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Protonated Alcohols Are Examples of Complete Charge-Shift Bonds

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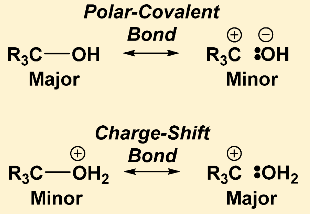
Supporting Information

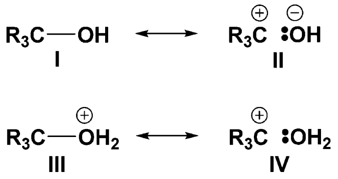
ABSTRACT: Accurate gas-phase and solution-phase valence bond calculations reveal that protonation of the hydroxyl group of aliphatic alcohols transforms the C−O bond from a principally covalent bond to a complete charge-shift bond with principally "no-bond" character. All bonding in this charge-shift bond is due to resonance between covalent and ionic structures, which is a different bonding mechanism from that of traditional covalent bonds. Until now, charge-shift bonds have been previously identified in inorganic compounds or in exotic organic compounds. This work showcases that charge-shift bonds can occur in common organic species.



INTRODUCTION

Alcohol C−O bonds are significantly altered by hydroxyl group protonation. For example, protonated alcohols (ROH_2^+) readily undergo substitution or elimination reactions via C−O bond heterolysis. Protonation also drastically increases the C−O homolytic bond dissociation energy (BDE), despite an increase in bond length.[1−4] Despite these significant reactivity and thermodynamic differences, textbooks portray the valence bond structure of ROH and ROH_2^+ species in a very similar way, with polar covalent C−O and O−H bonds.[5] The C−O bond of ROH species are considered to have a principal electron spin-paired (↑↓) covalent resonance structure **I** and a minor ionic structure **II** that accounts for the polar character (Scheme 1). The covalent bonding in **I** is due to spin-exchange resonance of the electron pair (i.e., C↑↓O ↔ C↓↑O), whereas the stabilization in **II** arises from the electrostatic interaction between the two charged fragments. Similar to that for neutral ROH species, there are two C−O bond resonance structures for ROH_2^+ species. In resonance structure **III**, which is usually assumed to be the principal resonance structure, the electrons have covalent pairing and the oxygen has a formal positive charge. In resonance structure **IV** the electron pair is localized on the oxygen atom and the carbon atom has a formal positive charge. Resonance structure **IV** is termed a "no-bond" resonance structure.

Scheme 1. C−O Valence Bond Structures for $R_3C{-}OH$ (I and II) and for $R_3C{-}OH_2^+$ (III and IV)



$$\underset{\textbf{I}}{R_3C{-}OH} \longleftrightarrow \underset{\textbf{II}}{\overset{\oplus}{R_3C}\ \overset{\ominus}{:OH}}$$

$$\underset{\textbf{III}}{R_3C{-}\overset{\oplus}{OH_2}} \longleftrightarrow \underset{\textbf{IV}}{\overset{\oplus}{R_3C}\ :OH_2}$$

Compared to neutral ROH alcohols, the dramatic change in reactivity, bond strength, and bond length of ROH_2^+ suggests the possibility that the C−O bond in protonated alcohols may be fundamentally different in nature. An early qualitative gas-phase valence bond analysis by Shaik also suggested that protonation of alcohols dramatically impacts resonance structure contributions.[6,7] Here we report high-level gas-phase and solution-phase valence bond calculations which demonstrate that protonation of the hydroxyl group of aliphatic alcohols changes the C−O bond from a polar covalent bond to a complete charge-shift bond where bonding is completely due to resonance between **III** and **IV**. This type of bonding mechanism is fundamentally different than classic covalent and ionic bonding.[8] Charge-shift bonds have been previously identified in inorganic compounds and in exotic organic compounds.[9] This work showcases that charge-shift bonds can occur in common organic species.

BRIEF GUIDE TO THEORY AND COMPUTATIONAL METHODOLOGY

All geometries were optimized with Gaussian 09[10] using the B3LYP/6-31G(d,p) density functional method and basis set. B3LYP/6-31G(d,p) geometries were selected because this level of theory predicts BDEs very similar to the G4 and CBS-QB3

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composite methods (see Supporting Information). Multistructure valence bond calculations with the 6-31G(d,p) basis set were performed using the XMVB[11] program interfaced with GAMESS.[12] The breathing orbital valence bond (BOVB) method of Hiberty was used because it provides accurate BDEs and resonance energies.[13]

