies on the parent ion (X = Y = Z = H), both in solution,[6] and as a crystalline salt[7,8] show it to be a symmetrical propeller shaped ion with a rotational angle, τ, of 31·8° (Fig. 1).

The triaryl carbinol–carbonium ion equilibrium shows a large dependence on the substituents X, Y and Z, and a series of carbinol indicators has been used to establish an acidity function.[1,3,4] The overall equilibrium is believed to involve the protonated alcohol as an unstable intermediate.[9,10]

$$R_3COH + H^{\oplus} \underset{}{\overset{1/K_1}{\rightleftharpoons}} R_3C - O^{\oplus}H_2 \overset{1/K_2}{\rightleftharpoons} R_3C^{\oplus} + H_2O$$

The pK_R+ values for the reverse of this equilibrium ($K_R+ = K_1K_2$), vary from

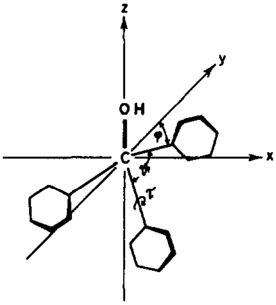


FIG. 1 Triphenyl carbinol in a cartesian coordinate system. Throughout the text ϑ, φ and τ are referred to as the bond angle, the out of plane angle and the rotational angle respectively. The carbonium ion has no hydroxyl group, $\varphi = 0°$ and $\vartheta = 120°$.

+9·36 for crystal violet ($X = Y = Z = N(CH_3)_2$)[11] to − 18·31 for 4,4′, 4″ trinitrotriphenyl carbinol,[4] the extremely wide variance usually being attributed to the ability of the substituents X, Y and Z to accommodate the positive charge through contributions from quinonoid structures.

The free energy change (ΔG_{298}) for the ionization reaction of the triaryl carbinols is proportional to the entropy change (ΔS_{298}) and hence to the enthalpy change (ΔH_{298}) for this reaction. Further, the gas phase ionizations of *m*- and *p*- substituted benzyl radicals give a good correlation with Brown's σ^+ values[12, 13] implying that the free energy contributions from solvation are also proportional to σ^+ and hence that the approximation ΔG (solution) is proportional to ΔH (gas phase) is valid.

Finally MO calculations produce estimates of ΔE_0 for gas phase reactions at 0°K. However, we have shown previously[14] that the approximation $\Delta H_{298} \simeq \Delta E_0$ is well within the limits of accuracy of even *ab initio* molecular orbital calculations. To summarise then, there are good reasons to expect a correlation between the ΔE_0 values calculated by molecular orbital theory and the experimental ΔG_{298} values for the ionization of carbinols in aqueous solutions.[15]

The UV spectra,[16, 17] charge distribution[18] and ionization equilibria[19, 20] of the benzyl and triphenylmethyl carbonium ions have been extensively studied using the Simple Hückel MO (SHMO) method. Hoffman has examined the charge distribution in the benzyl cation[21] using the Extended Hückel MO (EHMO) method and has also recently reported results on the triphenylmethyl carbonium ion.[22] The EHMO method has the reputation of being unreliable for the comparison of charged and uncharged species[21, 23] and in the present study we further examine the validity of this procedure by comparing the mono positively charged carbonium ions with the corresponding neutral carbinols, using a wide variety of para substituents.

COMPUTATIONAL DETAILS

A modified version of Hoffman's EHMO program[24] was used on an IBM 7094-II computer. The Slater orbital exponents[25, 26] and the ionization potentials used for the H_{ii} values are given in Table I. The off-diagonal elements (H_{ij}) were evaluated using the Wolfsberg–Helmholtz formula[24, 27] $H_{ij} = 0·5K\,(H_{ii} + H_{jj})\,S_{ij}$, with $K = 1·75$.

