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Effect of Hyperconjugation on Ionization Energies of Hydroxyalkyl Radicals

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On the basis of electronic structure calculations and molecular orbital analysis, we offer a physical explanation of the observed large decrease (0.9 eV) in ionization energies (IE) in going from hydroxymethyl to hydroxyethyl radical. The effect is attributed to hyperconjugative interactions between the σ_{CH} orbitals of the methyl group in hydroxyethyl, the singly occupied p orbital of carbon, and the lone pair p orbital of oxygen. Analyses of vertical and adiabatic IEs and hyperconjugation energies computed by the natural bond orbital (NBO) procedure reveal that the decrease is due to the destabilization of the singly occupied molecular orbital in hydroxyethyl radical as well as structural relaxation of the cation maximizing the hyperconjugative interactions. The stabilization is achieved due to the contraction of the CO and CC bonds, whereas large changes in torsional angles bear little effect on the total hyperconjugation energies and, consequently, IEs.

1. Introduction

Hydroxyalkyl radicals are important intermediates in combustion and atmospheric processes.[1,2] The most studied of these radicals are the hydroxymethyl and 1-hydroxyethyl radicals.[3−12] They are produced in reactions of the corresponding alcohols with atoms (F, Cl, O) and OH by abstracting a carbon-bound H atom and are the most stable structural isomers among the CH_3O and C_2H_5O species, which have been implicated as important reaction intermediates.

One of the notable characteristics of hydroxyalkyl radicals, as compared for example with the corresponding alcohols or the isomeric alkoxy radicals, is their low ionization energies (IEs). The adiabatic IEs of the hydroxymethyl and hydroxyethyl radicals are 7.56 and 6.64 eV, respectively,[13,14] while the corresponding values for methanol, ethanol, methoxy, and ethoxy radicals are 10.85, 10.41, 10.72, and 9.11 eV, respectively.[15−18] What is striking is not only the large reduction in ionization energy in going from the closed- to the open-shell compounds but also the large decrease (about 0.9 eV) in going from hydroxymethyl to the hydroxyethyl radical, which is much larger than the 0.4 eV difference between the corresponding alcohols.

The goal of the present work is to offer a physical explanation for this decrease in IE by using high-level electronic structure calculations and in particular by comparing the highest occupied, singly occupied, and lowest unoccupied molecular orbitals (HOMO, SOMO, and LUMO, respectively) of the radicals and the cations. Specifically, our analysis highlights the role of hyperconjugation in stabilizing the hydroxyethyl cation and destabilizing the radical, compared to hydroxymethyl.

Hyperconjugation is a concept used often in physical organic chemistry to describe conjugation effects that involve σ-bonds in addition to π-bonds. Both conjugation between double or triple bonds and hyperconjugation involve delocalization of charge density over several atoms or groups of atoms. This correspondence was recognized early on by Mulliken and others,[19,20] who considered the CH_3 group in a molecule as equivalent to one triple bond with respect to electron donation. Hyperconjugation is responsible, for example, for the stability of secondary and tertiary radicals and cations,[19] the changes in bond strengths[21] and conformations[20] upon substitutions, the vibrational spectra and structures of hydrocarbon radicals,[22,23] the trends in electronically excited states in alkylperoxy radicals,[24] and more. There is also a strong evidence that the torsional barrier in ethane is due to hyperconjugation[25−27] rather than steric repulsion, although this view on the primary cause for the staggered conformation is not uniformly accepted.[28,29]

With the advent of high-level electronic structure models, it is now possible to analyze the delocalization of electronic density in terms of electronic configuration and changes in nuclear geometry. Such insight can help understand trends in IEs and stability of ions in a homologous group. In general, a reduction in IE can originate from the stabilization of the cation and/or destabilization of the neutral, and electronic structure models can help analyze the contributions of different factors. In the case of the hydroxyethyl radical and its cation, we show below that both factors above contribute to the observed large decrease in IE in going from hydroxymethyl to hydroxyethyl.

