

An Evaluation of Additivity Schemes for the Estimation of Heats of Formation of Distonic Radical Cations†

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The validity of additivity schemes for the determination of the heats of formation of distonic radical cations, $\text{CH}_2^{\cdot}(\text{CH}_2)_{n-1}\text{OH}_2^+$ ($n=1-4$), has been examined using high level [G2(MP2,SVP) and G2(MP2)] *ab initio* calculations. The additivity schemes in essence assume that either (a) the dissociation energy of a C–H bond in a protonated molecule (e.g., CH_3OH_2^+) is the same as that of the corresponding unprotonated molecule (e.g., CH_3OH), or that (b) the proton affinity of a radical (e.g., $\text{CH}_2^{\cdot}\text{OH}$) is the same as that of the corresponding molecule (e.g., CH_3OH). These assumptions are found *not* to hold well for α -distonic radical cations (e.g., $\text{CH}_2^{\cdot}\text{OH}_2^+$), i.e., species for which the charge and radical sites are formally located on adjacent atoms ($n=1$). However, they lead to reasonable estimates for the heats of formation of larger distonic radical cations ($n>1$). A rationalization of these observations in terms of orbital interactions is presented.

Knowledge of the heats of formation (ΔH_f) of ions is important in understanding gas-phase ionic processes. In this respect, a variety of experimental procedures have been used to obtain heats of formation for a large number of ions.¹ However, in some instances the experimental determination of the heat of formation can be quite difficult and approximation schemes are used to obtain such information.²⁻⁵ These approximation schemes often exhibit quite useful accuracy.

Distonic radical cations (e.g., $\text{CH}_2^{\cdot}\text{OH}_2^+$), i.e., radical cations in which the charge and radical sites are formally separated, represent a class of ions for which the direct determination of ΔH_f is not always straightforward. A principal reason is that distonic radical cations do not generally have stable neutral counterparts and are therefore often produced by more complex rearrangement–fragmentation reactions.^{6,7} Moreover, any experimental determination of ΔH_f (e.g., by measuring an appearance energy) requires that the pure distonic ion be unambiguously generated. An approximation scheme has therefore been used^{4-6,8,9} in which it is in essence assumed either that (a) the bond dissociation energy (BDE) of a C–H bond in a protonated molecule (e.g., CH_3OH_2^+) is the same as that for the corresponding unprotonated molecule (e.g., CH_3OH), or that (b) the proton affinity (PA)

of a radical (e.g., $\text{CH}_2^{\cdot}\text{OH}$) is the same as that for the corresponding molecule (e.g., CH_3OH). In this way, the heat of formation of a distonic radical cation can be estimated from generally known quantities. For example, the ΔH_f of $\text{CH}_2^{\cdot}\text{OH}_2^+$ can be obtained from the ΔH_f , BDE and PA of methanol on the basis of such assumptions (see Fig. 1).

There are examples in the literature where these assumptions have appeared to be satisfactory, but it has been anticipated that they may fail when the charge and radical sites are adjacent (i.e., for α -distonic radical cations).^{5,6} Indeed, a recent experimental study¹⁰ found the proton affinity of $\text{CH}_2^{\cdot}\text{OH}$ (695 kJ mol⁻¹) to differ markedly from that of the neutral analogue CH_3OH

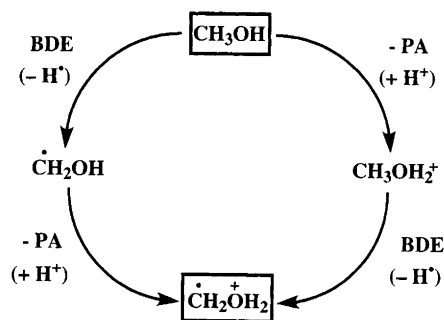


Fig. 1. Thermochemical cycle for the determination of the heat of formation of $\text{CH}_2^{\cdot}\text{OH}_2^+$ using known thermochemical data and additivity approximations.

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(760 kJ mol⁻¹), casting general doubt on the validity of assumption (b) above.

In the present study, we have employed high levels of *ab initio* molecular orbital theory to examine the reliability of these approximation schemes. Specifically, we have calculated and compared bond dissociation energies for the terminal C–H bonds in the series CH₃(CH₂)_{n-1}OH and CH₃(CH₂)_{n-1}OH₂⁺, and proton affinities at oxygen in the series CH₃(CH₂)_{n-1}OH and CH₂[·](CH₂)_{n-1}OH (*n* = 1–4).

