References and Notes

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Does a Methyl Substituent Stabilize or Destabilize Anions?

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Abstract. Ab initio molecular orbital calculations show that whereas methanol is a stronger acid than water, propyne is a weaker acid than acetylene, and acetic acid is a weaker acid than formic acid, in agreement with gas-phase experimental data. A rationalization for this capability of a methyl substituent to sometimes stabilize and sometimes destabilize anions relative to their parent acids is provided within the framework of perturbation molecular orbital theory.

Introduction

Although the methyl-substituent effect is of fundamental importance in the understanding of organic reactions in general and substituent effects in particular, the subject remains poorly understood even today. Traditionally, a methyl group has been thought to be solely electron releasing, resulting in the stabilization of cations and the destabilization of anions.[2] This supposition was based in part on the increasing stabilities of successively methyl-substituted carbocations and the decreased acidities in solution of acetic acid compared with that of formic acid and methanol compared with that of water.

More recently, both experimental and theoretical studies have shown that the experimentally observed lower acidity of methanol compared to that of water is a solvent effect: in the gas phase the reverse order is found, i.e., methanol is *more* acidic than water.[3] This observation has been attributed to the ability of alkyl groups to both donate and accept electrons as the charge site demands, resulting in the stabilization of both positive and negative charge through a polarization-type process.[3]

However, there are glaring exceptions to this generalization. Notably, acetic acid has recently been found to be less acidic than formic acid[4] and propyne, a weaker acid than acetylene,[5] *even in the gas phase*. Clearly, in these two instances the methyl substituent appears to have a destabilizing effect on the corresponding anions highlighting the inadequacy of the present picture of the methyl-substituent effect. Surprisingly, these exceptions have gone relatively unnoticed and have not yet been satisfactorily explained.

In this paper, we utilize ab initio molecular orbital theory to provide a quantitative confirmation of these results and then present a qualitative rationalization within the framework of perturbation molecular orbital (PMO) theory. Our model enables a more general prediction of the effect of a methyl substituent on the stability of anions.

Method and Results

Standard ab initio molecular orbital calculations were carried out using a modified version of the Gaussian 70 system of programs[6] and the 4-31G basis set.[7] Subject to certain symmetry constraints, all structures were fully optimized at the 4-31G level using a gradient optimization procedure.[8] Theoretical geometries are compared with corresponding experimental parameters[9,10] in Table I while calculated total energies, including relevant previously reported values,[11-15] are shown in Table II. Theoretical and experimental heats of proton-transfer reactions are compared in Table III.

Discussion

Although the calculated structures are not of primary concern in this paper, we note several points. First, the 4-31G C≡C and C—C bond lengths for propyne are in substantially better agreement with experimental values (cf. Table I) than are previously reported[16] STO-3G lengths (1.170 and 1.484 Å, respectively). In a similar manner, the 4-31G values of the C—O and C=O lengths in formic acid show considerable improvement over the STO-3G results[17] (1.385 and 1.214 Å, respectively). For acetic acid, no complete experimental

Table I. 4-31G Optimized Structural Parameters[a]

| species	symmetry	parameter	4-31G	exptl
CH_3O^-	C_{3v}	C—O	1.361	
		C—H	1.122	
		∠HCO	115.7	
$CH_3C\equiv C^-$	C_{3v}	C≡C	1.232	
		C—C	1.464	
		C—H	1.093	
		∠HCC	112.8	
$HC\equiv C^-$	$C_{\infty v}$	C≡C	1.234	
		C—H	1.057	
$CH_3C\equiv CH$	C_{3v}	C≡C	1.190	1.206[b]
		C—C	1.459	1.459
		C—H	1.051	1.056
		C—H[c]	1.083	1.105
		∠HCC	110.9	110.3
HCOOH	C_s	C—O	1.342	1.343[d]
		C=O	1.200	1.202
		C—H	1.072	1.097
		O—H	0.956	0.972
		∠HCO[e]	110.5	111.0
		∠OCO	124.6	124.9
		∠HOC	114.9	106.3
CH_3COOH	C_s[f]	C—O	1.352	
		C=O	1.206	
		C—C	1.488	
		C—H	1.079	
		O—H	0.955	
		∠HCX	109.7	
		∠XCC	0.1	
		∠CCO[e]	111.8	
		∠OCO	121.8	
		∠HOC	113.8	

[a] Bond lengths in Å; bond angles in deg. [b] Reference 9. [c] Methyl C—H. [d] Reference 10. [e] Angle involving the C—O single bond. [f] In addition, the methyl group is taken to have local C_{3v} symmetry. X is a point on the C_3 axis so that ∠XCC is the *tilt* of the C—C bond from this axis (away from C=O).

structure is available. However, a point of interest for this system is that our 4-31G results suggest that methyl substitution in formic acid (yielding acetic acid) leads to a slight elongation of each of the C—O lengths.