Ab initio calculations of the geometry and energy of hydroxymethyl[30,31] and hydroxyethyl[10,32] radicals and cations have been published before, and our calculations (see Figure 1) agree with previous results within error bars of the theoretical methods employed. The CH_2OH radical has C_1 nuclear symmetry with strongly coupled OH torsional and CH_2 wagging motions.[31] In contrast, the cation has a planar C_s symmetry and can be viewed as protonated formaldehyde. The major change upon ionization is the reduction in the C−O bond length, which acquires π-bond character upon removal of an electron from the antibonding SOMO centered on the C−O bond. Thus, ionization creates a closed-shell cation that is quite stable. Similar behavior has been observed in the cations of halogenated methyl radicals.[33,34] Adding a methyl group does not change this situation qualitatively, although the shape of the HOMO, SOMO, and LUMO change due to admixture of σ_{CH}. The hydroxyethyl radical has an unpaired electron in an antibonding orbital and possesses C_1 symmetry, whereas the cation can be viewed as a protonated acetaldehyde having C_s symmetry. As in hydroxymethyl, the main effect of ionization is a large contraction of the C−O bond, which (in hydroxyethyl) is accompanied by a small contraction of the C−C bond. Both

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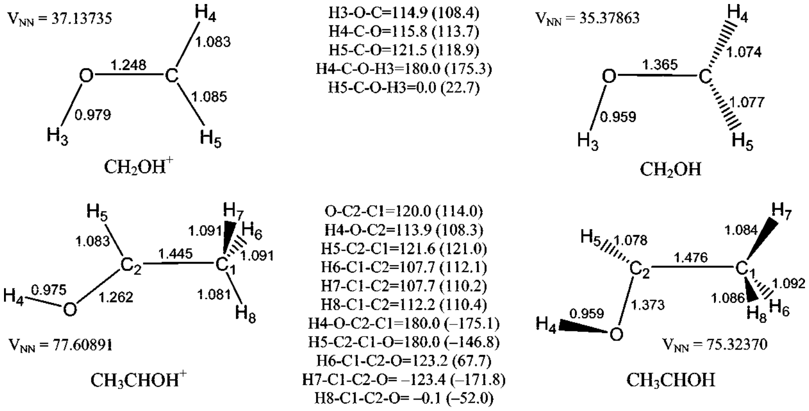

Figure 1. Equilibrium structures and nuclear repulsion energies (V_{NN}) of the CH_2OH and CH_3CHOH radicals and their cations optimized at the CCSD(T)/cc-pVTZ level of theory. Angles listed in parentheses correspond to the neutral radicals.

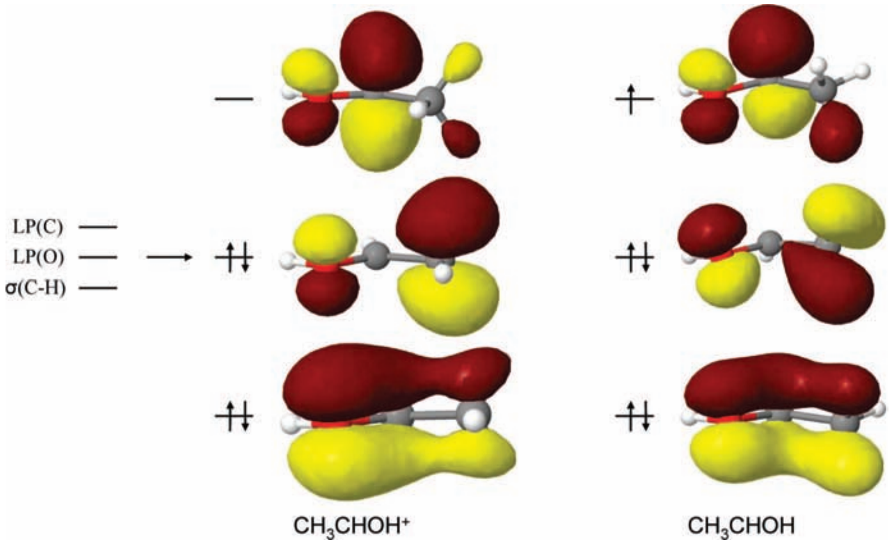

Figure 2. Three MOs resulting from hyperconjugation of σ_{CH}, LP(O), and LP(C) in CH_3CHOH at the cation and radical geometries. The bonding and nonbonding MOs are doubly occupied in both the cation and the neutral. The antibonding orbital is singly occupied in the radical and is unoccupied in the cation. At the neutral geometry (right), the shape of the orbitals is slightly different, but their character is preserved. For the sake of clarity, we refer to these three orbitals as SOMO, HOMO, and HOMO-1 of the radical, although energetically there are other MOs (which do not participate in hyperconjugation) in between the nonbonding and bonding MOs.

bonds acquire additional double-bond character upon removal of the unpaired electron.

