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AB INITIO CALCULATIONS OF THE ACIDITIES OF SOME ALCOHOLS AND HYDROCARBONS

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Pople and co-workers[1] have presented a basis set that is very useful for *ab initio* SCF calculations of organic molecules. This method consists of sets of linear combinations of Gaussian functions to simulate minimum basis sets of Slater type orbitals. We present here results of some calculations using Pople's method relating to the inductive effects of methyl groups on the gas phase acidities of some alcohols and hydrocarbons.

The absolute energy values resulting from this method are known to be poor, both because of the use of Gaussian functions and because a minimum basis set is used; nevertheless, a study of a series of first row hydrides by this method demonstrated that the calculated proton affinities give an excellent linear correlation to experimental values if both Slater exponents and molecular geometries of all species are optimized to minimum energy.[2] The derived structures after complete optimization had bond distances and bond angles that were generally within 1% of experimental values.

Alcohols. Complete optimization of Slater exponents and molecular geometries of water, hydroxide ion, methanol and methoxide ion was accomplished at the STO-3G level. The derived structures of methanol and water differed from the average experimental values by no more than .005 Å and 0.7°. Use was made of these results in a partial optimization of ethanol and ethoxide ion.

Table I lists the energies and proton affinities of these hydroxy compounds.

Table I. Proton Affinities of Hydroxy Compounds[a]

Compound	-E (Hartrees) alcohol parameters	-E (Hartrees) alkoxide parameters	Proton Affinity (Kcal/mole) alcohol parameters	Proton Affinity (Kcal/mole) alkoxide parameters
Water	74.96910	---	---	---
Hydroxide	74.06553	74.15573	567.2	510.6
Methanol	113.55281	---	---	---
Methoxide	112.72146	112.76245	521.9	496.2
Ethanol	152.14130	---	---	---
Ethoxide	151.29684	151.35383	530.1	494.3

[a] Total energies are at the STO-3G level with the 2s and 2p ξ values optimized separately.

Two sets of energies are listed for the anions. In one series the exponents and geometry of the anion were those of the parent hydroxy compound; in the second set the anions were separately optimized. In both series hydroxide ion has a greater proton affinity than methoxide ion in agreement with gas phase experimental results[3] and related *ab initio* SCF calculations using assumed standard exponents and geometries.[4] However, the two series give a different order for the acidity of methanol and ethanol. The fully optimized calculations give the result that ethanol is more acidic than methanol in agreement with the gas phase experimental results and carries the trend that methyl groups are effectively electron-attracting in alkoxide anions; the calculated difference is so small as to inspire little confidence in the generalization of this conclusion to larger systems.

Alkanes. This approach was extended to methane and ethane and their anions. Calculations were made both with the use of standard geometries[5] and standard Slater ξ values as proposed by Pople[1] and for the fully optimized systems. The optimized molecular geometries of the hydrocarbons again showed excellent agreement with experiment. This optimization resulted in pyramidal carbanions. Total energies and the corresponding proton affinities for the

standard and optimized series are given in Table II. These results show clearly

Table II. Proton Affinities of Hydrocarbons[a]

	-E (Hartrees)		Proton Affinity (Kcal/mole)	
Compound	Standard	Optimized	Standard	Optimized
CH_4	40.00739	40.01213	---	---
CH_3^-	39.10784	39.21230	562.2	499.9
C_2H_6	78.86222	78.87077	---	---
$C_2H_5^-$	77.97977	78.06765	554.7	502.0

[a] Total energies are at the STO-4G level with the 2s and 2p ξ values constrained to be equal.

that the predicted effect of a methyl group is sensitive to the degree of optimization; with assumed "standard" values we determine that methyl groups are effectively electron-withdrawing whereas the optimized parameters produce an electron-donating role for the methyl group although the calculated difference again is rather small. This reversal of the effect of a methyl group upon optimization parallels that reported above for the ethanol-methanol series. Our results with the optimized alkoxide anion and carbanion calculations yield different results for the effective inductive effect of a methyl group. Although the direction of the calculated inductive effect is variable its magnitude is small in these SCF calculations. We note that in this SCF method, electron correlation is neglected; such electron correlation is a form of polarization and could well have important significance in ions in the gas phase. Such correlation provides an effective mechanism for electron-attraction by methyl groups in anions that is not accessible to calculations by Hartree-Fock SCF methods.

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