Typical bond lengths and angles from the literature[28] were used for the neutral molecules. Also, since little data is available for charged species, the same geometries were retained as for the neutral species. This procedure seemed justified since (a) the total energies obtained from EHMO calculations are not very sensitive to small changes in bond length[24] and (b) any such error would be systematic and be unimportant in this *comparative* study. Also, EHMO calculations on benzyl alcohols were used to establish the most stable conformation for the —$N(CH_3)_2$, OCH_3, CH_2OH and $CH_2O^{\oplus}H_2$ groups as para substituents and these were used in all subsequent calculations on the diarylmethyl and triarylmethyl systems. The triarylmethyl carbonium ions were taken to be propeller shaped with a rotational angle of 30°[8] and the diarylmethyl ions were assumed to have the same rotational angle. The carbinols were all taken to have a tetrahedral exocyclic carbon atom and the phenyl rings of the triaryl compounds were assumed to be also in the propeller form, but with the C_1 and C_4 atoms, which are coplanar in the ion, now bent out of the plane by 19° 18′ corresponding to a tetrahedral arrangement ($\vartheta = 109°28,$) on the central carbon according to the equation

$$\cos 2\vartheta = \tfrac{1}{2}(3\sin^2\varphi - 1).$$

RESULTS AND DISCUSSIONS

1. *Conformational study on the parent carbonium ion*

The EHMO method is successful in predicting the most stable conformer for neutral hydrocarbons,[24] and in the present study was used to determine the rotational angle of the three parent carbonium ions (Fig. 2). The angle refers to rotation of the phenyl group about the bond from the exocyclic carbon atom to the benzene ring. All the phenyl rings of both the diphenylmethyl (II) and triphenylmethyl (I) ions were rotated simultaneously by the same amount, making a symmetrical propeller for the triphenylmethyl ion.[8]

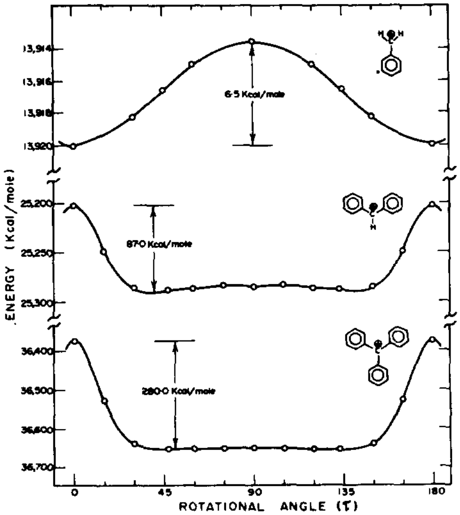


FIG. 2 Conformational studies on the unsubstituted carbonium ions. (Note the change in the vertical calibration for the three carbonium ions).

The benzyl ion (III) was found to be *planar* with a rotational barrier of 6·5 Kcal/mole. An experimental value for this barrier is not available in the literature, although Olah[29] has shown that benzyl ions substituted in the ortho positions have magnetically ono-equivalent hydrogens on the exocyclic C atom. The nmr signals from these hydrogens do not coalesce up to 0° (where decomposition becomes appreciable), indicating that the rotational barrier, at least in the ortho substituted benzyl carbonium ion, is larger than the 6·5 Kcal/mole estimated by the calculation.

Both the diphenylmethyl and triphenylmethyl ions are predicted to be non-planar, the release of steric interaction resulting in stabilisations of 87·0 and 280·0 Kcal/mole respectively. The calculated rotational angles, τ, are 30° for the diphenylmethyl ion and 48° for the triphenylmethyl ion, the latter being somewhat larger than the experimental value of 31·8° obtained from crystallographic studies on the perchlorate salt.[8] On increasing the rotational angle, τ, loss of conjugation results in small destablisations of the ions. However, this is very small (5·6 Kcal/mole for the diphenylmethyl ion, 2·1 Kcal/mole for the triphenylmethyl ion) compared with the large steric repulsions associated with lower values of ϑ. Consequently it may be concluded that the EHMO method overemphasises steric effects and that the calculated equilibrium out of plane angles are mainly determined by steric interactions between the *ortho* H atoms of the different phenyl groups. On this basis it appeared to be reasonable to use an out of plane angle of 30° (approximately the experimental value[8] of 31·8° ± 0·6) in the comparative study of the substituted diarylmethyl and triarylmethyl ions.