Examination of Table III shows qualitative agreement with experimental heats of proton-transfer reactions although the magnitudes tend to be overestimated. In agreement with the gas-phase experimental data, the effect of the methyl substituent is to *increase* the acidity of water but to *decrease* the acidities of both acetylene and formic acid. In other words, relative to the corresponding neutral species, the methyl substituent *stabilizes* the hydroxide anion but *destabilizes* the formate and acetylide ions.

This behavior can be readily rationalized in terms of a simple PMO treatment of the interaction between a methyl group and the appropriate neutral or anionic moieties. The interaction diagrams are displayed in Figures 1-3.

We begin by noting that a methyl group may be considered to possess two pairs of degenerate orbitals exhibiting π symmetry. One pair (π_{Me}) is occupied and the other (π_{Me}^*) is
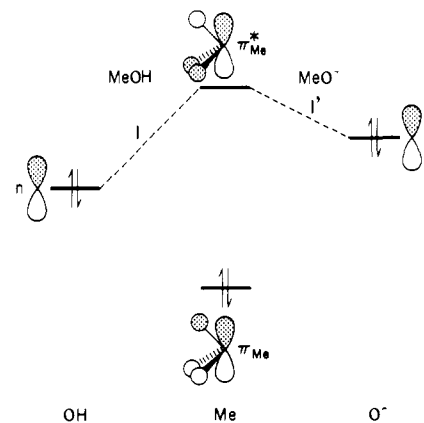
Figure 1. Energy diagram illustrating the interaction of π_{Me} and π_{Me}^* orbitals of methyl with a lone-pair orbital (n) of the OH and O$^-$ groups.

Table III. Theoretical (4-31G) and Experimental Heats (ΔE, kcal mol^{-1}) for Proton-Transfer Reactions

reaction	4-31G	exptl
$CH_3O^- + H_2O$ $\rightarrow OH^- + CH_3OH$	+16.2	+12.3[a]
$CH_3C\equiv C^- + HC\equiv CH$ $\rightarrow HC\equiv C^- + CH_3C\equiv CH$	−4.8	−3.1[b]
$CH_3COO^- + HCOOH$ $\rightarrow HCOO^- + CH_3COOH$	−4.9	−3.2[c]

[a] Reference 3c. [b] Reference 5b. [c] Reference 4.

unoccupied.[18] It is convenient in the interaction diagrams and the arguments that follow to consider just one member of each pair.[19]

For methanol and methoxide anion, the primary interaction (1, Figure 1) occurs between a filled lone-pair orbital (n) on oxygen and an unoccupied π_{Me}^* orbital of the methyl group resulting in a two-electron stabilizing effect. Deprotonation of OH (giving rise to O$^-$) leads to an increase in the energy of the n orbitals on oxygen and a decreased energy separation between the interacting orbitals n and π_{Me}^* and hence a greater stabilizing interaction (1′). Thus methyl is more effective in stabilizing the OH$^-$ anion compared with the neutral water molecule, and methanol is consequently more acidic (in the gas phase) than water.[20]

For propyne, the primary interaction (1, Figure 2) occurs between a filled π_{Me} orbital of the methyl group and an empty π_A^* orbital of the acetylene fragment. This picture corresponds, of course, to methyl acting as a π-electron donor and may be more conventionally (though less precisely) expressed in terms of the hyperconjugative interaction (I). There is also a secondary interaction between the filled π_A orbital of the triple bond and the empty π_{Me}^* orbital (2). However, this is less important due to the greater separation between π_A and π_{Me}^* than between π_{Me} and π_A^*.[21] Deprotonation to form the anion leads to an increase in the energy of the π_A and π_A^* levels in the C≡C$^-$ fragment and hence an increased separation

Table II. Calculated Total Energies (hartrees) for 4-31G Optimized Structures

species	energy	species	energy
CH_3O^-	−114.218 41[a]	$HC\equiv C^-$	−76.060 76
H_2O	−75.908 64[b]	$CH_3C\equiv CH$	−115.701 33
OH^-	−75.229 79[c]	CH_3COO^-	−226.888 76[c]
CH_3OH	−114.871 52[d]	HCOOH	−188.475 61
$CH_3C\equiv C^-$	−115.041 46	$HCOO^-$	−187.901 98[c]
$HC\equiv CH$	−76.711 41[e]	CH_3COOH	−227.470 24

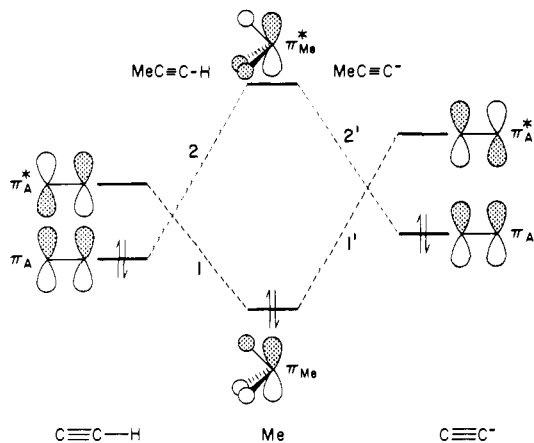[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 14. [e] Reference 15.

