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A THEORETICAL STUDY OF THE ANOMALOUS SUBSTITUENT EFFECT OF THE HYDROXYL GROUP

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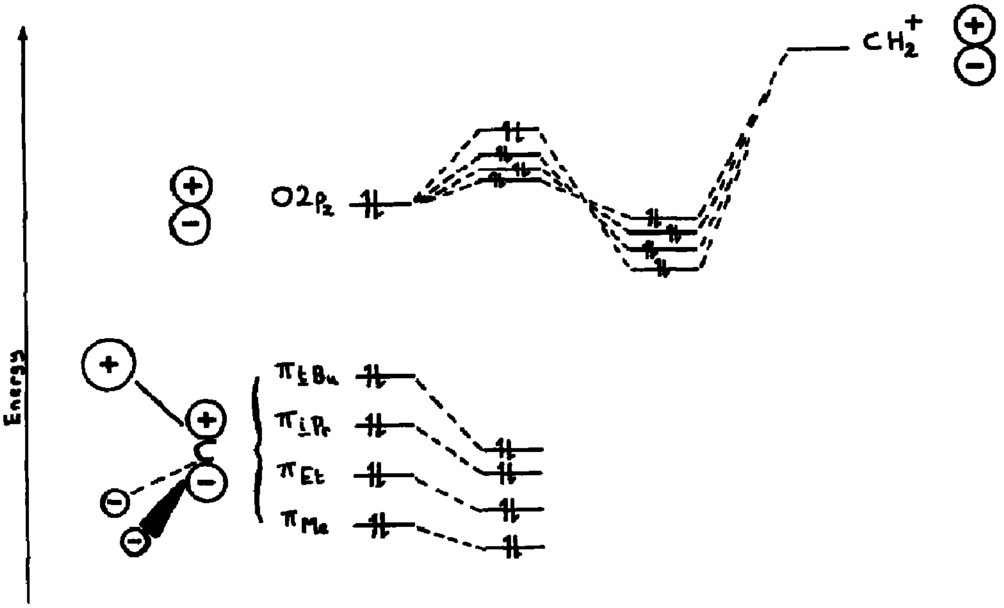
Abstract - A theoretical study by MINDO/3 and STO-3G SCF calculations has been used to examine the effect of a H-bonded water molecule on the ability of the hydroxyl group to stabilise a carbocation centre. Alkoxy groups are better stabilising groups in the gas phase, hydroxyl is more effective in protic solvents.

The ability of the hydroxyl group to stabilise a carbocation centre more effectively than methoxyl in protic solvents has been well documented; the effect is enhanced when direct conjugative interaction is possible, e.g. σ_p^+ (OH) = -0.92 [protic solvents], σ_p^+ (OMe) = -0.78 [protic solvents and gas phase][1]. This contrasts with the greater effectivenes of OMe in the gas phase where σ_p^+ (OH) has been estimated at ~ -0.5.[2]

Reaction of OH substituted carbocations through the presence of a fraction of the ionised O^- species may be excluded by the work of Eaborn[3] on the protonolysis of substituted phenyltrimethylisilanes in which the rate of the hydroxy substituted compound was unaffected by added perchloric acid.

The effect of substituents on the cations in the gas phase may be seen in Fig.I.

Fig.I - Interaction between orbitals of π symmetry for RO-$\overset{+}{C}H_2$



The interaction can be expressed by the perturbation expression[4]

$$E = E_{(OH)} + Hij^2/_{\Delta E}$$

Increasing homologation of the ether carbon raises the energy of the O $2p_z$ by a hyperconjugative interaction with alkyl group m.o.'s of π symmetry. Lowering of O $2p_z$ by interaction with alkyl π^* m.o.'s is unlikely owing to the high energy of the latter; however this 'negative' hyperconjugative interaction stabilises alkoxide ions[5].

Table I presents stabilisation energies for some substituted cations using MINDO/3 SCF calculations[6]. The geometries of all species were fully optimised. The results indicate a clear confirmation of the qualitative analysis presented above, where increasing homologation increases the stability of the cation.

