The Effects of Protonation on the Structure, Stability, and Thermochemistry of Carbon-Centered Organic Radicals

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Abstract: The effects of protonation on the geometries and stabilization energies of prototypical $^{\bullet}CH_2X$ radicals (X = NH_2, OH, OCH_3, PH_2, SH, F, Cl, Br, CN, CHO, and NO_2) have been studied with the use of ab initio molecular orbital calculations at the G2 level. The proton affinities at X of the $^{\bullet}CH_2X$ radicals and the analogous substituted methanes, CH_3X, are compared and the corresponding heats of formation calculated. For π-donor substituents (X = NH_2, OH, OCH_3, PH_2, SH, F, Cl and Br), protonation at X leads to considerable ^{+}C :XH character for both CH_3XH^+ and $^{\bullet}CH_2XH^+$, resulting in substantially lower heterolytic bond dissociation enthalpies and longer C−X bonds. Protonation also strengthens the C−H bonds in CH_3XH^+ and, in combination with the reduced interaction of the lone pair on X with the singly-occupied orbital at the radical center in the radicals, results in negative radical stabilization energies for $^{\bullet}CH_2XH^+$. For the π-acceptor substituents (CN, CHO, and NO_2), protonation enhances hyperconjugative electron donation from the methyl group to the π^* orbital of X, thereby resulting in C−X bonds in CH_3XH^+ and $^{\bullet}CH_2XH^+$ that are shorter than those in the unprotonated species. This also leads to weaker C−H bonds and, together with enhanced delocalization of the unpaired electron in the radical, leads to positive radical stabilization energies for $^{\bullet}CH_2XH^+$. The proton affinities of the radicals with π-donor substituents are 30−70 kJ mol^{-1} lower than those of their closed-shell counterparts. This may be attributed to the decreased availability of the lone-pair orbital(s) on X, resulting from interaction with the singly-occupied orbital at the radical center. The $^{\bullet}CH_2CHO$ and $^{\bullet}CH_2NO_2$ radicals have proton affinities that are similar to those of their closed-shell counterparts because protonation takes place in a plane almost orthogonal to the singly-occupied orbital on C, and so there is less effect in going from CH_3X to $^{\bullet}CH_2X$.

Introduction

Protonated molecules are of interest to chemists since they are often important intermediates in reaction mechanisms. The proton affinity (PA) is a key thermochemical quantity of relevance to the chemistry of protonated molecules. It is defined as the negative of the enthalpy change in the protonation reaction:

$$A + H^+ \rightarrow AH^+ \qquad (1)$$

The proton affinities (PA) of many molecules have been compiled in widely-used thermochemical compendia by Lias et al.,[2,3] and more recent experimental studies by Mautner[4] and McMahon[5] have led to a number of firmly established values. Uggerud[6] has recently reviewed the experimental techniques used to study the thermochemistry and reactivity of protonated molecules. Most recently, Hunter and Lias[7] have produced an updated compendium of proton affinities.

The effect of protonation on molecular structure has been studied computationally by Yáñez, Mó, and co-workers.[8−10] They found that protonation of an electronegative atom in a molecule usually leads to lengthening of the bonds to that atom. This behavior was rationalized by first noting that protonation of a substituent leads to an increase in its electronegativity. For first-row groups, the Pauling-type electronegativities are 3.98 for X = F and 5.22 for X = FH^+; 3.44 for OH and 4.13 for OH_2^+; and 3.04 for NH_2 and 3.58 for NH_3^+.[11] Yáñez et al. argued that since protonation increases the electronegativity of X, the surrounding bonds are depopulated and therefore lengthened.[8−10] Interestingly, Boyd et al.[11−13] have shown computationally that the C−X *homolytic* bond dissociation enthalpy (BDE) is actually larger in CH_3XH^+ than in CH_3X, a result seemingly at variance with the lengthening of the C−X bond. They explained this behavior by noting that heterolysis rather than homolysis is generally the lower energy dissociation process in the protonated species, particularly for highly electronegative X, and that the *heterolytic* BDEs are indeed

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(2) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(3) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(4) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448 and references therein.

(5) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839 and references therein.

(6) Uggerud, E. *Mass Spectrom. Rev.* **1992**, *11*, 389.

(7) Hunter, E. P.; Lias, S. G. *Proton Affinity Evaluation*; in NIST Standard Reference Database Number 69; Mallard, W. G., Linstrom, P. J., Eds.; February 1997; National Institute of Standards and Technology: Gaithersburg, MD.

(8) Bordejé, M. C.; Mó, O.; Yáñez, M.; Herreros, M.; Abboud, J.-L. M. *J. Am. Chem. Soc.* **1993**, *115*, 7389.

(9) Alcamí, M.; Mó, O.; Yáñez, M.; Abboud, J.-L. M.; Elguero, J. *Chem. Phys. Lett.* **1990,** *172*, 471.

(10) Bouchoux, G.; Drancourt, D.; Leblanc, D.; Yáñez, M.; Mó, O. *New J. Chem.* **1995**, *19*, 1243.

(11) Boyd, R. J.; Glover, J. N. M.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5152.

(12) Boyd, S. L.; Boyd, R. J.; Bessonette, P. W.; Kerdraon, D. I.; Aucoin, N. T. *J. Am. Chem. Soc.* **1995**, *117*, 8816.

(13) Boyd, S. L.; Boyd, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 4214.

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much lower in protonated molecules than they are in neutral molecules.[12,13] The lengthening of the C−X bond following protonation is thus associated with a weaker heterolytic BDE leading to CH_3^+ and :XH.[12,13]

A closely related rationalization of the effect of protonation on the C−X bond length and BDE comes from noting that there are two major resonance contributors to the C−X bond, namely a covalent (single-bond) structure (**a**) and an ionic (no-bond) structure (**b**):

$$\underset{\mathbf{1a}}{CH_3{-}X} \leftrightarrow \underset{\mathbf{1b}}{{}^+CH_3 :X^-}$$

$$\underset{\mathbf{2a}}{CH_3{-}XH^+} \leftrightarrow \underset{\mathbf{2b}}{{}^+CH_3 :XH}$$

In unprotonated molecules (**1**), the bonded structure (**1a**) dominates, but when a molecule is protonated on X (**2**), the contribution from the no-bond resonance structure (**2b**) can become significant, resulting in lower C−X heterolytic BDEs and longer C−X bonds.