Figure 2. Energy diagram illustrating the interaction of π_{Me} and π_{Me}^* orbitals of methyl with π_A and π_A^* orbitals of C≡C—H and C≡C⁻.

Figure 3. Energy diagram illustrating the interaction of π_{Me} and π_{Me}^* orbitals of methyl with the π_1, π_2, and π_3 orbitals of COOH and COO⁻.

between π_{Me} and π_A^*. The stabilizing interaction $\pi_{Me}\cdots\pi_A^*$ (1′) is consequently reduced in the anion. Again, this corresponds to the reduced desirability of the hyperconjugative interaction (II) in the anion. By a similar argument, there is a
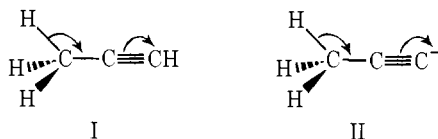
concomitant increase in the secondary interaction $\pi_A\cdots\pi_{Me}^*$ (2′), but because π_A^* is raised to a greater extent than π_A on deprotonation,[22] the net effect is dominated by a decreased $\pi_{Me}\cdots\pi_A^*$ interaction. The overall result is that methyl has a greater stabilizing interaction with the neutral acetylenic group than with the anionic acetylide function. Thus, methyl substitution *decreases* the acidity of acetylene.

The lower acidity of acetic compared with that of formic acid may be rationalized in similar terms (Figure 3). Here again, the primary interaction (1) occurs between a filled π_{Me} orbital and an unoccupied π^* orbital (π_3) of the COOH group. Deprotonation raises the energy of π_3, resulting in a decreased interaction (1′). Note that interaction 2′ is zero and 2 is near zero because of the symmetries of the orbitals π_{Me}^* and π_2.

The importance of symmetry considerations is reflected in the acidity predictions for the butenes. An interaction diagram similar to that of Figure 3 would predict that *less* acidic than the methyl protons of isobutene are those of propene.[23] In contrast, but-1-ene would be predicted to be *more* acidic than propene. Thus, whereas for methyl substitution at the 3-position in propene no significant interactions are expected between the methyl and neutral propenyl moieties, corresponding substitution in the allyl anion results in stabilization through 1′ and 2′. Since methyl substitution stabilizes the anion more than the neutral molecule, an increase in acidity is expected.

Similar arguments apply to the effect of methyl substitution on the acidity of acetaldehyde. Terminal substitution (yielding propionaldehyde) would be expected to lead to increased acidity. Central substitution (giving acetone) would be expected, on the other hand, to lead to decreased acidity. Experimental results are in agreement with these predictions.[24]

Conclusions

We note in conclusion that any attempt to provide too general a classification of the methyl substituent effect, even within such a restricted class of substrates such as anions, is doomed to failure. It is clear that a methyl substituent can either sta-
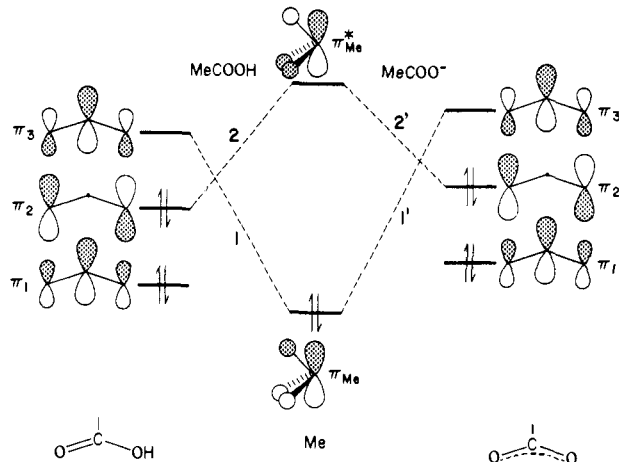
bilize or destabilize an anion relative to its parent acid. We recognize that the present treatment is simplistic in that we consider just one of perhaps several contributions affecting anion stabilities. For example, we do not discuss here the effect of four-electron destabilization terms. A more complete treatment including additional examples will be presented in due course. The arguments we have put forward nevertheless allow the following generalizations to be made: stabilization of an anion is likely to occur when the acid function has high-lying occupied orbitals which can interact effectively with the methyl-group orbitals; destabilization is likely to occur when the acid function has low-lying orbitals of appropriate symmetry.[25]

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fragments and just one of the π and π^* pairs in the C≡CH and C≡C⁻ fragments. This simplification in presentation does not, however, affect the rigor of our argument.