A valence bond wave function (Ψ_{VB}) is calculated using a set of valence bond resonance structures (Φ) with localized bonding (eq 1). For example, the Ψ_{VB} for the C−O bond in alcohols comprises resonance structures Φ_I and Φ_{II} (Scheme 1). The electron pair in the C−O bond is considered "active" because the occupation differs between resonance structures **I** and **II**. Active electron pairs were described using strictly localized nonorthogonal orbitals. The inactive C−C, C−H, and O−H electron pairs were treated as pairs of delocalized doubly occupied molecular orbitals. Test calculations show that involving active O−H electrons did not significantly alter the valence bond wave function. In the BOVB method, the resonance structure coefficients (C_N, eq 1) and all the orbital coefficients are simultaneously optimized to minimize the total energy following the variational principle. Flexibility was provided for different sets of orbitals to be used to describe different resonance structures. This allows the orbitals for each resonance structure to optimize size and shape, which provides accurate treatment of electron correlation.

$$\Psi_{VB} = C_1\Phi_1 + C_2\Phi_2 + \ldots C_N\Phi_N \qquad (1)$$

The weights of the valence bond structures (W_K) was calculated using the optimized valence bond coefficients (C_K and C_L for resonance structures K and L) with the Coulson−Chirgwin formula shown in eq 2, where $\langle\Phi_K|\Phi_L\rangle$ is the overlap integral between resonance structures K and L.

$$W_K = C_K^2 + \sum_{L\neq K} C_K C_L \langle\Phi_K|\Phi_L\rangle \qquad (2)$$

RESULTS AND DISCUSSION

We decided to focus on *tert*-butyl alcohol (*t*-BuOH) and protonated *tert*-butyl alcohol (*t*-$BuOH_2^+$) because this represents a model for aliphatic alcohols used in acid-catalyzed dehydration, substitution, and other classic organic transformations. Inclusion of explicit solvent molecules can potentially alter the composition of the valence bond wave function;[14] therefore, along with gas-phase calculations, two models for water solvent were used. In the first solvent model, geometries were optimized in a polarized continuum (PCM) followed by valence bond calculations also using PCM. This level of theoretical treatment is referred to as "PCM". In the second solvent model, two water molecules were explicitly inserted with the alcohol, which is embedded into a PCM continuum to describe outer solvation shells. This level of theoretical treatment is referred to as "explicit".

The B3LYP geometries calculated in the gas phase, PCM, and explicit solvents are displayed in Figure 1. The solution-phase (PCM and microsolvated) geometries for *t*-BuOH are highly similar to the gas-phase geometry, and the C−O bond lengths differ by less than 0.01 Å. For *t*-$BuOH_2^+$, the gas phase C−O bond length is 1.69 Å and decreases in PCM solvent to 1.61 Å and further decreases to 1.51 Å when two water molecules are explicitly considered.

Accurate and quantitative valence bond theory provides direct insight into the nature of the chemical bonding from the structure weights that naturally arise from optimization of the valence bond wave function. Table 1 lists the contributions of resonance structures **I**/**II** and **III**/**IV** for the C−O bond of *t*-BuOH and *t*-$BuOH_2^+$ in the gas phase and water solvent. The valence bond structures with reverse charge polarization (e.g., $R_3C^-/^+OH$) were excluded from Table 1 because they have negligible contribution.

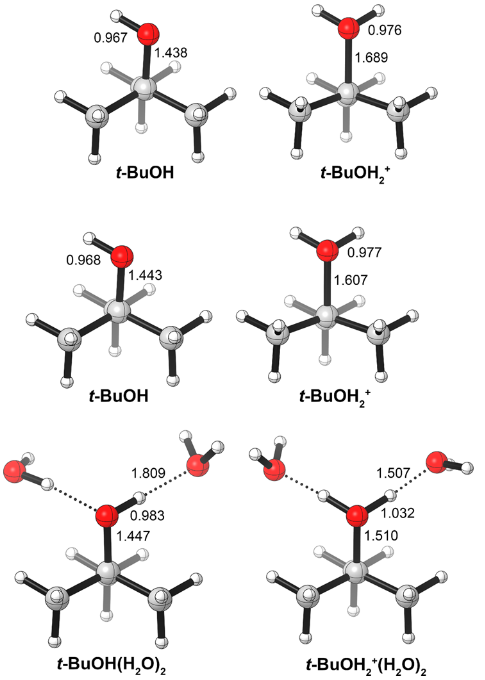

Figure 1. B3LYP/6-31G(d,p) geometries. Calculated bond lengths reported in angstroms. Top row: gas-phase geometries. Middle row: PCM geometries. Bottom row: explicit geometries.