Organic free radicals represent another important class of reactive intermediates. They are more difficult to study experimentally than closed-shell species and there have been comparatively few experimental determinations of free radical structures, heats of formation ($\Delta_f H°$), proton affinities (PA), and radical stabilization energies (RSE). Theory, therefore, has an important role to play in understanding the properties of these species. Protonated forms of $^\bullet CH_2X$ radicals can have either the $CH_3X^{\bullet+}$ or the $^\bullet CH_2XH^+$ structure. The latter are the so-called distonic radical cations in which the charge and radical sites are formally separated.[14−16] The distonic ions are more stable than the conventional $CH_3X^{\bullet+}$ isomers for the first-row systems, while the latter are preferred for the second-row substituents.[17]

The aims of the present study are to compare protonated species with unprotonated species and to compare radicals with the corresponding closed-shell molecules. Specifically, we seek to examine the effects of protonation on the structure, stability, and thermochemistry of organic carbon-centered free radicals using ab initio molecular orbital calculations at the G2 level of theory[18] and to compare the results with those of their closed-shell counterparts. Do the trends observed in BDE and geometry noted above for closed-shell molecules carry over to the open-shell systems? How does the radical center influence the proton affinity at adjacent heteroatoms? How does the effect of a π-donor substituent (e.g., X = NH_2) compare with that of a π-acceptor substituent (e.g., X = CHO)? We have chosen for this study a set of prototypical free radicals, $^\bullet CH_2X$, substituted with groups X that cover a range of chemical characteristics, including the halogens (X = F, Cl, and Br), several other first- and second-row π-donor groups (X = NH_2, OH, OCH_3, PH_2, and SH), and several π-acceptor groups (X = CN, CHO, and NO_2).[19] To facilitate comparison of the present results for radicals with those for the protonated forms of the closed-shell CH_3X molecules (CH_3XH^+), this paper deals only with the distonic forms of the protonated radicals ($^\bullet CH_2XH^+$).

Computational Methods

Standard ab initio molecular orbital calculations[20] were carried out at the G2 level of theory[18] with the use of the GAUSSIAN 92[21a] and GAUSSIAN 94[21b] programs. G2 theory corresponds effectively to a QCISD(T)/6-311+G(3df,2p) energy calculation, with the inclusion of zero-point vibrational energy (ZPE) and the incorporation of an empirical higher-level correction (HLC) employed to overcome residual basis set deficiencies. Geometries are optimized at the MP2(full)/6-31G(d) level of theory and zero-point vibrational energies are calculated from HF/6-31G(d) harmonic vibrational frequencies, scaled by 0.8929.[18] Unrestricted open-shell reference wave functions were used for open-shell species throughout the study. The G2 total energies at 298 K, along with $\langle S^2 \rangle$ values (for the underlying UHF/6-31G(d) wave function) for the open-shell systems, are listed in Table S1 of the Supporting Information. Complete geometries of the species dealt with in this study are given in the form of GAUSSIAN archive entries in Table S2 of the Supporting Information.

G2 theory has been employed successfully in calculating proton affinities of closed-shell molecules.[22] One problem encountered when studying open-shell systems is spin-contamination in the reference unrestricted Hartree−Fock wave function. In a recent assessment of theoretical procedures for calculating free radical thermochemistry,[23] we concluded that for radicals exhibiting low levels of spin-contamination ($\langle S^2 \rangle \leq 0.80$ compared with 0.75 for a pure doublet state), G2 theory might generally be expected to be adequate for obtaining reliable $\Delta_f H°$ values. Most of the radicals in the present study fall into this category. We also concluded that obtaining reliable $\Delta_f H°$ values for highly spin-contaminated radicals can require a more sophisticated theoretical treatment and we presented details of a recommended procedure.[23] Such a treatment would be expected to lead to improved results for 4 of the 22 radicals under consideration in the present study, namely $^\bullet CH_2CN$, $^\bullet CH_2CNH^+$, $^\bullet CH_2CHO$, and $^\bullet CH_2NO_2H^+$, but we have not included calculations of this type here.

Proton affinities at 0 K have been evaluated from G2 total energies as the negative of the energy changes for reaction 1. We note that G2 PAs are completely ab initio since the HLC in G2 theory is the same on both sides of the protonation reaction. To obtain theoretical PAs at 298 K, vibrational contributions to thermal corrections[19,24] were calculated with the use of HF/6-31G(d) harmonic frequencies, scaled by 0.8929 according to the G2 scheme.[18] Theoretical heats of formation

(14) (a) Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225. (c) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2250.

(15) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

(16) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. *Chem. Rev.* **1992**, *92*, 1649.

(17) For a discussion of the relative stabilities of $CH_3X^{\bullet+}$ and $^\bullet CH_2XH^+$ structures calculated at the G2 level, see: Gauld, J. W.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 777.

(18) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (b) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C., Jr.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104. For reviews of the applications of G2 theory, see: (c) Curtiss, L. A.; Raghavachari, K. *Quantum Mechanical Electronic Structure Calculations with Chemical Acuracy*, Langhoff, S. R., Ed.; Kluwer Academic Press: The Netherlands, 1995. (d) Raghavachari, K.; Curtiss, L. A. *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995.

(19) The effect of protonation on the $^\bullet CH_2OH$ radical has been discussed in a recent study that also examines the $^\bullet CH_2CH_2OH$ and $^\bullet CH_2CH_2CH_2OH$ systems: Gauld, J. W.; Holmes, J. L.; Radom, L. *Acta Chem. Scand.* **1997**, *51*, 641.

(20) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory;* Wiley: New York, 1986.

(21) (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Gaussian Inc.: Pittsburgh, PA, 1992. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez C.; Pople, J. A. GAUSSIAN 94; Gaussian Inc.: Pittsburgh, PA, 1995.

(22) For a detailed study, see: Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

(23) Mayer, P. M.; Parkinson, C. J.; Smith, D. M.; Radom, L. *J. Chem. Phys.* In press.

(24) Daudel, R.; Leroy, G.; Peeters, D.; Sana, M. *Quantum Chemistry;* Wiley: New York, 1983.