In hydroxyethyl, the H atom in O−H prefers the anti position, as shown in Figure 1, although the gauche isomer is less than 1 kcal/mol higher in energy.[32] The orientation of the methyl hydrogens relative to the OCC plane changes upon ionization, with one of the methyl hydrogens in the cation being in the same plane as OCC, whereas none is in that plane in the neutral (Figure 1). Again, the anti isomer is only marginally more stable than the syn structure.[32] In agreement with the analysis of Hoffman et al.,[20] the barriers to internal rotation of the methyl group are less than 2 kcal/mol both in the neutral and in the cation. Thus, the minimum-energy positions of the methyl hydrogens are determined by subtle effects related to the removal of the unpaired electron and the concomitant skeletal rearrangement, in particular, the contraction of the O−C and C−C bonds.

Because of the presence of the OH group, the hyperconjugation in hydroxyethyl involves three rather than two interacting MOs, which is the case in the ethyl radical. The participating orbitals are the p-like orbitals on C and O and one σ_{CH} MO of the methyl group that has favorable overlap with the p-like orbitals. In molecular orbital language, these orbitals, which have the same symmetry, can interact, creating a new set of three allyl-like delocalized orbitals as shown in Figure 2. The bonding and antibonding character of these delocalized MOs and the extent to which they are filled are responsible for the low IE of 1-hydroxyalkyl radicals and for the stabilization/destabilization of the neutral and cation species relative to the case of no hyperconjugation interaction. The NBO analysis confirms this qualitative picture, and the computed hyperconjugation energies are in qualitative agreement with the estimates derived from a simple Hückel-like model. Our main conclusion is that hyperconjugation destabilizes the neutral hydroxyethyl radical due to the antibonding character of the SOMO (Figure 2), while stabilizing the cation by lowering the energies of the HOMO and HOMO-1 relative to hydroxymethyl. Additional stabilization is achieved owing to the more extensive charge delocalization in hydroxyethyl.

2. Computational Details

All geometries were optimized by the coupled-cluster method with single and double substitutions and perturbative account of triples [CCSD(T)][35,36] with the cc-pVTZ basis set[37] using the ACES II electronic structure package.[38] Optimized geometries are summarized in Figure 1. The optimized geometry of

TABLE 1: Computed Vertical and Adiabatic IEs (eV) of CH_3CHOH and CH_2OH

	vertical		adiabatic	
method	CH_2OH	CH_3CHOH	CH_2OH	CH_3CHOH
CCSD(T)/cc-pVTZ	7.897	7.292	7.285	6.516
RCCSD(T)/cc-pVTZ	7.865	7.260	7.282	6.532
Koopmans' theorem	9.198	8.724		
expt[a]	8.14	7.29	7.56	6.64

[a] References 13 and 14.

CH_3CHOH deviates by 0.1° from C_s symmetry. Unrestricted Hartree–Fock references were used in all radical calculations. The spin contamination was found to be small; e.g., $\langle S^2 \rangle$ equals 0.76 for both radicals at their equilibrium geometries. To account for possible effect of spin contamination, we also computed IEs using restricted open-shell reference and partially spin-adapted CCSD(T) method, R-CCSD(T).[39] R-CCSD(T) energies were calculated by MOLPRO[40] with the same basis set, at the CCSD(T) optimized geometries. All other calculations were performed with Q-CHEM,[41] again using the cc-pVTZ basis set, except for some of the NBO analyses, as noted below. R-CCSD(T) energies were computed with frozen core. In all other calculations, all electrons were correlated.