2. *Charge distribution in parent carbonium ions*

The benzyl carbonium ion, one of the simplest odd alternant hydrocarbons, has been the subject of many theoretical investigations. The EHMO method predicts a similar π-charge distribution to the SHMO method,[18] the ω technique,[18] and the Pople's SCF method.[30] The *ortho, para, exocyclic,* and the substituent-carrying C atoms are all positively charged (Fig. 3). However, unlike in many other methods of calculation the meta carbon is predicted to have a negative charge. This arises from the σ-framework, which is not included in the other treatments.

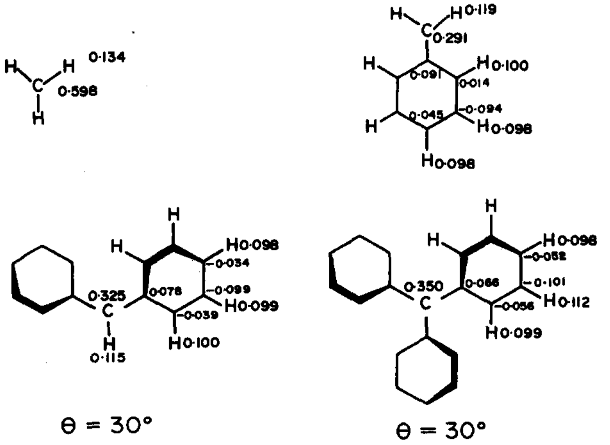


Fig. 3 Charge distributions in the unsubstituted carbonium ions.

The diphenylmethyl and triphenylmethyl ions have similar charge distributions to the benzyl ion, although all the positive charge is carried by the H atoms and the exocyclic and substituted C atoms. Twisting the phenyl groups out of the plane results in less overlap between the π systems of the phenyl groups and the $2p_z$ orbital of the exocyclic C atom, thereby isolating more positive charge on the exocyclic C atom.

3. *Diarylmethyl and triarylmethyl carbonium ions*

Introduction of electron donating substituents into one or more phenyl rings of both the diphenylmethyl and triphenylmethyl carbonium ions results in a lowering of the positive charge on the exocyclic C atoms. A plot of the electron density on the exocyclic C atom of the triarylmethyl ions against the experimental pK_{R+} values for the ionisation equilibria (Fig. 4) was linear ($r = 0{\cdot}972$). The less stable carbonium ions have larger charges on the exocyclic C atoms and are therefore more likely to undergo nucleophilic attack by water thereby reversing the equilibrium. The pK_{R+} values for the diphenyl carbinols and for 4,4′,4″ trifluoro triphenyl carbinol were not used in Fig. 4 since they had been evaluated using Deno's older acidity function.[11]

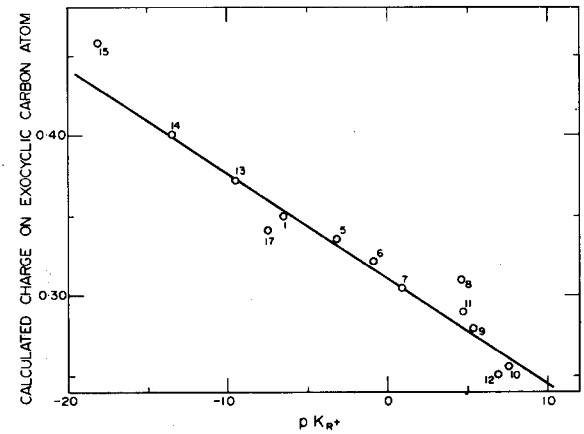


FIG. 4 Plot of the calculated charge on the exocyclic carbon atom of the triarylmethyl ions against the experimental pK_R^+ values. (The numbering system is given in Table 3).

