Bond Dissociation Energies and Radical Stabilization Energies Associated with Substituted Methyl Radicals

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Bond dissociation energies (BDEs) and radical stabilization energies (RSEs) associated with a series of 22 monosubstituted methyl radicals ($^\bullet CH_2X$) have been determined at a variety of levels including, CBS-RAD, G3(MP2)-RAD, RMP2, UB3-LYP and RB3-LYP. In addition, W1′ values were obtained for a subset of 13 of the radicals. The W1′ BDEs and RSEs are generally close to experimental values and lead to the suggestion that a small number of the experimental estimates warrant reexamination. Of the other methods, CBS-RAD and G3(MP2)-RAD produce good BDEs. A cancellation of errors leads to reasonable RSEs being produced from all the methods examined. CBS-RAD, W1′ and G3(MP2)-RAD perform best, while UB3-LYP performs worst. The substituents (X) examined include lone-pair-donors (X = NH_2, OH, OCH_3, F, PH_2, SH, Cl, Br and $OCOCH_3$), π-acceptors (X = BH_2, $CH{=}CH_2$, $C{\equiv}CH$, C_6H_5, CHO, COOH, $COOCH_3$, CN and NO_2) and hyperconjugating groups (CH_3, CH_2CH_3, CF_3 and CF_2CF_3). All substituents other than CF_3 and CF_2CF_3 result in radical stabilization, with the vinyl ($CH{=}CH_2$), ethynyl ($C{\equiv}CH$) and phenyl (C_6H_5) groups predicted to give the largest stabilizations of the π-acceptor substituents examined and the NH_2 group calculated to provide the greatest stabilization of the lone-pair-donor groups. The substituents investigated in this work stabilize methyl radical centers in three general ways that delocalize the odd electron: π-acceptor groups (unsaturated substituents) delocalize the unpaired electron into the π-system of the substituent, lone-pair-donor groups (heteroatomic substituents) bring about stabilization through a three-electron interaction between a lone pair on the substituent and the unpaired electron at the radical center, while alkyl groups stabilize radicals via a hyperconjugative mechanism. Polyfluoroalkyl substituents are predicted to slightly destabilize a methyl radical center by inductively withdrawing electron density from the electron-deficient radical center.

1. Introduction

The effect of substituents on the stability of free radicals is important in understanding the nature of reactions involving radicals as reactants, products or intermediates. In particular, the stabilities of substituted methyl radicals ($^\bullet CH_2X$) have been widely investigated, both experimentally[1] and theoretically.[2,3]

A measure of the stability of a substituted methyl radical ($^\bullet CH_2X$) is provided by the C−H bond dissociation energy (BDE) of the corresponding substituted methane (CH_3X). This is given by the enthalpy change of reaction 1:

$$CH_3X \rightarrow {}^\bullet CH_2X + {}^\bullet H \qquad (1)$$

Stabilization energies relative to $^\bullet CH_3$ are often referred to as radical stabilization energies (RSEs) and are given by the difference between the C−H bond dissociation energy in methane and the C−H BDE in the substituted methane (CH_3X):

$$\mathrm{RSE}({}^\bullet CH_2X) = \mathrm{BDE}(CH_4) - \mathrm{BDE}(CH_3X) \qquad (2)$$

This is equivalent to the enthalpy change of the isodesmic[4] reaction 3:

$$CH_4 + {}^\bullet CH_2X \rightarrow {}^\bullet CH_3 + CH_3X \qquad (3)$$

Defined in this way, a positive RSE indicates that the radical $^\bullet CH_2X$ is stabilized relative to $^\bullet CH_3$, resulting in a smaller C−H BDE in CH_3X than in CH_4.

In previous work,[3] we investigated the performance of a variety of theoretical methods for the calculation of RSE values of six substituted methyl and vinyl radicals. We found that the commonly used UMP procedure, and to a lesser extent UHF and PMP, performed poorly for radicals with significant spin contamination in their wave functions. On the other hand, RSEs calculated with RMP2/6-311+G(2df,p) single-point energies on RMP2/6-31G(d) or B3-LYP/6-31G(d) optimized geometries were found both to be relatively computationally cheap and generally good (yielding RSE values within 7 kJ mol^{-1} of benchmark results).

