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Theoretical Studies of the Oxy Anionic Substituent Effect[1]

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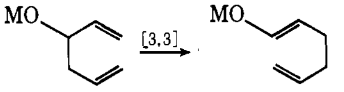
Abstract: Employing ab initio generalized valence bond and configuration interaction theoretical methods, we calculated C–H bond energies for H_3COH, H_3CONa, H_3COK, and H_3CO^- leading to bond energies (at 0 K) of 90.7 (the experimental value is 91.8 ± 1.2), 80.6, 79.0, and 74.2 kcal/mol, respectively. This dramatic decrease in the adjacent bond strength due to an oxy substituent helps explain the oxy anionic substituent effect in which very marked rate enhancements have been obtained.

Introduction

One of the fundamental pursuits in chemistry is the acquisition of greater insight into the processes of bond making and bond breaking. Questions dealing with mechanism and the interrelationship of structure and reactivity have been probed by both theory and experiment for a great body of chemical reactions. It is now well established that reaction rates may be strongly affected by structure; nonetheless, in many cases the effect of substituents on bond making and breaking is still poorly understood.

One of the most striking examples of a substituent-promoted rate acceleration for a sigmatropic rearrangement has recently been documented in these laboratories (eq 1).[3-5] For the general [3,3] sigmatropic rearrangement (1), numerous cases document the trend that a powerful rate acceleration (ca. 10^{12}–10^{17}) is attendant with a substituent change of M = H to M = K. Recent stereochemical studies indicate that there is *no* change in mechanism[5] so that a direct comparison of the two oxy substituents -OH and -OK is meaningful. In addition, recent related observations have been made on the acceleration of [1,3] sigmatropic rearrangements (cf. eq 2).[6]



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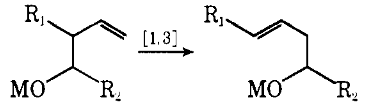

(2)

Two questions immediately arise: (1) What are the detailed electronic mechanisms of these particular sigmatropic rearrangements? (2) What is the general effect of various oxy substituents (-OH, -ONa, -OK, -O⁻) on neighboring center chemistry? In reaction 1 a carbon–carbon bond adjacent to the carbon–oxygen bond is (formally) broken. Thus, to answer the second question, one might determine the effects of oxy substituents (OM) on the strengths of adjacent bonds as in (3).

$$MOCH_2\text{-}R \rightarrow MO\text{-}\dot{C}H_2 + R\cdot \qquad (3)$$

Herein we report ab initio theoretical calculations of the carbon–hydrogen bond strengths for methanol, sodium methoxide, potassium methoxide, and the methoxide anion. The comparison among these bond energies provides part of the explanation of the substituent effect noticed, for example, in the oxy-Cope rearrangement (1).

Details of the Calculations

Basis Set. For all calculations we employed the Dunning[7] valence double ζ Gaussian basis set. This was supplemented with polarization functions on the carbon and oxygen atoms (d functions: $\alpha_{\text{carbon}} = 0.75$, $\alpha_{\text{oxygen}} = 0.85$) and on the hydrogen atom whose bond to carbon was to be broken (p functions: $\alpha = 1.00$). In order to describe the anionic oxygen center, sets of diffuse[8] s and p functions were added to the oxygen basis (except for methanol). Ab initio effective potentials[9] were used for the metal atoms.

SCF Calculations. To calculate the bond energies, we carried out generalized valence bond (GVB) calculations[10] on the closed-shell species, correlating each of the seven valence electron pairs. Two natural orbitals were included for each electron pair, except for the C–H bond being broken, for which additional correlation effects were included by allowing five natural orbitals to describe this electron pair. The resulting calculation is referred to as GVB (7/17), indicating that seven electronic pairs are described by 17 natural orbitals. For the radical, the corresponding level of calculation is GVB (6/12) in which the six valence pairs are described by 12 orbitals.

CI Calculations. The prime consideration in the configuration interaction (CI) calculations was to provide sufficiently balanced descriptions of both H_3COM and H_2COM as to yield a reliable C–H bond energy. Harding and Goddard[11] have shown that the minimal level of calculation leading to reliable bond energies for cases such as $D(H_3C\text{–}CH_3)$ can be obtained by first partitioning the electrons into an *active set* and an *inactive set* where the active set (the C–C pair in the ethane case) includes electrons that are affected directly by bond scission and where the inactive set (the C–H pairs in the ethane case) includes the electrons not directly affected by the scission (but which may be involved in correlations that do affect the bonding electrons). The electrons having been thus partitioned, a high level of correlation s allowed among the active electrons while a lower level of correlation is allowed within the inactive set.