Vertical IEs were calculated as the difference between the total energies of the cation and the neutral radical at the equilibrium geometry of the latter, at CCSD(T) and R-CCSD(T) levels. Adiabatic IEs were computed as the total energy differences at the CCSD(T)/cc-pVTZ optimized geometries. The calculated IEs are summarized in Table 1. Table 1 also lists Koopmans IEs computed as the absolute value of the energy of the UHF SOMO of the neutral radical. Although less accurate, these values are directly related to the orbital energies and are therefore useful for the interpretation.

The NBO[42] calculations were performed using the CCSD density computed by analytic gradients and properties code.[43] The effect of rotation of the CH_3 group on the magnitude of hyperconjugative interactions in CH_3CHOH was examined using the 6-31G(d) basis set, assuming a rigid molecular structure (i.e., no geometrical relaxation of any coordinate was allowed upon rotation) using parameters from Figure 1. All the other NBO calculations employed the cc-pVTZ basis set.

3. Results and Discussion

In the discussion below, we analyze the results of electronic structure calculations of the radicals and cations in a molecular orbital framework. We also employ the NBO analysis[42] to support the qualitative conclusions obtained on the basis of the molecular orbital analysis. The NBO procedure allows one to represent the total molecular electron density (either correlated or not) in terms of contributions from core, lone pairs, localized bonding, and antibonding orbitals. The advantage of NBO is that it produces a Lewis structure from delocalized electron density, thus providing chemical insight. For well-behaved closed-shell molecules, a large fraction (more than 95%) of the electron density fits a single Lewis structure consistent with chemical bonding theories. However, in the case of open-shell and electronically excited species, the results of NBO decompositions are not always meaningful. We found that the NBO interpretation of the bonding in the hydroxymethyl and hydroxyethyl cations is consistent with the molecular orbital analysis and molecular properties (e.g., structures), whereas in the case of the radicals the NBO picture was less clear.

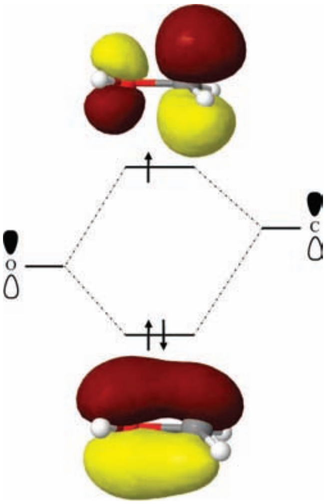

Figure 3. Frontier MOs of hydroxymethyl. Oxygen lone pair, LP(O), and LP(C) form bonding and antibonding π-like orbitals hosting three electrons in the radical.

Moreover, NBO is capable of quantifying interactions between different bonding and antibonding orbitals. This allows one to compute energies of hyperconjugation as the interaction energies (computed by a second-order perturbation scheme) resulting from charge delocalization among relevant bond orbitals. In CH_3CHOH^+, we computed hyperconjugation energies as the *sum* of the interaction energies of the three σ_{CH} of CH_3 with the π^*_{CO} orbital.

These energies can be compared with estimates of hyperconjugation effects derived from IEs using a simple Hückel-like picture, as described below. We emphasize that even though the NBO analysis is based on a well-defined mathematical procedure and uses highly accurate electron density, the resulting energy estimates are only semiquantitative, partly because of the simplicity of the underlying Lewis picture and partly because of the nonadditivity of different contributions to the total energy.

We begin by considering the relevant MOs of the hydroxymethyl radical and its cation shown in Figure 3. Although hydroxymethyl can be described as an OH-substituted methyl radical, its electronic structure is considerably different. The lone pair of oxygen is sufficiently close in energy to the carbon p_z orbital such that they form bonding and antibonding π-type orbitals. Consequently, the CO bond acquires partial π-bond character, which further increases upon ionization. This interaction destabilizes the SOMO, which results in a rather low IE of 7.56 eV (8.14 eV vertically), much lower than methyl's IE of 9.84 eV and slightly lower than the 8.12 eV IE of CH_3CH_2.[44,45]

In hydroxyethyl, the character of the SOMO changes further due to hyperconjugation interactions with the σ_{CH} orbitals of the CH_3 group. As described above, in hydroxyethyl and other radicals in which the radical center is adjacent to a lone pair (LP), one needs to consider the interactions of three orbitals, LP(O), LP(C), and σ_{CH}, yielding the bonding, nonbonding, and antibonding orbitals shown in Figure 2, which are remarkably similar to the allylic orbitals. This pattern differs from the more familiar hyperconjugation scenario involving two interacting orbitals, e.g., LP(C) and σ_{CH} in hydrocarbon radicals.[23] The vertical IE of CH_3CHOH is 7.29 eV, which is 0.85 eV lower than that of CH_2OH.