Table 1. Optimized C−X and C−XH$^+$ Bond Lengths in the Substituted Methanes (CH_3X), Methyl Radicals ($^\bullet CH_2X$), and Their Protonated Forms (CH_3XH^+ and $^\bullet CH_2XH^+$)[a,b]

	r(C−X)	r(C−XH$^+$)
CH_3-NH_2	1.465 (1.471)	1.508
$^\bullet CH_2-NH_2$	1.402	1.471
CH_3-OH	1.424 (1.429)	1.516
$^\bullet CH_2-OH$	1.373	1.468
CH_3-OCH_3	1.414 (1.415)	1.494
$^\bullet CH_2-OCH_3$	1.363	1.437
CH_3-F	1.390 (1.383)	1.603
$^\bullet CH_2-F$	1.350	1.550
CH_3-PH_2	1.860 (1.858)	1.800
$^\bullet CH_2-PH_2$	1.790	1.764
CH_3-SH	1.814 (1.814)	1.818
$^\bullet CH_2-SH$	1.728	1.762
CH_3-Cl	1.778 (1.776)	1.845
$^\bullet CH_2-Cl$	1.718	1.773
CH_3-Br	1.949 (1.934)	2.001
$^\bullet CH_2-Br$	1.863	1.925
CH_3-CN	1.461 (1.468)	1.448
$^\bullet CH_2-CN$	1.412	1.407
CH_3-CHO	1.502 (1.501)	1.457
$^\bullet CH_2-CHO$	1.456	1.408
CH_3-NO_2	1.486 (1.489)	1.480
$^\bullet CH_2-NO_2$	1.431	1.330

[a] MP2(full)/6-31G(d) values, in Å. [b] Experimental values in parentheses from ref 27.

at 0 K ($\Delta_f H°_0$) were derived from the G2 energies by the atomization method as outlined by Nicolaides et al.[25] and using the experimental heats of formation of the atoms.[3] Heats of formation at 298 K ($\Delta_f H°_{298}$) were evaluated with the use of calculated thermal corrections for the species of interest together with the experimental enthalpy increments ($H°_{298} - H°_0$) of the elements in their standard states.[26]

Results and Discussion

Changes in C−X Bond Length in Going from CH_3X to $^\bullet CH_2X$. The C−X bond lengths for the substituted methanes (CH_3X) and substituted methyl radicals ($^\bullet CH_2X$) are listed in Table 1. There is close agreement between the theoretical values and available experimental data,[27] despite the fairly simple level of theory used (MP2/6-31G(d)). The mean absolute difference between theoretical and experimental bond lengths is just 0.004 Å.

An important observation is that in all cases the C−X bond is significantly shorter in the radicals than in their closed-shell counterparts. This result can be rationalized by noting that hyperconjugative interaction between the CH_3 group and X in CH_3X is not as strong as the interaction between $^\bullet CH_2$ and X in $^\bullet CH_2X$. In the case of π-donor substituents, the hyperconjugative interaction in CH_3X takes the form of donation from the lone pair on X, n(X), to an antibonding orbital of π-symmetry on the methyl group, $\pi^*(CH_3)$.[28] For the π-acceptor substituents (X = CN, HCO and NO_2), hyperconjugative donation takes place from a $\pi(CH_3)$ orbital to a π^* orbital on X.[28] For the π-donor-substituted methyl radicals, overlap between the formally singly-occupied orbital at C (p(C)) and n(X) is possible, leading to a net-bonding three-electron interaction.[28−30] This is generally a more favorable interaction than the hyperconjugation in CH_3X, thereby shortening the C−X bond.[28] For X = CN, HCO, and NO_2, more effective delocalization of the unpaired electron through a three-center three-electron interaction means that the C−X bond in $^\bullet CH_2X$ will have greater partial-double-bond character than in CH_3X, again leading to a relative bond shortening.

Table 2. Comparison of Calculated (G2) and Experimental Electron Affinities of X and Ionization Energies of XH, CH_3, and CH_2

	EA(X)[a]			IE(XH)[b]	
X	G2[c]	exptl[d]	XH	G2[c]	exptl[d]
NH_2	0.77	0.75 ± 0.06	NH_3	10.19	10.16 ± 0.01
OH	1.87	1.829 ± 0.010	H_2O	12.63	12.612 ± 0.010
CH_3O	1.62	1.62 ± 0.14	CH_3OH	10.97	10.85 ± 0.01
F	3.48	3.399 ± 0.003	HF	16.08	16.004 ± 0.003
PH_2	1.25	1.19 ± 0.14	PH_3	9.87	9.869 ± 0.002
SH	2.30	2.32 ± 0.10	H_2S	10.43	10.453 ± 0.008
Cl	3.61	3.617 ± 0.003	HCl	12.71	12.747
Br	3.10	3.365 ± 0.003	HBr	11.58	11.66 ± 0.03
CN	3.97	3.74 ± 0.17	CNH	12.06	12.5 ± 0.1
CHO	0.34	0.313 ± 0.005	CHOH	8.95	
NO_2	2.34	2.30 ± 0.10	NO_2H	10.98	
			CH_3	9.77	9.84 ± 0.01
			CH_2	10.31	10.396

[a] Energies for the reaction $X^\bullet \rightarrow X^-$, in eV, at 0 K. [b] Energies for the reaction $XH \rightarrow XH^{\bullet+}$, in eV, at 0 K. [c] Many of these values can also be found in Curtiss et al.[18a,b] [d] Lias et al.[3]

Changes in C−X Bond Length Due to Protonation at X. The changes in C−X bond length in CH_3X and $^\bullet CH_2X$ following protonation at X are compared in Table 1. Our MP2(full)/6-31G(d) geometries are essentially identical with the MP2/6-31G(d) geometries calculated by Boyd et al.[11] for X = NH_2, OH, and F, and are similar to their MP2/6-31+G(d,p) results for X = PH_2, SH, and Cl.[13] For the π-donor substituents X, the C−X bond lengths in the substituted methanes generally increase with protonation, sometimes quite markedly, as observed previously by Yáñez[9] and Boyd.[11−13] Protonation of the π-donor group X serves to reduce the hyperconjugative electron donation from X to the $\pi^*(CH_3)$ orbital, thereby reducing the extent of double-bond character in the C−X bond. Also, as noted above, protonation of the heteroatom serves to increase the contribution of the no-bond resonance structure, $^+CH_3$:XH (**2b**), to the C−X bond. This behavior can be readily understood from a consideration of the electron affinities (EA) of X and ionization energies (IE) of XH (Table 2). In the unprotonated molecule (CH_3X), the C−X bond is best described by the bonded resonance structure **1a** because the IE of $^\bullet CH_3$ is considerably greater than the EA of X. The two electrons forming the bond will be shared by the CH_3 group and X, thus making the no-bond resonance structure **1b** relatively unimportant. In the protonated molecule (CH_3XH^+), the IE of XH becomes comparable to, or in some cases (e.g., X = F) much greater than, the IE of $^\bullet CH_3$. This increases the contribution of the no-bond resonance structure **2b** to the C−X bond, resulting in a longer bond length than in the unprotonated species. The only exception to this behavior occurs for the PH_2 substituent.