Theoretical procedures

Standard *ab initio* molecular orbital calculations¹¹ were carried out with the GAUSSIAN 92/DFT¹² and GAUSSIAN 94¹³ series of programs. Geometries and harmonic vibrational frequencies were optimized using both Hartree–Fock (HF) and second-order Møller–Plesset (MP2) theory, with the 6–31G(d) basis set.

Theoretical heats of formation, bond dissociation energies and proton affinities were obtained using slightly modified G2(MP2)¹⁴ and G2(MP2,SVP)^{15,16} procedures. These methods are similar in approach and accuracy to G2¹⁷ but are computationally less demanding. All three procedures effectively correspond to QCISD(T)/6–311 + G(3df,2p) energy calculations on MP2(full)/6–31G(d) optimized structures, with zero-point energy corrections determined from scaled (by 0.8929) HF/6–31G(d) vibrational frequencies and a so-called higher level correction term included. Our minor modification corresponds to using optimized geometries obtained at the MP2/6–31G(d) level with the frozen-core approximation, i.e., MP2(fc)/6–31G(d), rather than MP2(full)/6–31G(d). This is not expected significantly to affect the results. Restricted (RHF, RMP2) and unrestricted (UHF, UMP2) procedures were used for closed- and open-shell systems, respectively. The frozen-core approximation (fc) was used throughout.

Standard procedures¹⁸ were used to obtain heats of formation at 0 K ($\Delta H_{f,0}$) from the calculated total energies via atomization reactions, and $\Delta H_{f,298}$ values were obtained from the $\Delta H_{f,0}$ values using our computed [scaled HF/6–31G(d)] vibrational frequencies. Throughout this paper, energy comparisons refer to 298 K values.

In an initial set of calculations, $\Delta H_{f,298}$, BDE and PA values were obtained, as appropriate, for CH₃(CH₂)_{n-1}OH, CH₃(CH₂)_{n-1}OH₂⁺ and CH₂[·](CH₂)_{n-1}OH (*n* = 1–3) at both the G2(MP2) and G2(MP2,SVP) levels, based on global minimum energy structures determined at the MP2/6–31G(d) level of theory. The G2(MP2) and G2(MP2,SVP) results were found to be in very good agreement with one another in all cases. The computationally cheaper G2(MP2,SVP) procedure was therefore used in subsequent calculations.

In a second set of calculations, BDEs and PAs were calculated at the G2(MP2,SVP) level for systems constrained to idealized all-*trans* conformations, possessing a plane of symmetry along the C–C_{n-1}–O chain [referred

to as the all-*trans* (C_s) conformations]. In addition, the range of systems examined was extended to *n* = 4. The idealized extended chain conformations were chosen in these calculations in order to examine the validity of the approximation schemes in the absence of effects associated with conformational changes. For CH₂[·]OH, however, there exists no minimum energy structure (i.e., global or local minimum) at either the HF/6–31G(d) or MP2/6–31G(d) level that satisfies these criteria, and the normal optimized structure was therefore used.

Results and discussion

Comparison of calculated and experimental heats of formation. A comparison of calculated [G2(MP2,SVP) and G2(MP2)] and experimental^{1,19} heats of formation is presented in Table 1. There is uniformly good agreement between the G2(MP2) and G2(MP2,SVP) values, the largest difference being just 4.3 kJ mol⁻¹ (for CH₃OH₂⁺). There is also good agreement in general between the theoretical and experimental heats of formation, with most values agreeing to within ± 10 kJ mol⁻¹. However, larger differences are found for CH₂[·]OH (8.2–11.3 kJ mol⁻¹), CH₂[·]CH₂OH (31.9–32.0 kJ mol⁻¹), CH₂[·](CH₂)₂OH (17.7–18.7 kJ mol⁻¹) and CH₂[·](CH₂)₂OH₂⁺ (18.6–20.8 kJ mol⁻¹). In the case of CH₂[·]OH, our calculated heat of formation (–14.6 to –17.7 kJ mol⁻¹) is in better agreement with more recent experimental determinations, which predict $\Delta H_{f,298}$ to lie in the region of –12 to –20 kJ mol⁻¹.^{20–24} For CH₂[·]CH₂OH, CH₂[·](CH₂)₂OH and CH₂[·](CH₂)₂OH₂⁺, a re-examination of the experimental heats of formation^{19,25} would seem desirable. As a result of these comparisons, we have chosen to use our calculated energies (rather than the experimental energies) as the basis for subsequent analysis of bond dissociation energies and proton affinities.