The observed trends in IEs can be analyzed in terms of a simple Hückel-like model. For the sake of simplicity, consider two interacting orbitals (e.g., LP(C) and σ_{CH}) producing bonding and antibonding combinations split by 2Δ. The case of three interacting orbitals is essentially the same, since the nonbonding allylic orbital does not contribute to the energies discussed below. In the radical, the bonding orbital is doubly occupied, and the antibonding orbital hosts one electron. Neglecting electron−electron interaction, the change in IE of the unpaired electron relative to the noninteracting orbitals is Δ, and the stabilization energy of the cation due to delocalization is 2Δ. Thus, in this simple model, the hyperconjugation energy in the cation is double the reduction in the IE of the radical. To evaluate the change in IE due to hyperconjugation, we take 0.85 eV (the observed drop in vertical IE between hydroxymethyl and hydroxyethyl) and subtract from it 0.32 eV, the change in vertical IEs between the two saturated compounds, ethanol (10.64 eV) and methanol (10.96 eV).[46,47] This allows us to separate the reduction in IE due to hyperconjugation from the reduction in IE due to the increase in molecular size. Thus, our estimate based on vertical IEs is $\Delta = 0.53$ eV. As will become evident below, this number is in remarkable agreement with simple NBO calculations of hyperconjugation energy.

Consistent with the MO picture, both radicals undergo significant geometrical relaxation upon ionization. As summarized in Figure 1, ionization induces changes in the CO bond length, which is consistent with removing an electron from an antibonding orbital. The effect is slightly larger in CH_2OH (0.117 Å) relative to CH_3CHOH (0.111 Å) because the participating σ_{CH} orbitals in the SOMO of the latter dilute its CO antibonding character. In agreement with this explanation, the CC bond is also contracted in the cation (by 0.032 Å). Ionization also induces rotation of the methyl group by 64°; however, the overall energy effect of this relaxation is small. Note that the CH bonds participating in hyperconjugation change accordingly, resulting in unequal bond lengths; i.e., the CH bonds involved in hyperconjugation are weakened due to the donation of some of their electron density into the π^* CO orbital; thus they are elongated.

Because of significant geometry relaxation, the adiabatic IEs of CH_2OH and CH_3CHOH are lower than the vertical values by 0.58 and 0.65 eV, respectively. Since the changes in CO bond lengths are very similar in both radicals, the difference between the two values, 0.07 eV, can be interpreted as the increase in Δ due to stronger hyperconjugation interactions at the cation geometry and can be compared with the increase in the hyperconjugation energy in the hydroxyethyl cation upon relaxation computed by NBO.

The NBO procedure confirms the bonding pattern described above. The Lewis structure of the cation includes a double CO bond at both the radical and the cation equilibrium geometries. The NBO calculation of the hyperconjugation energy (the delocalization energy between π^*_{CO} and all σ_{CH}) of the hydroxyethyl cation at the equilibrium geometry of the radical is 0.98 eV, yielding $\Delta = 0.49$ eV, which is in a good agreement with the value of 0.53 eV estimated from the IE differences. At the cation equilibrium geometry, the hyperconjugation energy increases by 0.23 eV and is 1.21 eV. Thus, the change in Δ due to the more favorable overlap at the relaxed geometry is 0.12 eV, which agrees nicely with 0.07 eV estimated from IEs.

Hyperconjugation energies as defined above are not equivalent to the change in the total molecular energy because of the nonadditivity of different contributions. However, the changes in the total molecular energies due to hyperconjugation are proportional to the NBO hyperconjugation energies. This has been demonstrated by Alabugin et al.,[48] who compared NBO hyperconjugation energies with changes in the total energy due to the deletion of the corresponding blocks from the Fock matrix at DFT level for series of molecules.