As discussed below, breaking the C–H bond leads to a strong

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Table I.[a] Geometries for H_3COM and H_2COM

	r_{CO}, Å	θ_{COM}, deg	r_{OM}, Å	r_{CH}, Å	θ_{HCH}, deg
H_3COH[d]	1.427	105.9	0.956	1.096	109.2
H_3CONa	1.398[c]	180[c]	1.930[c]	(1.096)	(109.0)[b]
H_3COK	(1.398)	(180)	(2.26)	(1.096)	(109.0)[b]
H_3CO[e]	(1.398)			1.125[c]	(109.0)[b]
H_2COH[f]	1.386[c]	106.09[i]	0.955[i]	1.090[i]	128.63[i]
H_2CONa	1.359[c]	180[c]	1.930[c]	(1.090)	120.7[c]
H_2COK	(1.359)	(180)	(2.26)	(1.090)	(120.7)
H_2CO[e]	(1.359)			1.116[c]	(120.7)
H_2CO[g]	1.2099			1.1199	118
$H_2CO(n\pi^*)$[h]	1.3068			1.0961	118

[a] Values in parentheses were estimated by comparison with previous results. [b] The CH_3 group was assumed to have axial symmetry. [c] These values were calculationally optimized. [d] Reference 10. The hydroxyl proton is staggered with respect to the CH_3 group [e] The methoxide anion was modeled by H_3CO–Na and the radical anion by H_2CO–Na both with r_{Na} = 4.5 Å; see text. [f] The CH_2 group in H_2COH was canted some 5° away from the hydroxyl proton.[15] [g] The formaldehyde values are added for comparison.[17] [h] An average of the values for the singlet and triplet states.[17] [i] Adjusted by comparing the methanol and radical geometries of ref 14 with the experimental methanol geometry.

Table II. Calculated CH Bond Energies (kcal/mol) of CH_3–OM

	theory[a]			
	D_e	D_0[b]	expt D_0	change in D_0
H-CH_2OH	100.5	90.7	91.8 ± 1.2[c]	0
H-CH_2ONa	90.4	80.6		−10.1
H-CH_2OK	88.7	79.0		−11.7
HCH_2O^-	84.0	74.2		−16.5

[a] Except for H_2CONa calculations were for the planar radical. In H_2CONa we found a 0.7 kcal/mol decrease in the energy upon pyramidalization and this correction was applied to the other systems. [b] To estimate the effect of zero-point energy on the lowest energy we used experimental vibrational frequencies for methanol [S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **6**, 105 (1977)], and we estimated vibrational frequencies for the radical by comparison with the vibrational frequencies of formaldehyde (J. G. Grasselli, Ed., "Atlas of Structural Data and Physical Constants of Organic Compounds," CRC Press, Cleveland, Ohio, 1973). The same zero-point energy corrections were used for all cases. We assumed that the O–H vibrations in the radical were the same as in the alcohol. [c] From ref 13a, $D(H\text{–}CH_2OH) \approx D(H\text{–}CH_2OCH_3)$ and $D(H\text{–}CH_2OCH_3)$ = 93.2 ± 1.2 kcal at 298 K; using C_p from ref 13b then leads to $D_0(H\text{–}CH_2OCH_3)$ = 91.8 ± 1.2 kcal at 0 K.

interaction between the radical orbital and the π lone pair on the oxygen. Consequently, we considered the active set to contain the electrons in the CH bond being broken (the unpaired electron in the radical) and one oxygen lone pair (the pπ O pair in the radical). In the CI basis we included all 17 GVB orbitals for H_3COM. Within this basis we allowed all quadruple (and all lower order) excitations of the active electrons from the dominant configuration of the SCF. For the radical we included as the CI basis all 13 GVB orbitals plus an additional carbon pπ orbital.[12] To be consistent with the closed-shell calculations we allowed all triple (and all lower order) excitations of the active electrons from the two dominant configurations.

A test of the sufficiency of this calculational scheme is provided by the CH bond energy of CH_3OH. The experimental value[13] for 0 K is 91.8 ± 1.2 kcalmol (93.2 kcal/mol at 298 K) where the calculated value is 90.7 kcal/mol.