Table 1. Calculated^a and experimental^b heats of formation at 298 K (kJ mol⁻¹).

Molecule	G2(MP2,SVP)	G2(MP2)	Exptl. ^b
CH ₃ OH	–204.9	–208.7	–201.6
CH ₃ CH ₂ OH	–238.6	–240.1	–234.8
CH ₃ (CH ₂) ₂ OH	–260.0	–259.0	–254.8
CH ₂ [·] OH	–14.6	–17.7	–25.9
CH ₂ [·] CH ₂ OH	–24.1	–24.0	–56 ^c
CH ₂ [·] (CH ₂) ₂ OH	–49.3	–48.3	–67 ^c
CH ₃ OH ₂ ⁺	571.5	567.2	567
CH ₃ CH ₂ OH ₂ ⁺	515.5	513.4	507
CH ₃ (CH ₂) ₂ OH ₂ ⁺	485.9	486.3	476
CH ₂ [·] OH ₂ ⁺	820.4	817.1	815
CH ₂ [·] CH ₂ OH ₂ ⁺	730.8	729.1	732
CH ₂ [·] (CH ₂) ₂ OH ₂ ⁺	693.2	695.4	714

^aCalculated using the lowest energy conformers located on the MP2/6–31G(d) potential energy surface (see the text).

^bExperimental values taken from Ref. 1, unless otherwise noted. ^cFrom Ref. 19.

Bond dissociation energies. The calculated values of the terminal C–H bond dissociation energies for the lowest energy conformations of $\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}$ and $\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}_2^+$ ($n=1-3$) are presented in Table 2. It is clear that the C–H BDE of protonated methanol (CH_3OH_2^+) is not equal to that of methanol (CH_3OH). The calculated difference is $58.6-59.0 \text{ kJ mol}^{-1}$, with the value in protonated methanol being much higher than in neutral methanol. However, in ethanol and its protonated form (i.e., $n=2$), the calculated C–H bond dissociation energies differ by just $0.3-0.6 \text{ kJ mol}^{-1}$, while for propanol and its protonated form ($n=3$), the difference is only $3.2-3.6 \text{ kJ mol}^{-1}$. Thus, the terminal C–H BDEs for the protonated alcohols are very close to those of the alcohols for all but the first pair in the series, even when conformational differences are allowed.

The trends in BDEs with increasing n , for the all-*trans* (C_s) conformations, are shown diagrammatically in Fig. 2. The results for $n=1-3$ parallel those observed in the conformationally unconstrained systems (Table 2). Thus, the C–H bond dissociation energies in CH_3OH and CH_3OH_2^+ are clearly significantly different. However, as soon as one or more methylene groups are interposed between the site of bond dissociation and the

Table 2. Calculated C–H bond dissociation energies at 298 K (kJ mol^{-1}).^a

Precursor	Product	G2 (MP2,SVP)	G2 (MP2)
H–CH ₂ OH	CH ₂ ·OH	408.2	408.9
H–CH ₂ OH ₂ ⁺	CH ₂ ·OH ₂ ⁺	466.8	467.9
H–CH ₂ CH ₂ OH	CH ₂ ·CH ₂ OH	432.7	433.3
H–CH ₂ CH ₂ OH ₂ ⁺	CH ₂ ·CH ₂ OH ₂ ⁺	433.3	433.6
H–CH ₂ (CH ₂) ₂ OH	CH ₂ ·(CH ₂) ₂ OH	428.8	429.0
H–CH ₂ (CH ₂) ₂ OH ₂ ⁺	CH ₂ ·(CH ₂) ₂ OH ₂ ⁺	425.2	425.8

^aCalculated using the lowest energy conformers located on the MP2/6–31G(d) potential energy surface (see the text).

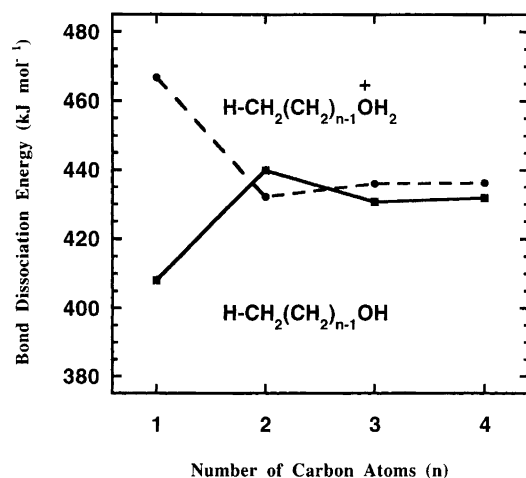


Fig. 2. Calculated G2(MP2,SVP) bond dissociation energies for all-*trans* (C_s) conformers of $\text{H-CH}_2(\text{CH}_2)_{n-1}\text{OH}$ and $\text{H-CH}_2(\text{CH}_2)_{n-1}\text{OH}_2^+$ for $n=1-4$.