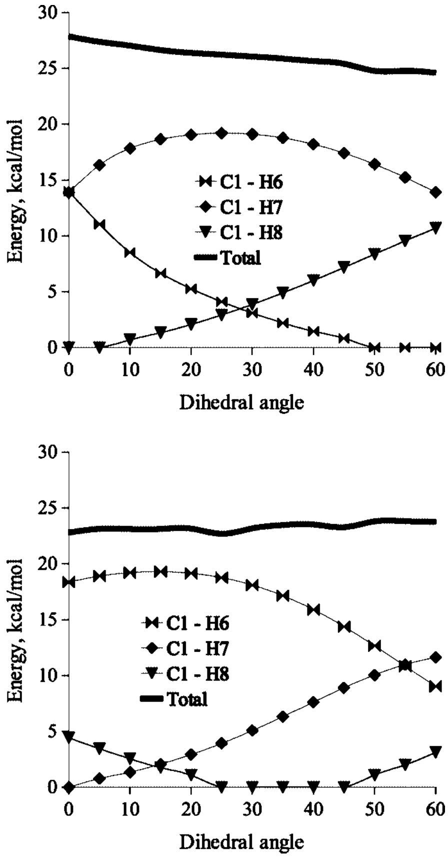

Figure 4. Hyperconjugation energies of the three CH bonds for various orientations of the CH_3 group in CH_3CHOH^+ at the cation (upper panel) and neutral (lower panel) geometries.

Hyperconjugation depends on the orientation of the interacting orbitals, which can be examined by calculating the hyperconjugation interactions at different positions of the CH_3 group produced by a rotation of the group around the CC axis. Figure 4 shows the individual hyperconjugation energies for each of the CH bonds, as well as their sum, along the torsional coordinate for CH_3CHOH^+ at the cation and radical geometries (only the torsional angle is varied, all other degrees of freedom are frozen; see section 2). Because of the different lengths of the three CH bonds, the torsional curves in Figure 4 are not symmetric. If the three CH bonds were identical, the period of rotation would be 120° and the potentials will be symmetric with respect to 60°.

As expected, the interaction between an individual σ_{CH} bond and the π^*_{CO} decreases as the angle between them increases; however, hyperconjugation as the *sum* of the individual interactions is almost constant, since as one CH bond leaves the zone of favorable overlap, another CH bond enters in. Thus, unless one of the hydrogens is appropriately substituted, the torsion potential is rather flat.[20] The total hyperconjugation energy is larger at the cation geometry because of the more favorable overlap at this geometry due to the shorter CC and CO bonds. Thus, significant energy relaxation upon ionization is largely due to the more efficient hyperconjugation at shorter bond lengths, whereas the changes in energy due to CH_3 group orientation are minor. This is in agreement with the analysis of the nature of the torsional barrier in ethane,[26] where hyperconjugation was found to be more efficient at the staggered configuration due to the shorter CC bond length rather than more favorable orientation of the CH_3 groups.

4. Conclusions

Hyperconjugation explains the observed large changes in the IE of the hydroxyethyl radical as compared to the hydroxymethyl radical by destabilizing the SOMO and stabilizing the HOMO-1 of the cation. At the radical geometry, the change in IE due to SOMO destabilization is estimated to be 0.53 eV, which is in excellent agreement with the hyperconjugation energy of the hydroxyethyl cation computed by NBO.

Upon geometry relaxation following ionization, the hyperconjugation energy increases by about 0.1 eV, which explains the larger difference between the vertical and adiabatic IEs in hydroxyethyl relative to hydroxymethyl. Thus, we can interpret the large change between the adiabatic and vertical IE in CH_3CHOH as the cumulative effects of the bonding interactions between the carbon's unpaired electron, the lone pair of oxygen, and hyperconjugation interaction with σ_{CH}. The energy relaxation upon ionization is due to more efficient hyperconjugation at shorter CC and CO bond lengths, whereas energy changes due to the CH_3 torsion are minor.

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