The calculated energy differences, ΔE_0, between the products (Ar_3C^+ and $2H_2O$) and the reactants (ArCOH and H_3O^+) are given in Tables 2 and 3. These are all negative, predicting the products to be more stable than the reactants by more than 100 Kcal/mole. However, the triphenylmethyl ion is not expected to be heavily solvated and, assuming the only contribution from solvation is to stabilise the reactant hydronium ion by approximately 100 Kcal/mole,[31] then all the reactions except that for the trinitro compound are predicted to be exothermic by only a few Kcal/mole. Experimentally the ionisation reaction is slightly endothermic[4] except for the three nitro containing compounds. Points for these compounds deviate seriously from the experimental plot of ΔG_{298} against ΔS_{298} showing that entropy effects, probably caused by the anomalous behaviour of nitro compounds in strong acid solutions,[32] are mainly responsible for the low pK_{R+} values. This interaction between the nitro group and the solvent will add an additional enthalpy term which should be separated from the experimental ΔH°_{298} terms for other carbinol equilibria.

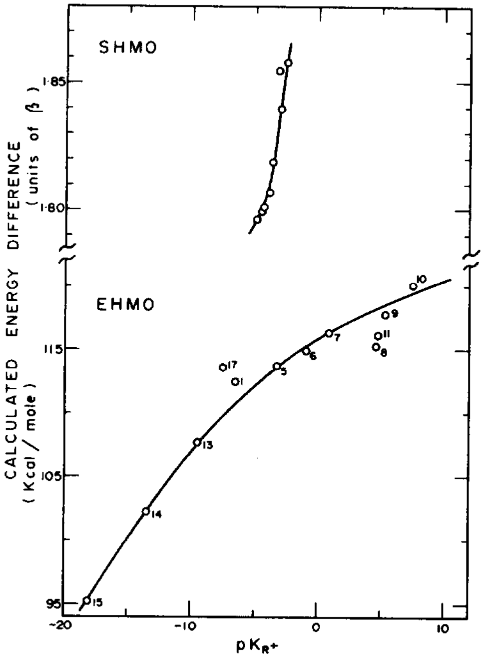


FIG. 5 Plots of the energy required to convert the triaryl ions into carbinols against the experimental pK_R^+ values for this reaction.
(a) SHMO results from Ref. 20.
(b) EHMO results from the present study.
(The numbering system refers to Table 3).

Previous authors[19, 20] have plotted the energy difference between the neutral hydrocarbon and the carbonium ion against the experimental free energy in an attempt to demonstrate that, for a set of compounds undergoing the same reaction, the free energy change is proportional to the change in resonance energy. Streitwieser,[20] using the SHMO method only on triphenylmethyl ions substituted with phenyl groups in the meta and para positions, obtained a slightly curved plot for the free energies of ionization of the triaryl chlorides. This data is reproduced along with EHMO results in Fig. 7. The slopes of both these plots are positive showing the ionization reaction to be most exothermic for the more basic compounds and the curves are relatively smooth showing that the calculated ΔE_0 is a function of the experimental ΔG_{298}. Both these observations are in agreement with experiment. More detailed comparison between the two sets of results is difficult since the SHMO data only cover a small pK_{R+} range and the curvature of the EHMO plot is partly caused by the nitro compounds which, due to their anomalous behaviour in sulphuric acid solutions, are not expected to give reliable results.

The experimental pK_{R+} data for the compounds used in this study do not correlate very well with either Hammett's σ values[33] ($r = 0{\cdot}973$) or Brown's σ^+ values[13] ($r = 0{\cdot}953$). This is partly due to a "saturation effect", the ρ value at large negative $\Sigma\sigma^+$ values being much smaller than when there are fewer substituents.[34] The calculated energy differences also correlate better with σ than with σ^+ ($r = 0{\cdot}932$ and

0·887 respectively), but the Hammet plot (Fig. 6) is slightly curved with the trihalogeno-triphenylmethyl compounds being the only ones to deviate seriously from the curve.