(25) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(26) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(27) Values taken from the following: Structure Data of Free Polyatomic Molecules. *Landolt-Börnstein, New Series*; Vol. II/23 (polyatomic molecules): Kuchitsu, K., Ed.; 1995, and earlier compendia in the series as referenced in II/23.

(28) See, for example: Radom, L. *Prog. Theor. Org. Chem.* **1981**, *3*, 1.

(29) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; D. Reidel: Dordrecht, 1986; p 1.

(30) (a) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469. (b) Bernardi, F.; Epiotis, N. D. In *Applications of Molecular Orbital Theory in Organic Chemistry*; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1977; p 47. (c) Crans, D.; Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1980**, *21*, 3681.

In this case, because the IE of PH_3 is only slightly greater than that of $^{\bullet}CH_3$ (9.87 eV vs 9.77 eV) (Table 2), the character of the C−P bond in $CH_3-PH_3^+$ will still be dominated by the bonded resonance structure (**2a**), leading to a C−P bond length that is shorter than in CH_3-PH_2.

The molecules with π-acceptor substituents (X = CN, CHO, and NO_2) all exhibit shortening of the C−X bond upon protonation. In the unprotonated species, hyperconjugative donation from a $\pi(CH_3)$ orbital to a $\pi^*(X)$ orbital strengthens the C−X bond. Protonation of X lowers the energy of the $\pi^*(X)$ orbital, thereby enhancing the extent of the hyperconjugative interaction with $\pi(CH_3)$. This generally leads to a further shortening of the C−X bond relative to that in the unprotonated species. In cases where XH has a large ionization energy (e.g., X = CN), the opposing effect of an increased contribution from the no-bond resonance structure **2b** becomes important so that the overall effect is quite small.

Similar arguments can be used to rationalize the effect of protonation on the C−X bond lengths in the $^{\bullet}CH_2X$ radicals (Table 1). The C−X bonds can again be described as having two major resonance contributors:

$$^{\bullet}CH_2-X \leftrightarrow {}^{+}{}^{\bullet}CH_2 :X^-$$
3a **3b**

$$^{\bullet}CH_2-XH^+ \leftrightarrow {}^{+}{}^{\bullet}CH_2 :XH$$
4a **4b**

As with the closed-shell species, the unprotonated radicals $^{\bullet}CH_2X$ bearing π-donor substituents X are dominated by the bonded resonance structure **3a**. Following protonation, however, there is an increase in the contribution of the no-bond resonance structure **4b** to the description of the C−X bond in such radicals because the XH molecules have ionization energies similar to or even higher than that of CH_2. There is a consequent increase in the C−X bond length. The only exception to this trend again occurs for X = PH_2, arising because the IE of PH_3 is considerably lower than that of CH_2. This results in the bonded resonance structure **4a** remaining the dominant contributor to the C−P bond.

The π-acceptor substituents CN, CHO, and NO_2 all permit efficient delocalization of the unpaired electron in $^{\bullet}CH_2X$ and thus the C−X bond in each case will have partial-double-bond character. This conjugative interaction is enhanced following protonation and as a result the C−X bond is shortened (as was also noted for the closed-shell systems).

Changes in C−X Bond Length vs X. The changes in C−X bond lengths across the first and second rows of the periodic table show opposite behavior depending on whether the molecules are unprotonated or protonated (Table 1). For the unprotonated molecules (CH_3X), the C−X bond gets shorter as one goes from left to right in the table, whereas for the protonated molecules (CH_3XH^+) the C−X bond lengthens. The shortening of the C−X bond across the first- and second-row substituents in neutral CH_3X molecules is well established and has been rationalized previously on the basis of electronegativity arguments:[9−13] the C−X bond shortens as the difference in electronegativity between CH_3 and X increases, i.e., the bond lengths are in the order X = NH_2 > OH > F and X = PH_2 > SH > Cl. For protonated molecules CH_3XH^+, the no-bond resonance structure **2b** becomes more important and the C−X bond length will increase as the contribution of this nonbonded structure increases. This contribution in turn will become more significant as the IE of XH increases. Thus, the C−X length will increase in the order X = NH_2 < OH < F and X = PH_2 < SH < Cl (Table 1).

Table 3. Calculated Homolytic and Heterolytic BDEs of CH_3X, $^{\bullet}CH_2X$, and Their Protonated Counterparts

	homolytic BDE[a]		heterolytic BDE[a]	
	C−X	C−XH^+	C−X	C−XH^+
CH_3NH_2	358.2	478.4	1226.3	437.7
$^{\bullet}CH_2NH_2$	429.8	483.5	1350.3	495.1
CH_3OH	391.5	552.7	1153.5	277.0
$^{\bullet}CH_2OH$	450.2	552.3	1264.4	328.8
CH_3OCH_3	359.4	452.6	1145.4	336.7
$^{\bullet}CH_2OCH_3$	418.3	456.9	1256.6	393.2
CH_3F	470.1	733.0	1077.3	123.7
$^{\bullet}CH_2F$	507.6	707.2	1167.1	150.3
CH_3PH_2	302.3	449.7	1124.7	440.2
$^{\bullet}CH_2PH_2$	352.7	468.9	1227.4	511.7
CH_3SH	313.4	401.0	1034.0	337.5
$^{\bullet}CH_2SH$	376.3	413.4	1149.2	402.2
CH_3Cl	353.6	483.6	948.8	199.6
$^{\bullet}CH_2Cl$	399.1	481.2	1046.6	249.4
CH_3Br	292.8	397.5	936.7	223.1
$^{\bullet}CH_2Br$	333.1	396.8	1029.3	274.7
CH_3CN	520.3	676.5	1079.6	455.2
$^{\bullet}CH_2CN$	578.0	714.9	1189.7	546.0
CH_3CHO	357.0	522.9	1267.2	602.0
$^{\bullet}CH_2CHO$	418.5	593.3	1380.9	724.8
CH_3NO_2	263.6	420.4	980.2	303.8
$^{\bullet}CH_2NO_2$	300.4	464.8	1069.2	400.5

[a] At 298 K in kJ mol^{-1}.