Table 1. BOVB/6-31G(d,p) Weights (%) of Resonance Structures for R_3COH and $R_3COH_2^+$ (R = CH_3)

	gas phase	water (PCM)	water (explicit)
$R_3C\bullet\!-\!\bullet OH$ (**I**)	61.1	60.2	60.0
$R_3C^+{:}OH^-$ (**II**)	38.9	39.8	40.0
$R_3C\bullet\!-\!\bullet OH_2^+$ (**III**)	36.4	41.7	49.2
$R_3C^+{:}OH_2$ (**IV**)	63.6	58.3	50.8

In the gas phase, the C−O bond of *t*-BuOH is principally covalent with 61% contribution from resonance structure **I** to the total valence bond wave function. The polarity of the bond is manifested by a minor, but substantial, 39% contribution from the ionic resonance structure **II**. In contrast, valence bond calculations reveal that the C−O bond in *t*-$BuOH_2^+$ is fundamentally different from that in *t*-BuOH. Surprisingly, the respective weights of the covalent (**III**) and no-bond (**IV**) resonance structures are reversed in *t*-$BuOH_2^+$ compared with *t*-BuOH. In *t*-$BuOH_2^+$ the "no-bond" resonance structure **IV** is the major contributor with a 64% weight in the total valence bond wave function.[6] The covalent resonance structure is a minor contributor at 36%.

In a fashion similar to that for *t*-BuOH and *t*-$BuOH_2^+$, the resonance structure weights for methanol and protonated methanol were also calculated. These showed that alkyl group substitution on the carbon, from primary to tertiary, enhances by ~5% the contributions of ionic structure **II** to methanol and the no-bond structure **IV** to protonated methanol. This is expected based on the hyperconjugation stabilization of methyl groups, which increases the contribution of the no-bond resonance structures.

The weights of the resonance structures for the solvated molecules are also presented in Table 1. For *t*-BuOH, water solvation has essentially no impact on the relative contributions of resonance structures **I** and **II**. For *t*-$BuOH_2^+$, PCM calculations show a ~5% increase in resonance structure **III** and a corresponding ~5% decrease in resonance structure **IV**. This moderate change in resonance structure contributions is consistent with the slight shortening of the C−O bond length in PCM solvent compared to the gas phase. Similar to the gas-phase calculations, the "no-bond" resonance structure is the major contributor. For the explicit solvated *t*-$BuOH_2^+(H_2O)_2$, the two resonance structures have almost equal weights, with **IV** slightly larger. This is again consistent with the further decrease in C−O bond length.

This valence bond analysis suggests that protonation in the gas phase and solvent localizes the C−O bond pair of electrons on the oxygen atom due to the effective increase in oxygen electronegativity.[2,3] The C−O bond transforms from principally covalent in *t*-BuOH to principally "no bond" in *t*-$BuOH_2^+$.[6] The major contribution of the "no-bond" resonance structure in *t*-$BuOH_2^+$ explains the tendency for heterolysis of this bond in classic organic reactions and simultaneously explains the very large homolytic BDE.[2,3] Our valence bond calculations show that as the C−O bond dissociates in a polar solvent there is a smooth change from the already major "no-bond" contribution of the wave function to 100% contribution from structure **IV** at the dissociation limit of the bond. Additionally, this quantitative valence bond assignment of resonance structure contributions is in accord with the larger amount of positive charge placed on the alkyl fragment rather than on the more electronegative OH_2 group.

The localized description of bonding in valence bond theory allows for the separate calculation of a single resonance structure and therefore accurate quantification of resonance energies.[15] This has led to the discovery of a third class of chemical bonds called charge-shift bonds, which are distinct from traditional covalent and ionic bonds.[9,16] In a charge-shift bond, resonance energy between covalent and ionic (or "no-bond") resonance structures constitutes the majority or all of the bonding energy. This type of bonding mechanism is fundamentally different from that of a classic covalent or polar-covalent bond that originates from the electron interchange between bonding atoms. It is also different from that of an ionic bond where classic electrostatic interactions dominate.

The covalent-ionic or charge-shift resonance energy (RE_{CS}, eq 3) is defined as the difference between the energy of the full multiresonance structure valence bond wave function (Ψ_{VB}) and the energy of the major valence bond resonance structure (Φ_{major}) calculated separately. This major valence bond structure has the lowest energy among all of the valence bond structures that constitute the full valence bond wave function.