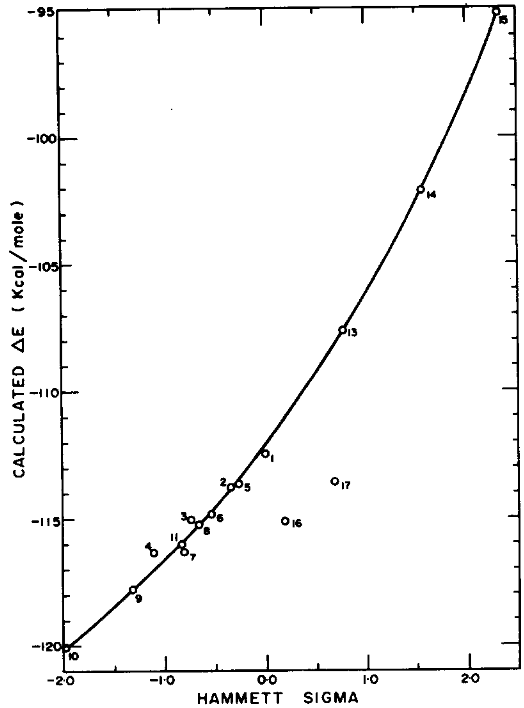


FIG. 6 Plot of the calculated $[E\,(R_3C^{\oplus} + 2H_2O) - E\,(R_3COH + H_3O^{\oplus})]$ against Hammett σ substituent constants for the triaryl carbinols. (The numbering system is given in Table 3).

4. *Mono substituted benzyl ions*

The rates of formation of the benzyl ions in the S_N1 solvolysis of benzyl chlorides has been used as a basis for a different set of substituent constants σ^+.[13] Gas phase results on the formation of benzyl carbonium ions,[12] and the proportionality of ΔH_{298} with ΔG_{298} for the ionization of triaryl carbinols,[4] indicate that there should be a correlation between σ^+ and the energy differences between substituted benzyl chloride molecules and the corresponding ions. The results of such a plot, using the carbinols instead of the benzyl chlorides, are given in Fig. 7. There is an appreciable amount of scatter (correlation coefficient, $r = 0{\cdot}926$), mainly caused by the halogen substituents again displaying their ability to stabilise the charge on the carbonium ion through their anomalously high π donation.

In these calculations the halogen atoms, usually considered to be overall electron withdrawing substituents, are predicted to be weak electron donors. Inclusion of d-orbitals for the chlorine and bromine atoms result in much larger charge donation from the filled p-orbital of the halogen atom and these orbitals were not considered in calculations on the larger ions.

Electron donating substituents in the *para* position of the benzyl ion result in a decrease in the total positive charge on the exocyclic carbon atom (C_7), the effect being

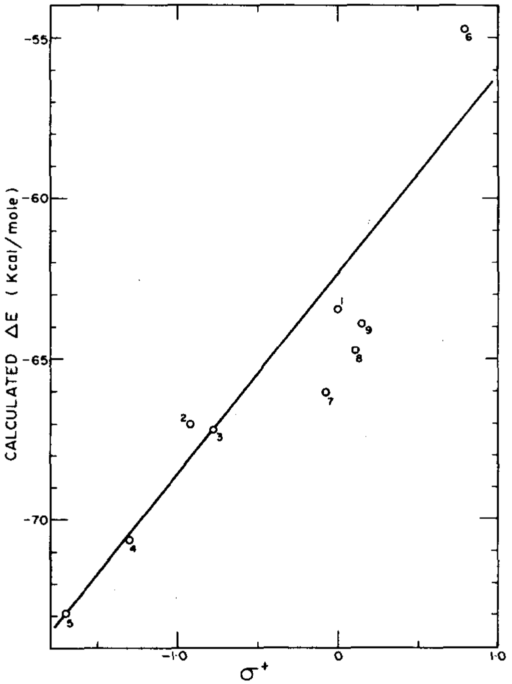


Fig. 7 Plot of the calculated [E ($RC^{\oplus}H_2 + 2H_2O$) − E ($RCH_2OH + H_3O^{\oplus}$)] against σ^+ substituents for the *para* substituted benzyl ions. (1 H; 2 OH; 3 OCH_3; 4 NH_2; 5 $N(CH_3)_2$; 6 NO_2; 7 F; 8 Cl (3s,3p orbitals only); 9 Br (4s,4p orbitals only).

more pronounced than in the triarylmethyl and diarylmethyl ions. This should stabilise the substituted benzyl carbonium ions relative to the parent ion, in accord with experiment.[12, 29]