The results for the unprotonated free radicals $^{\bullet}CH_2X$ follow the trend set by their closed-shell counterparts, i.e., the C−X bond gets shorter as the electronegativity of X increases. The protonated free radicals $^{\bullet}CH_2XH^+$, however, show bond length changes that reflect two competing effects: first, the intrinsic tendency for the C−X bond to shorten as XH becomes more electronegative, and second, the tendency for the C−X bond to lengthen as the contribution of the no-bond structure **4b** increases, i.e., as the IE of XH increases. The net result of these two effects is a very slight shortening of the C−X bond in going from X = NH_2 to OH and from PH_2 to SH (by 0.003 and 0.002 Å, respectively), followed by a lengthening of the bond for the halogen substituents. It appears that the added significance of the nonbonded resonance structures in the two protonated free radicals $^{\bullet}CH_2OH_2^+$ and $^{\bullet}CH_2SH_2^+$ is insufficient to overcome the electronegativity increase of the XH group, resulting in the slight calculated bond shortening compared with $^{\bullet}CH_2NH_3^+$ and $^{\bullet}CH_2PH_3^+$.

Changes in C−X BDE Due to Protonation at X. The homolytic and heterolytic bond dissociation enthalpies (BDEs) for the C−X bond in the substituted methanes, methyl radicals, and their protonated counterparts, calculated at the G2 level of theory, are listed in Table 3. The most striking observation from Table 3 is the dramatic drop in heterolytic BDE for the protonated species. This behavior has been observed previously for the closed-shell systems by Boyd et al.[11−13] Heterolytic cleavage of a C−X bond in a protonated molecule CH_3XH^+ does not result in the unfavorable charge separation that occurs for a neutral molecule CH_3X, and thus is associated with a smaller heterolytic BDE. The effect will be largest for substituents XH having large IEs. Indeed, the lowest heterolytic BDE for protonated closed-shell species is exhibited by CH_3FH^+ and for protonated free radicals by $^{\bullet}CH_2FH^+$ (Table 3).

The homolytic C−X BDEs exhibit the opposite trend to the heterolytic values, i.e., they tend to increase upon protonation. This behavior for closed-shell species has been rationalized by Yáñez et al.[8−10] and Boyd et al.[11−13] in terms of the increased

Table 4. Comparison of Calculated and Experimental Radical Stabilization Energies for $^{\bullet}CH_2X$ Radicals and Their Protonated Forms, $^{\bullet}CH_2XH^+$ [a]

X	RSE($^{\bullet}CH_2X$) G2	RSE($^{\bullet}CH_2X$) exptl[b]	RSE($^{\bullet}CH_2XH^+$) G2
NH_2	46.9	38.3 ± 9[c]	−19.7
OH	33.9	35.3 ± 7[d]	−25.2
OCH_3	34.1	50 ± 5	−20.5
F	12.7	6.3 ± 9	−50.6
PH_2	25.6		−5.6
SH	38.1	49.1 ± 10[e]	−12.4
Cl	20.7	21.0 ± 4.1[f]	−27.2
Br	15.5	8 ± 3	−25.5
CN	33.0	50 ± 11	13.7
CHO	36.7		45.7
NO_2	12.0		19.6

[a] Enthalpies for the reactions 2 and 3, respectively, at 298 K in kJ mol^{-1}. [b] Using values from Lias et al.[3] unless otherwise stated. [c] Griller and Lossing[34] give 41.4 kJ mol^{-1} while Bordwell et al.[35] give 43.1 kJ mol^{-1}. [d] Using $\Delta_f H°_{298}(^{\bullet}CH_2OH) = -16.6 \pm 0.9$ kJ mol^{-1} (Ruscic and Berkowitz).[36] [e] Using $\Delta_f H°_{298}(^{\bullet}CH_2SH) = 150.0 \pm 8.4$ kJ mol^{-1} (Ruscic and Berkowitz).[37] [f] Using $\Delta_f H°_{298}(^{\bullet}CH_2Cl) = 117.3 \pm 3.1$ kJ mol^{-1} (Seetula).[38]

electronegativity of the X group following protonation: the homolytic BDE of CH_3X increases upon protonation of X since protonation increases the electronegativity difference between CH_3 and X.

In many of the cases in Table 3, the heterolytic BDEs in the protonated molecules and protonated free radicals are actually lower than the corresponding homolytic BDEs. This is a consequence of the added importance of the no-bond resonance structures $^{+}CH_3$:XH and $^{+\bullet}CH_2$:XH in describing the C−X bond. As was observed for the C−X bond lengths, however, there are a small number of cases in which this does not occur, specifically $^{\bullet}CH_2NH_3^+$, $^{\bullet}CH_2PH_3^+$, CH_3CHOH^+, and $^{\bullet}CH_2$-$CHOH^+$. In each of these cases, the IE of XH (XH = NH_3, PH_3, or CHOH, see Table 2) is similar to or lower than that of CH_3 or CH_2, and hence the C−X bonds in these systems are still influenced to a large extent by the bonded resonance structure.

Stabilization Energies of the $^{\bullet}CH_2X$ Radicals and Their Protonated Forms $^{\bullet}CH_2XH^+$. To evaluate the effect of substituents on the stability of the $^{\bullet}CH_2X$ radicals and their X-protonated forms, we have calculated radical stabilization energies (RSEs),[19,29,31−33] as defined by the enthalpy changes for the following isodesmic reactions:

$$^{\bullet}CH_2X + CH_4 \rightarrow CH_3X + {}^{\bullet}CH_3 \quad (2)$$

$$^{\bullet}CH_2XH^+ + CH_4 \rightarrow CH_3XH^+ + {}^{\bullet}CH_3 \quad (3)$$

The calculated RSEs are compared with available experimental values[34−38] in Table 4. Agreement between theoretical and experimental RSEs is generally quite reasonable but discrepancies of up to 17 kJ mol^{-1} may be seen. We note that the experimental uncertainties are not insignificant and that, for strongly spin-contaminated systems (e.g., X = CN), the G2 values may be less reliable than normal.[23]

Table 5. Comparison of Calculated and Experimental C−H Bond Dissociation Enthalpies in CH_3X and CH_3XH^+ [a]