oxygen atom, there is an *immediate* and marked reduction in the difference in the BDEs between the neutrals and their protonated analogues. The two curves in Fig. 2 both appear to converge quickly towards a limiting value of approximately 435 kJ mol^{-1} . The assumption that the bond dissociation energy of a C–H bond in the protonated alcohol is the same as that for the corresponding unprotonated alcohol thus fails for $n=1$ but appears to hold well for $n>1$. The possible failing of such approximations for $n=1$ has been suggested previously.⁶ The convergence behavior for other related properties of distonic ions has been discussed previously.²⁶

The trends shown by the two bond dissociation curves in Fig. 2 suggest that the ‘anomalous’ behavior in the BDEs of methanol and protonated methanol is due mainly to short-range effects. A rationalization is provided by orbital interaction arguments²⁷ involving the p-type lone pair orbital on the oxygen atom in neutral methanol (see Fig. 3). Hyperconjugation between this orbital and the appropriate pseudo- π^* antibonding orbital of the methyl group leads to weakening of the C–H bonds. Protonation of the hydroxy group (as in CH_3OH_2^+) lowers the energy of the p-type lone pair orbital on oxygen. This leads to a reduced hyperconjugative interaction with the methyl π^* orbital and hence leads to a reduction in the extent of bond weakening. In addition, contributions from the ‘no-bond’ resonance structure CH_3^+OH_2 result in a lengthening of the C–O bond in CH_3OH_2^+ (to 1.518 \AA), also leading to a reduction in the extent of bond weakening. Thus, protonation of methanol will lead to an increase in the C–H homolytic bond dissociation energy. As soon as one or more methylene groups are interposed, however, the possibility of hyperconjugative interaction with oxygen is effectively removed and hence the effect of protonation on the BDE becomes very small. Alternative arguments based on electronegativity effects have been used in previous studies of the effects of protonation on bond dissociation energies.²⁸

The hyperconjugative bond weakening in methanol is reflected in a C–H₂ bond length of 1.097 \AA compared with a length of 1.090 \AA for the C–H₁ bond (see Fig. 3). The latter cannot interact with the p-orbital at oxygen because of orthogonality of the potentially interacting orbitals; only interaction with the less effective sp^2 -type

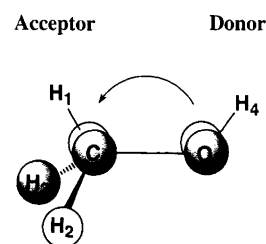


Fig. 3. Schematic representation of hyperconjugative interaction between the p-type lone pair on oxygen and the pseudo- π^* antibonding orbital of the methyl group in methanol.

donor orbital at oxygen is possible. In contrast, the C–H bonds in protonated methanol are 1.086–1.087 Å. So the C–H bonds in CH_3OH_2^+ are shorter than those in CH_3OH , consistent with the reduction in hyperconjugative bond weakening. In the ethanol–protonated ethanol pair and in the extended all-*trans* (C_s) conformations of propanol–protonated propanol and butanol–protonated butanol, all the C–H bond lengths lie within the fairly narrow range of 1.091–1.094 Å, reflecting the absence of strong hyperconjugative interaction with oxygen. On the other hand, in the unconstrained protonated propanol structure, one of the C–H bonds is as long as 1.097 Å, possibly as a result of direct interaction with the bonds at the oxygen center.

Proton affinities. The calculated values of the proton affinities at oxygen for the lowest energy conformations of $\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}$ and $\text{CH}_2^{\cdot}(\text{CH}_2)_{n-1}\text{OH}$ ($n = 1-3$) are presented in Table 3 and show exactly parallel behavior to that noted for the bond dissociation energies. For the smallest species, CH_3OH and $\text{CH}_2^{\cdot}\text{OH}$, we see a significant difference in the proton affinities of 58.6–59.1 kJ mol^{-1} . For those systems corresponding to $n = 2$ and 3, i.e., ethanol and propanol and their corresponding radicals, the differences are markedly smaller (0.3–0.7 and 3.2–3.5 kJ mol^{-1} , respectively).