The benzyl ions are only generated in very strongly acidic media and, unless they are polysubstituted, tend to decompose.[29] Consequently there are no experimental values for the free energy of the ionisation reaction. However, it has been shown that the electron density on the exocyclic C atom of the triphenylmethyl carbonium ion gives a good correlation with the experimental pK_{R+} values. This encouraged us to plot the charge on the exocyclic carbon atom against the calculated energy difference between the *para* substituted benzyl alcohols and their ions. The result was a smooth curve (Fig. 8) similar to those obtained both for the triphenyl carbinol-triphenylmethyl ion equilibria discussed above and by Streitwieser[20] in the correlation of π-energy differences with the experimental free energies for the ionisation of trityl chlorides. A detailed study on meta substituted ions are not undertaken due to the lack of experimental data on these ions.

5. *Alcohols and protonated alcohols*

Protonation of the carbinol is postulated to be the initial step in the formation of the carbonium ion.[9, 10] The protonation of *para* substituted benzyl alcohols was studied in detail using the same conformations for both the neutral and protonated alcohol groups as was found to be most stable in the unsubstituted molecule and conjugate acid. The charges on the oxygen atoms (δ_0) of the alcohols ($-1{\cdot}235 < \delta_0 < 1{\cdot}237$) and

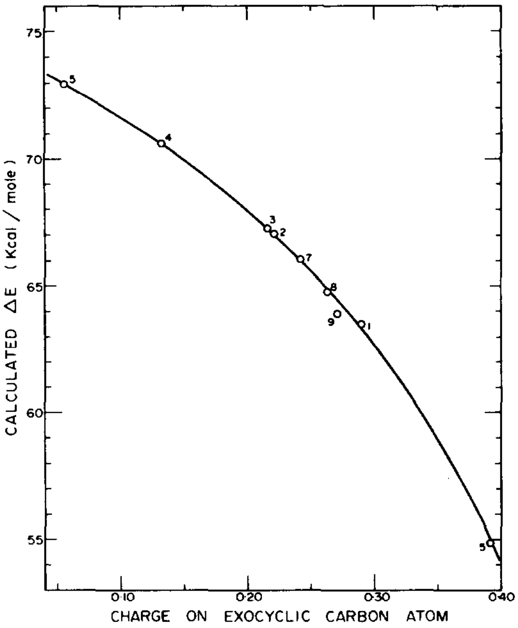


FIG. 8 Plot of the calculated $[E(\mathrm{RCH_2OH} + \mathrm{H_3O}^{\oplus}) - E(\mathrm{RCH_2^{\oplus}} + 2\mathrm{H_2O})]$ against the calculated charge density on the exocyclic carbon atom of para substituted benzyl ions. (The numbering system is given at the foot of Fig. 7).

the conjugate acids ($-0{\cdot}902 < \delta_0 < -0{\cdot}804$) were found to be almost independent of the substituents whilst those on the exocyclic carbon (δ_c) atoms ($0{\cdot}386 < \delta_c < 0{\cdot}405$ for the alcohol and $0{\cdot}363 < \delta_c < 0{\cdot}380$ for the conjugate acid) were much more invariant than in the corresponding benzyl (δ_{c+}) ions ($0{\cdot}056 < \delta_{c+} < 0{\cdot}392$).

The calculated proton affinity (ΔH_0 for the protonation reaction in the gas phase) was also found not to be strongly dependent on the substituent ($-72{\cdot}30 < \Delta H_0 < -67{\cdot}93$ Kcal/mole). These predicted proton affinities are much smaller than the experimental values for aliphatic alcohols (around 170 Kcal/mole).[35] The EHMO method predicts the proton affinities of water and methanol to be $-74{\cdot}0$ and $-77{\cdot}6$ Kcal/mole[23] compared with experimental values of -151[36] and -167 Kcal/mole, i.e. proton affinities are generally underestimated by approximately a factor of two.