$$RE_{CS} = E(\Phi_{major}) - E(\Psi_{VB}) \tag{3}$$

For *t*-BuOH, Ψ_{VB} is the optimized superposition of resonance structures **I** and **II**, and Φ_{major} is resonance structure **I** optimized separately. For *t*-$BuOH_2^+$, Ψ_{VB} is the optimized superposition of resonance structures **III** and **IV**, and Φ_{major} is resonance structure **IV** optimized separately. Table 2, column 1, reports the valence bond calculated bond dissociation energies, D_e. For *t*-BuOH, this involves separation of the C−O bond into geometry-relaxed radical fragments. For *t*-$BuOH_2^+$, this involves geometry-relaxed bond heterolysis. Table 2, column 2, reports the bond dissociation energies with consideration of only the major resonance structure (Φ_{major}), D_{major}. The total bond dissociation energy is the sum of D_{major} and RE_{CS} (Table 2, column 3, and eq 4). The last column in Table 2 reports the percentage of charge-shift resonance energy relative to the bond dissociation energy, which is defined by eq 5 and is used as a quantitative measure of the charge-shift character of a chemical bond.[13]

Table 2. BOVB/6-31G(d,p) Dissociation Energies (D_e, D_{major}) and Charge-Shift Resonance Energy (RE_{CS}) Reported in kcal/mol

	D_e	D_{major}	RE_{CS}	% RE_{CS}
t-BuOH				
gas phase	88.2	28.1	60.1	68
water (PCM)	86.7	26.2	60.5	70
water (explicit)	82.0	21.9	60.1	73
t-$BuOH_2^+$				
gas phase	34.5	−23.3	57.8	167
water (PCM)	32.6	−37.8	70.4	216
water (explicit)	31.4	−57.3	88.8	282

$$D_e = D_{major} + RE_{CS} \tag{4}$$

$$\%RE_{CS} = \frac{RE_{CS}}{D_e} \times 100 \tag{5}$$

For *t*-BuOH, the covalent resonance structure **I** provides ~20−30 kcal/mol (D_{major}) of the total 82−88 kcal/mol bond energy (D_e). This indicates that resonance structure **I** alone is able to provide a stable bond relative to radical fragments and that further resonance structures improve the quantitative description of the bond. The charge-shift resonance energy is the main contributor to the dissociation energy D_e, which is not unexpected for highly polar bonds between atoms involving an electronegative atom with nonbonding lone electron pairs.[13]

The calculated bond dissociation energies and RE_{CS} in Table 2 further reveals that C−O bonds in alcohols are fundamentally altered upon protonation. Not only does protonation of *t*-BuOH change the major resonance structure from covalent to "no-bond" (**IV**), more importantly, the major resonance structure alone is repulsive and unable to provide any bonding. This is indicated by the *negative* D_{major} values. This means that the C−O bond described by only the major "no-bond" resonance structure would lead to spontaneous dissociation into fragments. This is likely because the electron steric repulsion is larger than the carbocation−water dipole interaction that is dominant in resonance structure **IV**. Not only is the resonance structure **IV** repulsive, but the minor covalent structure **III** is even more repulsive. This means that neither resonance structure **III** nor resonance structure **IV** alone accounts for any bonding between the carbon and oxygen atoms in *t*-$BuOH_2^+$. As a result, the $\%RE_{CS}$ values are *larger than 100%*. In the gas phase the $\%RE_{CS}$ is 167% and increases to over 200% in solvent. The charge-shift resonance energies indicate that the C−O bond in *t*-$BuOH_2^+$ is an example of a complete charge-shift bond where resonance between covalent and "no-bond" resonance structures is the *only* source of bonding. This type of complete charge-shift bond has only been identified in very few cases such as the prototype case of F_2, HF, the inverted bond of propellane, and more recently, hypervalent compounds such as XeF_2, PF_5, SF_4, or ClF_3.[17−19] The discovery that the C−O bond in $t\text{-BuOH}_2^+$ is a complete charge-shift bond suggests that this type of bonding may occur in common organic molecules and reactive intermediates.

CONCLUSION AND BROADER MEANING OF CALCULATIONS

Accurate gas-phase and solution BOVB calculations have revealed that protonation of the hydroxyl group of alcohols transforms the C−O bond from a polar bond with principally covalent character to a complete charge-shift bond with principally "no-bond" character. This showcases the electrophilic power of the proton that induces a considerable effective increase in group electronegativity. Because the "no-bond" structure is the principal contribution to the molecular ground state, it also explains the relative ease of heterolysis of the C−O bond in classic organic reactions. More importantly, neither resonance structure **III** nor resonance structure **IV** can account by themselves for carbon−oxygen bonding in $t\text{-BuOH}_2^+$. These results indicate that the common textbook description of protonated alcohols by resonance structure **III** with extra polarity compared to nonprotonated alcohols is incomplete. Rather, the description that has emerged from this work is that of a charge-shift bond with a critical **III** ↔ **IV** resonance energy contribution to bonding.

ASSOCIATED CONTENT

Supporting Information

B3LYP BDEs and *xyz* coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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