Results and Discussion

Geometries. The geometries calculated for the various species are listed in Table I. The experimental[14] gas-phase geometry of methanol was used in all of the methanol calculations. Pople et al.[15] carried out STO-3G Hartree-Fock calculations for the hydroxymethyl radical, H_2COH. We used this geometry as a starting point, making the following changes: (1) Comparing calculated[15] and experimental geometries for methanol, we adjusted the calculated[15] geometry of the radical. The pyramidalization of the CH_2 group in H_2COH should resemble that which is in the nπ states of H_2CO. In the latter case the optimum angle is ~30° out of the plane[17] but the decrease in energy from the planar configuration is only ~1 kcal.[17d] Consequently we assumed a planar geometry for the hydroxyl methyl radical. (2) We reoptimized the CO bond length, finding r_{CO} = 1.386 Å as compared with r_{CO} = 1.394 Å from ref 15. For the methoxides and corresponding radicals we completely reoptimized the geometries.

Some points to note follow.

(1) The C–O–H angle of methanol is 106°, but the methoxides (as well as the corresponding radicals) have linear C–O–M arrays. This change arises from the very large electron transfer from the alkali atom to the oxygen atom (0.83 electrons[16] transferred in H_3CONa).

(2) On going from methanol to sodium methoxide the C–O bond becomes 0.029 Å shorter. This decrease in the C–O bond as the O–M system becomes more ionic appears to be due to the delocalization of the (excess) electronic density back onto the "empty space" around the carbon atom (that is, anionic hyperconjugation). In the case of the corresponding radicals, the C–O bond shrinks some 0.027 Å, which can also be attributed to increased bonding in the three-electron π space of C–O (vide infra).

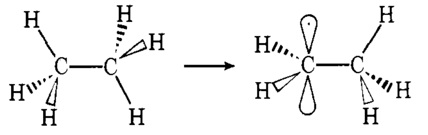
(3) We allowed the CH_2 group of H_2CONa to pyramidalize, finding an angle of 14° but a stabilization (with respect to planar) of only 0.7 kcal/mol. Thus, pyramidalization in this radical has little effect on $D(H\text{–}CH_2ONa)$. Analogous systems are the nπ states of formaldehyde which have the CH_2 group bent out of plane ($^3A_2$, θ = 43°;[17a] $^1A_2$, θ = 20.5[17b]). Here also the energy lowering due to bending is small (~1 kcal/mol).[17d]

(4) The C–H bonds become longer as the systems become more ionic, with an increase of 0.03 Å for the anions (H_3CO and H_2CO) over the hydroxy case.

(5) In the gas phase the extra electron of CH_2O^- is not bound,[18] which presents some problems in calculating the CH bond energy of CH_3O^-. To circumvent such difficulties we placed an Na at 4.5 Å from the O. In H_2CONa and H_3CONa this leads to less than 0.01 electrons[16] on the Na so that the H_2CO fragment is indeed anionic. Ths presence of the long-range $1/R$ potential due to the M^+ ion keeps the "anionic" electron bound.

CH Bond Energies. Our results for the C–H bond energies are reported in Table II.[19] The C–H bond is weakened by 10–12 kcal/mol on going from methanol to the alkali methoxides, and by 17 kcal/mol on going to the anion. (Recent thermochemical estimates[10] also predict a bond weakening in the anion of ~17 kcal/mol.)

In order to understand the origin of this effect, consider the C-H bonds of ethane (4), methanol (5), and sodium methoxide (6). The number of electron pairs on the center adjacent to the CH bond is the same in all of these cases. To a first-order approximation, orthogonality (induced by the Pauli principle) and electron-repulsion effects are the same in these cases. In the hydroxymethyl radical, though, the oxygen pπ lone pair overlaps the carbon radical orbital leading to a weak three-electron bond. This can be envisioned as a carbon-centered radical (5b) building in some zwitterionic character (1). This π bonding is worth ~6 kcal/mol so that $D(\mathrm{H{-}CH_2OH}) = 92$ kcal/mol while $D(\mathrm{H{-}CH_2CH_3}) = 98$ kcal/mol.[13]



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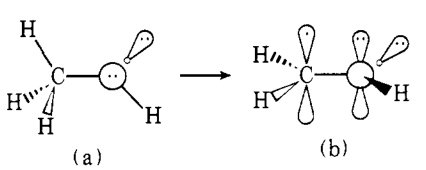