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(22) This result is readily demonstrated by a simple PMO argument.

(23) Experiments carried out in part to test this prediction have indeed confirmed the result: R. T. McIver, paper PHYS-093, 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978.

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Theoretical ab Initio SCF Investigation of the Photochemical Behavior of Three-Membered Rings. 1. Diazirine

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Abstract: Ab initio SCF CI methods (minimal basis STO-3G and limited CI) are used to calculate the potential energy surfaces of the ground and low-lying excited states of the diazirine–diazomethane system when various distorsions are simulated: (1) the continuous "out of plane" bending of linear diazomethane followed by its closure into diazirine; (2) the "in-plane" bending of linear diazomethane and the breaking of the N–C bond; (3) the elongation of the N–C linkage in linear or bent diazomethane and the concerted two-bond scission in diazirine.

In a previous paper[3] we have investigated the successive and concerted scissions of the pair of NH bonds in *cis*-diimide. This molecule is the simplest acyclic system which contains the –N=N– chromophore which, however, can also appear in cyclic species. Such is diazirine **3**. In the present study we will simulate theoretically the major processes occurring in the photochemistry of this three-membered ring[4] and related species such as linear[5] **1** or bent diazomethane **2** and **4**.

Substituted diazomethane and diazirine are known to cleave, whether thermally or photochemically, into a carbene fragment and a nitrogen molecule.[6] The intimate mechanism of this fragmentation remains somewhat obscure. On the other hand, substituted diazomethane and the primary products of diazirine decomposition exhibit 1,3-dipolar cycloadditions with various dipolarophiles.[7] It is therefore interesting to obtain some information pertaining to all these species and their interconversions.

The reactions we will consider are summarized in Figure 1. To facilitate their discussion we will choose linear diazomethane **1** as the starting point of our investigations.

The first distortion (path a) is the bending of diazomethane **1** which results in its closure into diazirine **3**, that is, the continuous decrease of the NNC angle from 180° (its value in linear diazomethane **1**) to 110° (in the corresponding bent form **2**) and finally to 64.8° (in diazirine **2**). The bisecting plane of the CH₂ group is the only symmetry element of the whole molecule conserved throughout this first process. Note here that the reverse process **3** → **2** should be qualitatively similar to the breaking of a single NH bond in *cis*-diimide, minor quantitative differences arising from the fact that (a) NC bonds (bond energy 78 kcal/mol) are now concerned instead of nh bonds (bond energy 92 ± 2 kcal/mol) and (b) a cyclic molecule is now considered which releases its ring strain energy (15–20 kcal/mol). Starting with species **1**, **2**, and **3** the elongation of the NC bond(s) will finally result in the complete breaking of the molecule into its constituent fragments: methylene and a nitrogen molecule (paths b, c, and d, respectively). Note again that, with similar quantitative restrictions, path d should be somewhat reminiscent of the concerted scis-

sion of *cis*-diimide into hydrogen and nitrogen molecules.

The second distortion is the in-plane bending of diazomethane (e) followed by the dissociation of the corresponding bent species **4** (path f). (This is now the plane of the CH₂ group which is the only symmetry element conserved during the bending.)

Methods of Calculations

From a technical point of view, the calculation of all these ground- and excited-state potential energy curves (PECs) requires two steps. The first is the familiar SCF part which will provide us with adequate MOs. This part was carried out with the usual GAUSS 70 series of program[8] in its STO-3G minimal basis version. Two different calculations were, however, done at each point. The first, using Roothaan's closed-shell formalism,[10] gives the best MOs in the reactant (closed-shell) regions of the reaction paths while the second, Nesbet brand[11] of open-shell treatments is more suited for regions where the dissociation of a bond is already well underway. Using these two approaches and their respective MO manifolds, we have then carried out the CI part of the treatment by allowing the mixing of all singly and doubly excited configurations obtained from the ground-state configuration by varying the population of the five highest occupied and the two (or three) low-lying empty MOs.[12] For each state, and at each point, Roothaan and Nesbet MOs give two different results. The lower in energy was conserved to draw the various PECs displayed in the figures. It will be obvious to the reader that this procedure is already more than adequate to obtain the qualitative features of these PECs. The quantitative information (activation energies) must be considered with care. They could be improved by (a) adding a diffuse basis set of atomic orbitals for the description of $n\pi^*$ singlet states (though these states do not play a prominent role in our analysis), (b) extending the scope of our CI step to include triply excited configurations, and (c) minimizing the molecular geometries at each point of a reaction path and for each state. Still the vertical excitation energies tabulated below agree fairly well with both experimental results[13] and SCF theoretical determinations[14] already published