Ab Initio Molecular Orbital Calculations on Anions. Determination of Gas Phase Acidities

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Summary Relative acidities deduced from *ab initio* molecular orbital calculations are found to be in reasonable agreement with experimental gas-phase values.

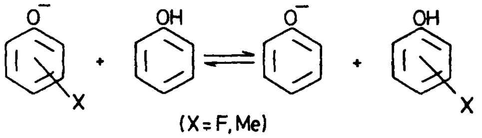
Ab initio MOLECULAR ORBITAL THEORY has been extensively and successfully applied to the calculation of heats of isodesmic reactions (*i.e.* bond type conserved) involving neutral and positively charged species.[1] We present results which suggest that the theory is equally successful for isodesmic reactions involving closed shell anions. Closed shell *ab initio* molecular orbital theory[2] has been used to examine isodesmic proton transfer reactions for four series of molecules (alkyl alcohols, alkylacetylenes, fluoro- and methyl-phenols, and xylenes) for which gas-phase data from ion cyclotron resonance (i.c.r.) studies have recently been reported.

The relative acidities of the molecules in question are conveniently described by the proton transfer reactions (1)—(4). Theoretical and experimental heats of reaction are summarized in Table 1.† The following points should be noted.

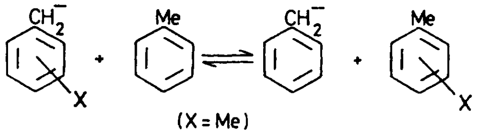
(i) The experimental[3] sequence of acidities of the alcohols ROH, R = Me < Et < Pr^i < Bu^t is reproduced theoretically. For R = Et, the theoretical proton transfer energy

$$RO^- + MeOH \rightleftharpoons MeO^- + ROH \qquad (1)$$
$$(R = Me, Et, Pr^i, Bu^t)$$

$$RCC^- + HCCH \rightleftharpoons HCC^- + RCCH \qquad (2)$$
$$(R = H, Me, Et, Pr^i, Bu^t)$$



(X = F, Me) (3)



(X = Me) (4)

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† Ideally, the experimental energies which are reported as ΔG^0_{298} values, should be converted into ΔH^0_0 values at 0 K with stationary nuclei before comparison with the theoretical results. In the absence of the data required to do this, no corrections have been applied.

(1·9 kcal mol^{-1}) agrees with a previous *ab initio* calculation[4] and with the experimental i.c.r. value.[3b] However, an attenuation of the effect of further methyl substitution is observed experimentally [3c] but is not provided theoretically.

TABLE. Theoretical and experimental heats (kcal mol^{-1}) of proton-transfer reactions.[a]

Reaction	Substituent	Theoretical	Experimental
(1)	Me	0	0[b]
	Et	+1·9	+1·9[b]
	Pr^{i}	+4·3	+3·1[b]
	Bu^{t}	+6·7	+3·8[b]
(2)	Me	−3·0	−3·1[b]
	Et	−2·3	
	Pr^{i}	−1·6	(−1·9)[b,c]
	Bu^{t}	−0·6	−1·2[b]
(3)	*o*-F	+2·7	+2·8[d]
	m-F	+5·0	+4·8[d]
	p-F	+1·7	+2·1[d]
	o-Me	+0·3	+0·3[d]
	m-Me	−0·6	−0·5[d]
	p-Me	−1·0	−1·2[d]
(4)	*o*-Me	(−0·9)[e]	
	m-Me	−0·5	
	p-Me	−1·4	(see text)

[a] Energies for neutral substituted benzenes required for heats of reactions (3) and (4) taken in part from W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496 and unpublished data. [b] From ref. 3c. [c] Experimental result for Pr^{n} rather than Pr^{i}. [d] From ref. 6. [e] This result may be influenced by steric distortion, not included in this standard model treatment.

(ii) For the acetylenes RCCH, i.c.r. measurements[3c,5] indicate an acidity sequence R = H > Bu^{t} > Pr^{n} > Me, *i.e.* methyl substitution decreases the acidity of acetylene but larger alkyl groups stabilize the acetylide anion (*i.e.* increase the acidity) when compared with smaller ones. It has been noted previously[5] that CNDO/2 calculations do not reproduce this sequence. On the other hand, the *ab initio* order, R = H > Bu^{t} > Pr^{i} > Et > Me is not only consistent with experiment, but there is also reasonable quantitative agreement.

(iii) For the fluoro- and methyl-substituted phenols, detailed quantitative experimental information has recently been reported.[6] The theoretical and experimental heats of proton transfer reactions (3) agree closely. Fluoro-substituents stabilize the phenoxide anion more than phenol because of the inductive effect although the extent of stabilization is somewhat reduced at the *ortho* and *para* positions through unfavourable mesomeric interaction. Methyl substitution in the *meta* and *para* positions is destabilizing. In the *ortho* position, there is a slight stabilizing effect probably due to the favourable interaction of the charge and dipole of C–O with the polarisable methyl group.

(iv) *p*-Xylene is less acidic than toluene.[5] CNDO/2 calculations do not reproduce this result[5] but *ab initio* calculations do; and this provides additional support for the suggestion[5] that a methyl group is generally destabilizing when attached to an unsaturated carbon in an anion.

The agreement between the calculations reported here and the results of experiment can be attributed in part to the nature of the reactions considered. Anions in general,[7] and heats of reactions involving anions in particular,[8] have not been extensively studied using single determinant M.O. theory. The inhibiting factor has been that the correlation error assumes special significance for anions and generally leads to a calculated energy for an anion which is greater than that of the corresponding radical with an electron at infinity. In the present study, an attempt has been made to circumvent this problem in two ways. First, a closed-shell self-consistent field procedure has been used so that a description of the anion in terms of a radical and separated electron, even though energetically favourable, is not possible. Additionally, calculations have been restricted to isodesmic reactions for which there is a reasonable prospect of cancellation of errors associated with electron correlation and with limitations in the basis set. Although a definitive assessment must await the results of further tests, the results reported in this communication are sufficiently encouraging to suggest that heats of isodesmic reactions involving closed shell anions may be reasonably described by single-determinant *ab initio* M.O. calculations, and further work to test the generality and limitations of this suggestion is in progress.

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[1] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4796; L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, 1972, **94**, 5935.

[2] Calculations were carried out using the Gaussian 70 system of programs, W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program No. 236, Q.C.P.E., University of Indiana, Bloomington, Ind., with the minimal STO-3G basis set and standard exponents, W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657. Geometries used were either standard J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253, or based on optimized geometries for model species and will be reported in the full paper.

[3] (a) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, 1970, **92**, 5986; D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 5153; (b) R. T. McIver, J. A. Scott, and J. M. Riveros, *J. Amer. Chem. Soc.*, 1973, **95**, 2706; (c) R. T. McIver, J. A. Scott, and J. H. Silvers, 'Twenty-First Annual Conference on Mass Spectrometry and Allied Topics,' San Francisco, California, May 1973, Abstract A2.

[4] P. H. Owens, R. A. Wolf and A. Streitwieser, *Tetrahedron Letters*, 1970, 3385.

[5] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, 1971, **93**, 4315.

[6] R. T. McIver and J. H. Silvers, *J. Amer. Chem. Soc.*, 1973, **95**, 8462.

[7] For a recent summary, see L. Radom and J. A. Pople, in M.T.P. International Review of Science (Theoretical Chemistry), ed. W. Byers Brown, Butterworths, London, 1972.

[8] See, for example, W. J. Hehre and J. A. Pople, *Tetrahedron Letters*, 1970, 2959.