X	BDE(H−CH_2X) G2	BDE(H−CH_2X) exptl[b]	BDE(H−CH_2XH^+) G2
H	442.6	438.3	
NH_2	395.7	400.0 ± 8.4	462.2
OH	408.7	403 ± 2[c]	467.8
OCH_3	408.5	389 ± 4	463.1
F	429.9	432.0 ± 8.4	493.1
PH_2	417.0		448.2
SH	404.5	390.9 ± 8.4[d]	455.0
Cl	421.9	417.3 ± 3.1[e]	469.8
Br	427.0	430 ± 1	468.1
CN	409.6	389 ± 10	428.9
CHO	405.9		396.9
NO_2	430.6	407.5[f]	422.9

[a] In kJ mol^{-1} at 298 K. [b] Using $\Delta_f H°_{298}$values from Lias et al.[3] unless otherwise stated. [c] Using $\Delta_f H°_{298}(^{\bullet}CH_2OH) = -16.6 \pm 0.9$ kJ mol^{-1} (Ruscic and Berkowitz).[36] [d] Using $\Delta_f H°_{298}(^{\bullet}CH_2SH) = 150.0 \pm 8.4$ kJ mol^{-1} (Ruscic and Berkowitz).[37] [e] Using $\Delta_f H°_{298}(^{\bullet}CH_2Cl) = 117.3 \pm 3.1$ kJ mol^{-1} (Seetula).[38] [f] Bordwell and Satish.[40]

Factors governing the stabilization of $^{\bullet}CH_2X$ radicals are well documented,[29−31,33,39] and include the n(X) → p(C) interaction when X is a π-donor substituent, and delocalization of the unpaired electron when X is a π-acceptor substituent.[28−30]

The RSEs for the protonated radicals with π-donor substituents are all negative, i.e., the stabilization is less in the $^{\bullet}CH_2$-XH^+ radicals than in CH_3XH^+ (Table 4). Protonation of X produces a smaller n(X) → p(C) interaction because of the lowering in energy of the lone-pair orbital. For the π-acceptor substituents (X = CN, HCO, and NO_2), delocalization of the unpaired electron is enhanced in the protonated forms of the radicals, and hence $^{\bullet}CH_2XH^+$ are stabilized to a greater extent than CH_3XH^+.

The absolute C−H BDE values in CH_3X and CH_3XH^+ are listed in Table 5. For all the π-donor substituents and CN, the C−H BDEs are larger for the protonated species than for the unprotonated species, whereas for X = CHO and NO_2, the reverse is true.

Proton Affinities of CH_3X and $^{\bullet}CH_2X$. Calculated G2 gas-phase proton affinities (PAs) of CH_3X and $^{\bullet}CH_2X$ are listed in Table 6. Agreement with the values quoted in Lias et al.[3] is quite variable, but there is considerable improvement when more recent experimental values are used, such as those of Szulejko and McMahon[5,44]and Audier and co-workers,[42,43] or those listed in a recent compendium by Hunter and Lias.[7]

Comparison of the PAs of $^{\bullet}CH_2X$ radicals with the PAs of the corresponding CH_3X molecules shows that for π-donor substituents, the proton affinities are 30−70 kJ mol^{-1} lower in the radicals than in the corresponding closed-shell molecules (Table 6). This behavior may be rationalized by noting that the n(X) → p(C) interaction in the radicals makes the lone pair

(31) Leroy, G.; Sana, M.; Wilante, C.; Nemba, R. M. *J. Mol. Struct.* **1989**, *198*, 159.
(32) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062.
(33) Hawari, J. A.; Kanabus-Kaminska, J. M.; Wayner, D. D. M.; Griller, D. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; D. Reidel: Dordrecht, 1986; p 91.
(34) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.
(35) (a) Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623. (b) Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 7558.
(36) Ruscic, B.; Berkowitz, J. *J. Phys. Chem.* **1993**, *97*, 11451.
(37) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1992**, *97*, 1818.
(38) Seetula, J. A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3069.
(39) (a) Sana, M.; Leroy, G. *J. Mol. Struct. (Theochem)* **1991**, *226*, 307. (b) Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct. (Theochem)* **1991**, *228*, 37. (c) Sana, M.; Leroy, G.; Hilali, M.; Nguyen, M. T.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1992**, *190*, 551.
(40) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1994**, *116*, 8885.
(41) (a) Fox, G. L.; Schlegel, H. B. *J. Phys. Chem.* **1992**, *96*, 298. (b) Walch, S. P. *J. Chem. Phys.* **1993**, *98*, 3076.
(42) Audier, H. E.; Fossey, J.; Mourgues, P.; Leblanc, D.; Hammerum, S. *Int. J. Mass Spectrom. Ion Proc.* **1996**, *157/158*, 275.
(43) Mourgues, P.; Audier, H. E.; Leblanc, D.; Hammerum, S. *Org. Mass Spectrom.* **1993**, *28*, 1098.
(44) Glukhovtsev, M. N.; Szulejko, J. E.; McMahon, T. B.; Gauld, J. W.; Scott, A. P.; Smith, B. J.; Pross, A.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 13099.

Table 6. Comparison of Calculated and Experimental Proton Affinities[a] of Substituted Methanes and Substituted Methyl Radicals

	PA			
	G2	Lias et al.[b]	Hunter and Lias[c]	other data
CH_3NH_2	900.9	896	899	901.2[d]
$^{\bullet}CH_2NH_2$	834.3	>848 ± 8	849.4	>839.6,[e] 829[f]
CH_3OH	753.2	761	754.3	760.2[d]
$^{\bullet}CH_2OH$	695.3		695	695 ± 8,[g] 695 ± 4,[f] 698 ± 9[h]
CH_3OCH_3	792.0	804	792.0	793.3[d]
$^{\bullet}CH_2OCH_3$	739.9		756.1	751 ± 6[f]
CH_3F	597.6	605	598.8	597.1[i]
$^{\bullet}CH_2F$	534.3	589 ± 8		532 ± 23[j]
CH_3PH_2	855.0	854	852.0	
$^{\bullet}CH_2PH_2$	823.8			797 ± 13[k]
CH_3SH	776.3	784	773.4	
$^{\bullet}CH_2SH$	725.8		735.1	764 ± 8,[l] <732.2[m]
CH_3Cl	649.7	682	648.2	650.6[i]
$^{\bullet}CH_2Cl$	601.1	631		605[n]
CH_3Br	663.3	693	664.2	662.3[i]
$^{\bullet}CH_2Br$	622.3	714		
CH_3CN	780.1	817	779.2	
$^{\bullet}CH_2CN$	763.0			
CH_3CHO	770.2	781	769.1	
$^{\bullet}CH_2CHO$	779.8		774.0	
CH_3NO_2	745.6		752.8	
$^{\bullet}CH_2NO_2$	752.1			