The trends in PAs with increasing n for the all-*trans* (C_s) conformations are shown in Fig. 4. Again, the results parallel those (Table 3) for the conformationally unconstrained systems with $n = 1-3$. Thus, as the distance between the site of protonation and the radical site is increased, the proton affinities of the radicals immediately approach the values for the corresponding neutrals. The proton affinities increase gradually with n and appear to be converging but it is not clear how far our values for $n = 3$ and 4 would lie from the ultimate ($n = \infty$) limit.

The rapid approach of the two curves in Fig. 4 to one another, suggests again that short-range effects are primarily responsible for the behavior with respect to protonation of $\text{CH}_2^{\cdot}\text{OH}$ vs. CH_3OH . This can be rationalized in terms of a two-center–three-electron interaction. In $\text{CH}_2^{\cdot}\text{OH}$, the lone pair on the oxygen interacts with the singly occupied p-type orbital on the carbon, the two orbitals being aligned almost parallel to one another.

Table 3. Calculated proton affinities at 298 K (kJ mol^{-1}).^a

Neutral species	Protonated species	G2 (MP2,SVP)	G2 (MP2)
CH_3OH	CH_3OH_2^+	754.3	754.9
$\text{CH}_2^{\cdot}\text{OH}$	$\text{CH}_2^{\cdot}\text{OH}_2^+$	695.7	695.8
$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{OH}_2^+$	776.6	777.2
$\text{CH}_2^{\cdot}\text{CH}_2\text{OH}$	$\text{CH}_2^{\cdot}\text{CH}_2\text{OH}_2^+$	775.9	776.9
$\text{CH}_3(\text{CH}_2)_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_2\text{OH}_2^+$	784.7	785.3
$\text{CH}_2^{\cdot}(\text{CH}_2)_2\text{OH}$	$\text{CH}_2^{\cdot}(\text{CH}_2)_2\text{OH}_2^+$	788.2	788.5

^aCalculated using the lowest energy conformers located on the MP2/6–31G(d) potential energy surface (see the text).

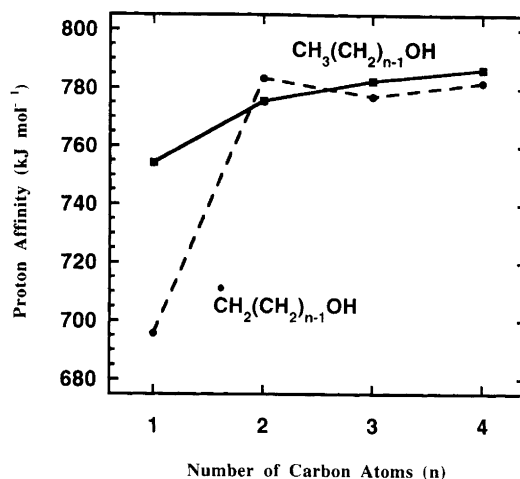


Fig. 4. Calculated G2(MP2,SVP) proton affinities for all-*trans* (C_s) conformers of $\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}$ and $\text{CH}_2^{\cdot}(\text{CH}_2)_{n-1}\text{OH}$ for $n = 1-4$.

This three-electron interaction results in a delocalization of the lone pair on the oxygen across the C–O bond, lowering its energy and making it less available for protonation. Thus, protonation in $\text{CH}_2^{\cdot}\text{OH}$ is less favourable than in CH_3OH . As n is increased, i.e., as soon as one or more methylene groups are interposed between the oxygen atom and the radical site, the interaction between the oxygen lone pair and the singly occupied orbital at carbon is drastically reduced. Thus, one can expect the proton affinities of the radicals immediately to approach those of the corresponding neutrals, as is observed (see Table 3 and Fig. 4).

Conclusions

Our results indicate that the approximations:

$$\begin{aligned} \text{BDE}[\text{H}-\text{CH}_2(\text{CH}_2)_{n-1}\text{OH}_2^+] \\ \approx \text{BDE}[\text{H}-\text{CH}_2(\text{CH}_2)_{n-1}\text{OH}] \end{aligned}$$

and

$$\text{PA}[\text{CH}_2^{\cdot}(\text{CH}_2)_{n-1}\text{OH}] \approx \text{PA}[\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}]$$

are poor when $n = 1$, i.e., these approximations should not be used in estimating heats of formation for α -distonic radical cations such as $\text{CH}_2^{\cdot}\text{OH}_2^+$. However, the approximations are found to hold well (i.e., to within 4 kJ mol^{-1}) when $n > 1$, i.e., when one or more methylene groups is interposed between the 'active sites'. These results can be rationalized using orbital interaction arguments.

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