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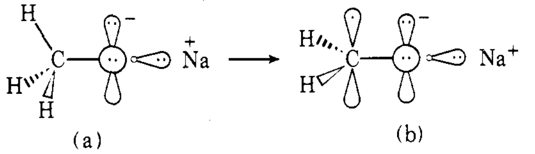

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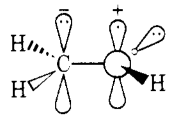

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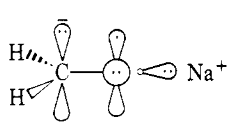
Now consider replacing the hydroxyl hydrogen atom with an alkali atom. The major effect of this is to increase the amount of charge transferred from M to the residual organic fragment (which in the case of $\mathrm{H_3CONa}$ reduces the population on the sodium atom to 0.17 electrons[16]). Because of this increased electronic population on the oxygen atom in $\mathrm{H_3CONa}$ and $\mathrm{H_2CONa}$, the oxygen pπ orbitals are destabilized (relative to those in $\mathrm{H_3COH}$ and $\mathrm{H_2COH}$). This is due to increased nuclear shielding by the oxygen σ electrons. As a result, there is an increased tendency for the oxygen pπ electrons to delocalize back onto the carbon. In the methoxide (6a) this delocalization tendency is thwarted by the presence of the three C-H bonds. However, in the radical, the delocalization of the O pπ electrons onto the carbon leads to greater contribution of the carbon-centered anionic configuration (2).



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That is, with an alkali atom present there is a strong admixture of **2**, leading to a stronger (~16-18 kcal/mol) three-electron π bond and thus a weaker C-H bond in $\mathrm{H_3CONa}$. In the case of the anion this effect is even more important owing to the complete charge transfer, and the CH bond in $\mathrm{H_3CO}$ correspondingly weaker.

Counterion Effect. It is observed experimentally that the rearrangement (1) is much faster with a potassium counterion than with sodium.[3] Our theoretical results show a weaker bond in $\mathrm{H_3COK}$ than in $\mathrm{H_3CONa}$. These facts may be rationalized as follows.

The tendency to transfer electrons from M to RO (in this case R = $\mathrm{CH_3}$ or $\dot{\mathrm{C}}\mathrm{H_2}$) is partially controlled by the energy of the ionic state ($\mathrm{RO^-\ M^+}$) relative to the covalent state (RO-M). An approximate formula for this energy difference is

$$\Delta E_{(6b)} = \mathrm{IP_M} - \mathrm{EA_{RO}} - \frac{332.1}{R_{\mathrm{OM}}} \qquad (7)$$

where $\mathrm{IP_M}$ = ionization potential of M, $\mathrm{EA_{RO}}$ = electron affinity of RO, and R_{OM} = oxygen-M internuclear distance. The conversion factor 332.1 allows energies to be in kcal/mol when R is in Å.

We must also consider the energy contribution of configurations such as **2**. The corresponding approximate energy formula is

$$\Delta E_2 = \mathrm{IP_M} - \mathrm{EA_C} - \frac{332.1}{R_{\mathrm{CM}}\ (\text{Å})} \qquad (8)$$

(with variables defined as above). The tendency to form a three-electron π bond is described (in this very approximate scheme) by the difference between (7) and (8). Thus, given a comparable amount of charge transfer from M, a larger cation (M) will lead to a greater incorporation of configuration similar to **2**. The more important this configuration, the stronger the three-electron bond and the weaker the corresponding CH bond, which is the observed tendency.

This argument is taken to its limit in the case of the methoxide anion. The absence of an alkali (or other positive) center frees the oxygen-centered electrons to delocalize further, making the C-H bond weaker still.

Summary

We have calculated the C-H bond strengths in several oxy-substituted methanes and find a sizable bond-weakening effect due to these substituents. This is expected to manifest itself in the chemistry of oxy-substituted substrates. It should be emphasized that the chemical effects of polar substituents are quite general, and our results may be applied to many chemical systems.

Reference and Notes

(1) This work was supported in part by a grant (DMR74-04965) from the National Science Foundation and by research grant No. GM-23971 from the NIH, National Institute of General Medical Sciences.

(2) National Science Foundation Undergraduate Research Participant, summer 1977.