TABLE I - MINDO/3 Stabilisation Energies

R^1	R	Stabilisation energy[a] (kcal/mol)	Appearance potential of cation[b] (ev)	π c–o bond order for cation	π c–o bond order for ether
H	H	0	22.37	-	-
H	OH	69.92[c]	19.63	0.802	0.235
H	OMe	83.18[d]	17.57	0.821	0.232
H	OEt	88.29	16.57	0.829	0.223
H	O*i*Pr	93.66	16.05	0.832	0.233
H	O*t*Bu	104.62	15.53	0.839	0.239
Me	OH-C_6H_4	106.65	13.35	0.460	0.308
Me	OMe-C_6H_4	109.34	12.98	0.486	0.313

a) Energy for the reaction
$R\overset{+}{C}(R^1)_2 + CH_4 \rightarrow R\,CH(R^1)_2 + CH_3^+$

b) by Koopman's theorem[7]

c) STO-3G value = 69.14 kcal/mol

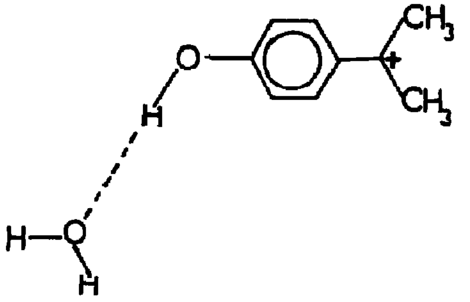
d) STO-3G value = 79.27 kcal/mol

There is a clear attenuation in the relative stabilising influence of OMe relative to OH in the cumyl case. The energy difference (2.69 kcal/mol) corresponding to a ρ value of ~ 7 assuming $[\sigma_p^+(OMe) - \sigma_p^+(OH)] \sim -0.28$ in the gas phase[2].

In order to assess the effect of solvation, calculations were performed using a STO-3G minimal basis set[8]; this method is known to give reliable estimates of hydrogen bond strengths in contrast to the deficiencies of MINDO/3 in this context[9].

The geometry chosen for the solvated hydroxyl cumyl cation is shown in Fig. II. The hydrogen bond distance was optimised, whilst the rest of the molecule retained the geometry obtained by MINDO/3 calculation.

Fig. II



It is assumed that the solvation of the cationic centre in the OH and OMe cumyl cases will be the same (any differences would further stabilise OH relative to OMe), the only difference being the extra solvent molecule in OH-cumyl. Table II presents STO-3G stabilisation energies for these systems.

TABLE II - STO-3G Stabilisation Energies[10]

R^1	R	Stabilisation[a] Energy (kcal/mol)	H-bond strength in cation (kcal/mol)	H-bond strength in ether (kcal/mol)
Me	$OH-C_6H_4$	108.39	-	-
Me	$OMe-C_6H_4$	110.59	-	-
Me	$H_2O...HO-C_6H_4$	120.21	19.88[b]	8.06[c]

a) defined as in Table I

b) H-bond length = 1.54 Å

c) H-bond length = 1.70 Å

Clearly the ability of OH to hydrogen bond more strongly on the cation than in the ether produces an enhanced stabilisation which makes OH a more effective stabilising group. Qualitatively this differental stabilisation in the OH-cumyl system may be traced to the more effective donation of electron density, in the cation, from the lone pair on the water molecule into the σ* orbital of the O-H group, with a concomitant increase in energy of O $2p_z$ and stabilisation of the cation centre cf. Fig. I.

Meaningful comparison of OH-cumyl with other alkoxy groups would be subject to difficulties arising from steric inhibition of solvation with the bulkier alkoxy groups, responsible for the Baker-Nathan order with alkyl substituents.[11]

The prediction of an extra solvent molecule in the OH-cumyl system is amenable to experimental investigation by means of the proton inventory method[12]. Significantly the methoxyl group is found to be a better conjugating group in non-protic solvents, for which σ° (OMe) = -0.16 and σ° (OH) = -0.13 and more negative ^{13}C chemical shifts are observed for OMe substituted benzenes, when the cmr spectra are recorded in CCl_4 solution[13].

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