All the protonation reactions are predicted to be exothermic, as expected for all gas phase processes. However, this is contrary to experimental observation for the reaction in solution and the difference is attributed to the effect of solvation on the protonation equilibrium.

$$\mathrm{ROH\ (solv)} + \mathrm{H_3O^{\oplus}(solv)} \rightleftharpoons \mathrm{H_2O\ (solv)} + \mathrm{RO^{\oplus}\,H_2\ (solv)}$$

The protonated water molecule is heavily solvated with a solvation energy of approximately 100 Kcal/mole.[31] The product, a protonated alcohol, has only two acidic hydrogens capable of hydrogen bonding with the solvent compared with the three of the hydronium ion and consequently will probably have a smaller solvation energy. Hence solvation will tend to make the protonation reaction in solution less exothermic than in the gas phase and possibly endothermic.

CONCLUSIONS

The results of the conformational studies on the carbonium ions agree with previous observations that the EHMO method overemphasises steric effects for hydrocarbons. However, the geometries predicted for the parent ions are in rough agreement with the limited experimental data[8] and chemical reasoning.[11] The calculations predict the energy from π-electron delocalisation to be much smaller than from the steric interactions between the ortho hydrogens of the aryl groups, and the latter are responsible for both the high rotational barrier and the predicted rotational angle being larger than the experimental value. Previous work on monosubstituted benzenes[37] and more detailed analysis of the benzyl results than presented in this paper have shown that the EHMO method predicts that the σ-inductive effect is not transmitted to the *para* position and only slightly to the *meta* position. Hence, in the absence of steric interactions, the calculations are essentially for the π-framework only. It may be concluded therefore, that, for *para* and *meta* substituents, EHMO calculations predict the order of relative importance to be steric effects $\gg$ resonance effects $>$ sigma-inductive effects.

The calculations predict the energy of the protonation reaction to be independent of substituents whilst the overall equilibrium is substituent dependent. Hence, according to the calculations, the position of the carbinol-carbonium ion equilibrium depends only on the second stage of the ionization, the loss of water from the conjugate acid.

$$R_3COH + H_3O^{\oplus} \rightleftharpoons R_3CO^{\oplus}H_2 + H_2O \rightleftharpoons R_3C^{\oplus} + 2H_2O$$

The good correlation between the experimental pK_{R+} value of the calculated positive charge on the central carbon (C_{19}) of the triarylmethyl carbonium ions coupled with the fact that the charge on the exocyclic carbon (C_7) of the protonated benzyl alcohols is independent of substituents, suggests that the second step in the equilibrium above is governed by the availability of the positive charge on the exocyclic carbon atom. Consequently, it may be concluded that the overall equilibrium, in the absence of any specific solvation effects, depends on the ability of the aryl rings to accommodate the positive charge, thereby stabilising the ion and preventing nucleophilic attack by water at the central C atom.

The experimental pK_{R+} values for the triarylmethyl ions do not correlate well with either the Hammett σ or Brown σ^+ substituent constants. Consequently, it is not surprising that the plots of the calculated energy differences against substituent constants show similar scatter, and even the plot for the benzyl ions (after omission of the unreliable halogen-containing compounds) against σ^+ is not linear. This, however, is to be expected since substituent constants are evaluated from equilibrium and rate data which include entropy terms and these are not necessarily proportional to the entropy changes in the ionization of carbinols. Further, the curves obtained when plotting the calculated ΔE_0 values against the experimental ΔG_{298} values, or against the charge on the exocyclic C atom, are similar to the results of Streitwieser's SHMO calculations[20] and only agree approximately with the experimental observation that the free-energy change is directly proportional to the enthalpy change for the ionization reaction.

The gas phase protonation of the alcohols is the only reaction not affected by solvation terms and, as has been reported previously,[23] the EHMO method estimates proton affinities to be about half the experimental value for alcohols. This could result from the use of incorrect ionization potential data for the atoms. The same H_{ii} values

TABLE 1. SLATER ORBITAL EXPONENTS AND IONIZATION POTENTIALS

Atom	A.O. type	Exponent	Coulomb Integral (eV)
H	1s	1·000[a]	−13·60[d]
C	2s	1·625[a]	−21·43[d]
	2p	1·625[a]	−11·42[d]
N	2s	1·950[a]	−27·50[d]
	2p	1·950[a]	−14·49[d]
O	2s	2·275[a]	−35·30[d]
	2p	2·275[a]	−17·76[d]
F	2s	2·600[a]	−39·00[e]
	2p	2·600[a]	−18·20[e]
Cl	3s	2·359[b]	−24·44[b]
	3p	2·039[b]	−13·26[b]
	3d	1·100[c]	−2·00[c]
Br	4s	2·638[b]	−26·40[g]
	4p	2·257[b]	−13·70[h]
	4d	1·200[c]	−2·50[c]

[a] Ref. 25

[b] E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).