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(12) In the SCF calculations on the $\mathrm{H_3COM}$ species the C-H bond to be broken was described by five natural orbitals. These natural orbitals were determined self-consistently in the calculation. For the $\mathrm{H_2COM}$ radicals, the radical electron is described by only one natural orbital. There being no "intrapair" correlation (since there is only one electron in this "pair"), no correlating natural orbitals can be self-consistently fixed to allow consistency with the closed-shell ($\mathrm{H_3COM}$) calculations; one extra orbital was added into the CI basis for the radical ($\mathrm{H_2COM}$). This orbital was a carbon pπ orbital which would account for the dominant (π in-out) dynamic correlation.

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Application of ab Initio Molecular Orbital Calculations to the Structural Moieties of Carbohydrates. 5.[1] The Geometry of the Hydrogen Bonds

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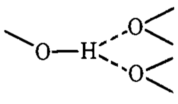
Abstract: Ab initio RHF/4-31G level molecular orbital calculations and Boltzmann factors are used to calculate the room temperature probability distribution of the O-H···O hydrogen-bond angle using a model consisting of two methanol molecules. The maximum in the distribution curve occurs at 163°. The data available from 18 neutron diffraction studies of carbohydrates yield a mean value of 166°. The energetics of symmetrical and asymmetrical bifurcated hydrogen bonds, which are not uncommon in carbohydrate crystal structures, were modeled with three water molecules. It is found that a symmetrical bifurcated hydrogen bond with typical geometry is more stable, relative to $3H_2O$, than an equilibrium linear bond, relative to $2H_2O$, by 1-2 kcal/mol. For a typical asymmetrical bifurcated geometry, the addition of a third water molecule to a "linear" bond with an O-H···O angle of 150° can lead to further stabilization of 1-4 kcal/mol, depending upon the geometry of the system.

I. Introduction

Simple monosaccharides are an excellent source of data for studying hydrogen bonding.[2] The molecules are approximately ellipsoidal and have an external surface which consists primarily of hydroxyl groups. Hydrogen bonding involving these groups can be expected to dominate the intermolecular cohesive forces, with other polar interactions and van der Waals forces playing only a secondary role. The molecules consist of singly bonded first-row elements and are therefore very suitable for modeling ab initio molecular orbital methods.[3] Although concentrated carbohydrate solutions are prone to form syrups, when nucleation is induced well-formed crystals of neutron diffraction quality and size can frequently be obtained. These crystals have relatively high melting points and the thermal motion of the molecules in the crystal lattice is relatively small and isotropic for molecular weights of less than 200 consisting of first-row elements only. These factors simplify the problems of obtaining the high-precision structural data relating to the hydrogen atoms necessary to understand the structure of the hydrogen bonds.

In this paper we consider from a theoretical point of view the factors which bear on the hydrogen-bond angle (∢OH···O) and compare our predictions with experimental data from single-crystal neutron diffraction analyses. We will address two questions: (1) What is the most probable O-H···O angle for a "linear" hydrogen bond? (We use the term "linear" in a general sense to refer to the simple open hydrogen-bonded structure, -O-H···O, and not simply to the limiting case when ∢OH···O = 180°.) (2) To what extent can departures from the most probable angle be facilitated by the involvement of an additional proton acceptor, in a configuration which we denote as a *bifurcated* hydrogen bond (i)? This is the standard usage of the term in the crystallographic literature.[4] Theoretical workers have tended to use "bifurcated" to denote a different double hydrogen-bond configuration;[5] i.e., the type ii. Since this is never observed in carbohydrate crystal structures, we shall not consider it in the present study.



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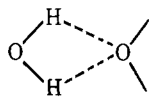

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A detailed comparison of theoretical and experimental aspects of hydrogen bonding based solely on neutron diffraction data is appropriate at the present time, since there have been four recent analyses[6-10] based primarily on X-ray diffraction results. In these X-ray data, the hydrogen positions are subject to large errors, usually in the direction of appearing closer to the covalently bound oxygen, by as much as 0.3 Å. In consequence, the O···O separations may be accurate to better than 0.005 Å, but the covalent O-H bond lengths and the hydrogen-bond H···O bond lengths can have errors as large as 0.3 Å and the O-H···O angles are subject to errors of ~5-10°.

There are now sufficient neutron diffraction crystal structure determinations of carbohydrates to permit an analysis of the geometry of the O-H···O bonds from data in which the hydrogen-atom positions are as accurately located as are those of the oxygen atoms. In general, all the bond lengths have standard deviations of 0.002-0.003 Å, and the angles of 0.3°. We shall defer discussion of the systematics which have

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