[a] Values given correspond to protonation at X, at 298 K in kJ mol^{-1}. [b] Either listed in, or derived using $\Delta_fH°_{298}$ values from Lias et al.[3] [c] Values listed by Hunter and Lias.[7] [d] Szulejko and McMahon.[5] [e] Using $\Delta_fH°_{298}(^{\bullet}CH_2NH_2)$ = 150.6 kJ mol^{-1} (Griller and Lossing)[34] and $\Delta_fH°_{298}(^{\bullet}CH_2NH_3^+) \leq$ 841 kJ mol^{-1} (Lias et al.).[3] [f] Audier et al.[42] [g] Mourgues et al.[43] [h] Using $\Delta_fH°_{298}(^{\bullet}CH_2OH) = -16.6 \pm 0.9$ kJ mol^{-1} (Ruscic and Berkowitz).[36] [i] Glukhovtsev et al.[44] [j] Calculated using $\Delta_fH°_{298}(^{\bullet}CH_2FH^+)$ = 965 ± 15 kJ mol^{-1} (J. L. Holmes, private communication, cited by Gauld et al.)[17] and $\Delta_fH°_{298}(^{\bullet}CH_2F) = -33 \pm 8$ kJ mol^{-1} (Lias et al.).[3] [k] Schweighofer et al.[45] [l] Using $\Delta_fH°_{298}(^{\bullet}CH_2SH)$ = 150.0 ± 8.4 kJ mol^{-1} (Ruscic and Berkowitz)[37] and $\Delta_fH°_{298}(^{\bullet}CH_2SH_2^+)$ = 916 kJ mol^{-1} (Lias et al.).[3] [m] Chou et al.[46] [n] Using $\Delta_fH°_{298}(^{\bullet}CH_2Cl)$ = 117.3 ± 3.1 kJ mol^{-1} (Seetula)[38] and $\Delta_fH°_{298}(^{\bullet}CH_2ClH^+)$ = 1029 kJ mol^{-1} (Lias et al.).[3]

less available for protonation. For the $^{\bullet}CH_2CHO$ and $^{\bullet}CH_2NO_2$ radicals, the orbital that accepts the incoming proton lies in the plane of the radicals and is relatively unaffected by the change in going from CH_3X to $^{\bullet}CH_2X$.

Heats of Formation. We compare the calculated G2 heats of formation for the CH_3X, CH_3XH^+, $^{\bullet}CH_2X$, and $^{\bullet}CH_2XH^+$ systems with available experimental data in Table 7. Closely related values for some of these systems have been reported elsewhere.[17] The agreement between theory and the most recent experimental values is generally reasonable with 25 of the 38 comparisons lying within the G2 target of ±10 kJ mol^{-1} and only three differences (namely those for $^{\bullet}CH_2BrH^+$, $^{\bullet}CH_2CN$, and $^{\bullet}CH_2CNH^+$) being greater than 20 kJ mol^{-1}.

Table 7. Comparison of Calculated and Experimental Heats of Formation[a]

	$\Delta_fH°_{298}$		
	G2	Lias et al.[3]	other exptl data
CH_3NH_2	−22.8	−23.0 ± 0.4	
$CH_3NH_3^+$	606.9	611	
$^{\bullet}CH_2NH_2$	154.3[b]	159 ± 8	150.6[c]
$^{\bullet}CH_2NH_3^+$	851.2	<841	
CH_3OH	−206.7	−201.6 ± 0.2	
$CH_3OH_2^+$	568.6	567	
$^{\bullet}CH_2OH$	−16.0	−25.9 ± 6	−16.6 ± 0.9,[d] −16.6 ± 1.3[e]
$^{\bullet}CH_2OH_2^+$	819.5	815 ± 8	818.4 ± 4[f]
CH_3OCH_3	−192.4	−184.0 ± 0.5	*g*
$(CH_3)_2OH^+$	546.3	542	
$^{\bullet}CH_2OCH_3$	−2.0	−13 ± 4	−5.4 ± 8,[g,h]
$^{\bullet}CH_2O(H^+)CH_3$	791.4		
CH_3F	−244.5	−247.0	*i*
CH_3FH^+	688.7	678	686[j]
$^{\bullet}CH_2F$	−32.6	−33 ± 8	−31.8 ± 8.4[k]
$^{\bullet}CH_2FH^+$	963.8	908.0	965 ± 15[l]
CH_3PH_2	−19.4	−18	
$CH_3PH_3^+$	656.4	658	
$^{\bullet}CH_2PH_2$	179.6		
$^{\bullet}CH_2PH_3^+$	886.6		908 ± 13[m]
CH_3SH	−20.4	−22.9 ± 0.6	
$CH_3SH_2^+$	733.9	723	
$^{\bullet}CH_2SH$	166.1		150.0 ± 8.4[n]
$^{\bullet}CH_2SH_2^+$	970.9	916	> 950[o]
CH_3Cl	−84.6	−82.0	
CH_3ClH^+	796.2	767	798[j]
$^{\bullet}CH_2Cl$	118.4	130	117.3 ± 3.1,[p] 116 ± 8[q]
$^{\bullet}CH_2ClH^+$	1048.0	1029.0	
CH_3Br	−34.0	−38.1 ± 1.3	−34.3 ± 0.8[r]
CH_3BrH^+	833.5	800	831[j]
$^{\bullet}CH_2Br$	175.1	174	168 ± 8[q]
$^{\bullet}CH_2BrH^+$	1083.6	990	
CH_3CN	75.7	74 ± 1	
CH_3CNH^+	825.6	817	
$^{\bullet}CH_2CN$	267.2	245 ± 10	243 ± 12,[s] 250 ± 8[t]
$^{\bullet}CH_2CNH^+$	1036.5	1004	
CH_3CHO	−174.3	−165.8 ± 0.4	
CH_3CHOH^+	589.3	583	
$^{\bullet}CH_2CHO$	16.6		
$^{\bullet}CH_2CHOH^+$	768.2		
CH_3NO_2	−86.7	−74.8 ± 1	
$CH_3NO_2H^+$	700.4	705	
$^{\bullet}CH_2NO_2$	125.9		
$^{\bullet}CH_2NO_2H^+$	905.3		