[c] S. A. Houlden and I. G. Csizmadia, *Tetrahedron* (In press).

[d] Averaged from experimental data (from H. A. Skinner and H. O. Pritchard, *Chem. Rev.* **55**, 745 (1955)), and calculated data (C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* p. 122. W. A. Benjamin Inc., (1964).)

[e] L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.* **43**, S160 (1965).

[f] L. C. Cusachs, J. W. Reynolds and D. Barnard, *Ibid.* **44**, 835 (1966).

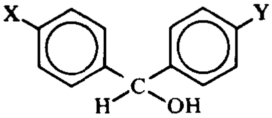
[g] A. Viste and H. Basch, tabulated in *Molecular Orbital Theory*, Ref. *d* above.

[h] H. A. Skinner and H. O. Pritchard, Ref. *d* above.

were used for the atoms in the EHMO calculations on both positively charged and neutral species, but intuitively the value for the former would be expected to be larger, thereby making the charged species more stable and increasing the proton affinity.

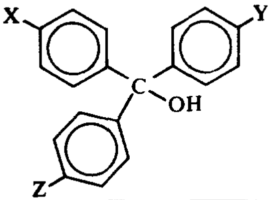
Finally, although comparisons between charged and neutral species are of limited value, confirming previous reports,[21] the good correlation between pK_{R+} and the charge on the exocyclic carbon atom of the triarylmethyl ions indicates that comparison of a mono-positively charged carbonium ion with others of like charge is a valid procedure.

TABLE 2. CHARGE DENSITIES AND ENERGY DIFFERENCES FOR PARA SUBSTITUTED DIARYLMETHYL CARBONIUM IONS.

Parent compound 	Charge on central carbon atom	Experimental pK_R^+
1. X = Y = H	+0·325	−8·30[a]
2. X = Y = NH_2	+0·210	—
3. X = Y = $N(CH_3)_2$	+0·159	+5·61[a]

[a] See Ref. 11.

TABLE 3. CALCULATED ENERGY DIFFERENCES FOR PARA SUBSTITUTED TRIARYLMETHYL CARBONIUM IONS.

	Calculated ΔE (Kcal/mole)	Calculated ΔH (Kcal/mole)	Experimental ΔH Kcal/mole)[a]
1. X = Y = Z = H	−112·44	−12·44	3·41
2. X = Y = H; Z = OH	−113·78	−13·78	—
3. X = H; Y = Z = OH	−115·06	−15·06	—
4. X = Y = Z = OH	−116·31	−16·31	—
5. X = Y = H; Z = O CH_3	−113·68	−13·68	6·48
6. X = H; Y = Z = O CH_3	−114·87	−14·87	5·68
7. X = Y = Z = O CH_3	−116·32	−16·32	2·49
8. X = Y = H; Z = NH_2	−115·28	−15·28	-
9. X = H; Y = Z = NH_2	−117·80	−17·80	—
10. X = Y = Z = NH_2	−120·05	−20·05	—
11. X = Y = H; Z = $N(CH_3)_2$	−116·04	−16·04	—
12. X = H; Y = Z = $N(CH_3)_2$	—	—	—
13. X = Y = H; Z = NO_2	−107·61	7·61	−0·87
14. X = H; Y = Z = NO_2	−102·15	−2·15	−6·06
15. X = Y = Z = NO_2	−95·18	+4·82	−16·80
16. X = Y = Z = F	−115·12	−15·12	—
17. X = Y = Z = Cl[b]	−113·60	−13·60	2·49

[a] See Reference 4.

[b] 3s and 3p orbitals only.

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