[a] Values at 298 K in kJ mol^{-1}. [b] This value is different from the G2 value quoted by Armstrong et al.[47] due to an erroneous G2 total energy quoted in their paper. [c] Griller and Lossing.[34] [d] Ruscic and Berkowitz.[36] [e] Dóbé et al.[48] [f] Using $\Delta_fH°_{298}(^{\bullet}CH_2OH) = -16.6 \pm 0.9$ kJ mol^{-1} (Ruscic and Berkowitz)[36] and PA($^{\bullet}CH_2OH$) = 695 ± 8 kJ mol^{-1} (Audier et al.).[42] [g] G2 value of −184.1 kJ mol^{-1} for CH_3OCH_3 and +3.8 kJ mol^{-1} for $^{\bullet}CH_2OCH_3$ using isodesmic reactions (Good and Francisco).[49] [h] Holmes and Lossing.[50] [i] Theoretical value of −240 ± 5 kJ mol^{-1} by Espinosa-Garcia.[51] [j] Using experimental PAs of the halomethanes (Glukhovtsev et al.).[44] [k] Pickard and Rogers.[52] [l] J. L. Holmes (private communication as quoted by Gauld et al.).[17] [m] Schweighofer et al.[45] [n] Ruscic and Berkowitz[37] corrected to 298 K. [o] Chou et al.[46] [p] Seetula.[38] [q] Holmes and Lossing.[53] [r] Ferguson et al.[54] [s] Holmes and Mayer.[55] [t] Matimba et al.[56]

Concluding Remarks

Several important points emerge from this study.

(1) As is well established, hyperconjugative interactions in CH_3X molecules can take the form of (a) hyperconjugative

(45) Schweighofer, A.; Chou, P. K.; Thoen, K. K.; Nanayakkara, V. J.; Keck, H.; Kuchen, W.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1996**, *118*, 11893.
(46) Chou, P. K.; Smith, R. L.; Chyall, L. J.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1995**, *117*, 4374.
(47) Armstrong, D. A.; Rauk, A.; Yu, D. *J. Am. Chem. Soc.* **1993**, *115*, 666.
(48) Dóbé, S.; Bérces, T.; Turányi, T.; Márta, F.; Grussdorf, J.; Temps, F.; Wagner, H. Gg. *J. Phys. Chem.* **1996**, *100*, 19864.
(49) Good, D. A.; Francisco, J. S. *Chem. Phys. Lett.* **1997**, *266*, 512.
(50) Holmes, J. L.; Lossing, F. P. *Int J. Mass Spectrom. Ion Proc.* **1984,** *58*, 113.
(51) Espinosa-Garcia, J. *Chem. Phys. Lett.* **1996**, *250*, 71.
(52) Pickard, J. M.; Rodgers, A. S. *Int. J. Chem. Kinet.* **1983**, *15*, 569.
(53) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343.
(54) Ferguson, K. C.; Okafo, E. N.; Whittle, E. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 295.
(55) Holmes, J. L.; Mayer, P. M. *J. Phys. Chem.* **1995**, *99*, 1366.
(56) Matimba, H. E. K.; Crabbendam, A. M.; Ingemann, S.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Proc.* **1992**, *114*, 85.

electron donation from an n(X) orbital to a $\pi^*(CH_3)$ orbital in the case of π-donor substituents X or (b) hyperconjugative electron donation from a $\pi(CH_3)$ orbital to a $\pi^*(X)$ orbital in the case of π-acceptor substituents X.

(2) For π-donor substituents, protonation of CH_3X generally leads to a lengthening of the C−X bond due to an increase in the contribution of the no-bond resonance structure $^+CH_3$:XH. This is accompanied by a sharp decrease in the heterolytic BDE of the C−X bond, to a value that is often lower than the corresponding homolytic BDE. Protonation also diminishes the hyperconjugative electron donation from n(X) to $\pi^*(CH_3)$, thereby increasing the C−H bond strengths.

(3) For π-acceptor substituents, protonation of CH_3X enhances the hyperconjugative electron donation from $\pi(CH_3)$ to $\pi^*(X)$, thereby shortening the C−X bond relative to that in the unprotonated species. As with the π-donor substituents, protonation also serves to increase the contribution of the no-bond resonance structure $^+CH_3$:XH, resulting in lower heterolytic BDEs.

(4) Conjugative interactions in $^\bullet CH_2X$ radicals can take the form of (a) two-center three-electron interactions involving the p(C) orbital and an n(X) orbital in the case of π-donor substituents X or (b) three-center three-electron interactions involving the p(C), π(X), and π^*(X) orbitals in the case of π-acceptor substituents X.

(5) For π-donor substituents, protonation of X in $^\bullet CH_2X$ generally leads to a lengthening of the C−X bond due to an increase in the contribution of the no-bond resonance structure $^+CH_2$:XH as for the CH_3X molecules. This is again accompanied by a marked decrease in the heterolytic BDE of the C−X bond, to a value that is often lower than the corresponding homolytic BDE. Because protonation diminishes the degree of interaction between the p(C) and n(X) orbitals, the radical stabilization energies (RSEs) calculated for the protonated radicals are negative, i.e., the $^\bullet CH_2XH^+$ radicals are destabilized.

(6) For π-acceptor substituents, protonation of X in $^\bullet CH_2X$ increases the conjugative interaction between p(C) and the π-(X) system, resulting in a reduction in the C−X length relative to that in the unprotonated radicals. Because protonation increases the degree of interaction between the p(C), π(X), and π^*(X) orbitals, the RSEs calculated for the protonated radicals are positive, i.e., the $^\bullet CH_2XH^+$ radicals are stabilized.

(7) The proton affinities of $^\bullet CH_2X$ radicals substituted by π-donor groups are found to be between 30 and 70 kJ mol^{-1} lower than those for their closed-shell counterparts. This can be understood in terms of a diminished availability of the lone-pair orbital resulting from interaction of n(X) with the p(C) orbital. For X = CHO and NO_2, protonation occurs in a plane orthogonal to that of the p(C) orbital and thus the PA is less influenced by the changes that occur in going from CH_3X to $^\bullet CH_2X$.

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Supporting Information Available: Total G2 energies and values of $\langle S^2 \rangle$ (Table S1) and GAUSSIAN archive entries for the MP2(full)/6-31G(d) optimized geometries (Table S2) (9 pages). See any current masthead page for ordering and Internet access instructions.

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