Since previous extensive studies of bond dissociation energies and radical stabilization energies have often used methods such as UMP, which do not always perform well, it is of interest to carry out a systematic study of RSEs with more reliable procedures. In this paper, we extend our previous investigations of RSEs by including a discussion of BDEs, by substantially broadening the range of radicals studied, and by including an assessment of additional theoretical procedures. We calculate BDE and RSE values associated with 22 substituted methyl radicals $^\bullet CH_2X$ (X = NH_2, OH, OCH_3, F, CH_3, CH_2CH_3, CF_3, CF_2CF_3, PH_2, SH, Cl, Br, BH_2, $CH{=}CH_2$, $C{\equiv}CH$, C_6H_5, CHO, COOH, $COOCH_3$, $OCOCH_3$, CN and NO_2). The methods used include UB3-LYP/6-311+G(3df,2p), RB3-LYP/6-311+G(3df,2p), RMP2/6-311+G(2df,p), G3(MP2)-RAD, CBS-RAD and, for a subset of these radicals, W1′.

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2. Theoretical Procedures

Standard ab initio molecular orbital theory[4] and density functional theory[5] calculations were carried out with the GAUSSIAN 94,[6] GAUSSIAN 98,[7] MOLPRO 98.1[8] and MOLPRO 2000.1[9] computer programs. Calculations on radicals[10] were performed either with a restricted-open-shell reference wave function, signified with an "R" prefix, as for RMP2,[11] or with an unrestricted-open-shell wave function, designated with a "U" prefix. The frozen-core (fc) approximation was employed in all calculations. Bond dissociation energies were calculated as the enthalpy change for reaction 1, while radical stabilization energies were evaluated as the enthalpy change of reaction 3. Unless otherwise noted, the calculated BDEs and RSEs were corrected with scaled (by 0.9806) UB3-LYP/6-31G(d) zero-point vibrational energy (ZPVE) values.[12]

Recently, DiLabio et al.[2s,t,w] have successfully applied restricted-open-shell DFT methods to the prediction of bond dissociation energies. Although it has been argued[13] that DFT calculations on open-shell systems should be performed with spin-unrestricted methods, it is of interest to examine the performance of both the RB3-LYP/6-311+G(3df,2p)//RB3-LYP/6-31G(d) and UB3-LYP/6-311+G(3df,2p)//UB3-LYP/6-31G(d) procedures in evaluating BDEs and RSEs of the present investigation.

We have noted previously[3] that RMP2/6-311+G(2df,p) single-point energies on RMP2/6-31G(d) or UB3-LYP/6-31G(d) geometries perform well in predicting RSEs. The assessment of this level was extended to include the calculation of BDEs and RSEs for the 22 species in the present study.

BDEs and RSEs were also determined at the CBS-RAD(B3-LYP,B3-LYP)[14] and G3(MP2)-RAD levels of theory. CBS-RAD(B3-LYP,B3LYP) is a variation of CBS-Q[15] which makes use of B3-LYP/6-31G(d) optimized geometries and scaled (by 0.9806) ZPVEs[12] and replaces the QCISD(T) single-point energy with CCSD(T). The G3(MP2)-RAD procedure closely resembles G3(MP2)//B3-LYP[16a] except that (a) UMP2 is replaced by RMP2 in the basis-set-extension scheme and (b) QCISD(T) is replaced by URCCSD(T), as implemented in MOLPRO. We make use of the optimized[12] scaling factor for B3-LYP ZPVEs (0.9806) and corresponding HLC coefficients ($A = 9.682$, $B = 4.900$, $C = 9.801$ and $D = 1.996$ mhartrees),[16b] rather than those for standard G3(MP2)//B3-LYP.[16a] The G3(MP2)-RAD level essentially corresponds to URCCSD(T)/G3MP2large//B3-LYP/6-31G(d) + ZPVE energies, obtained using additivity approximations.

Finally, we have carried out W1′ calculations[17] in a number of cases to try to resolve apparent discrepancies between theory and experiment. The W1′ level of theory attempts to extrapolate to infinite basis set URCCSD(T) results, again with incorporation of ZPVE, and has been found in test calculations to give total atomization energies with a mean absolute deviation from experiment of 1.3 kJ mol^{-1}.

The RMP2/6-31G(d), RB3-LYP/6-31G(d) and UB3-LYP/6-31G(d) optimized geometries for the substituted methyl radicals ($^{\bullet}CH_2X$), and the corresponding substituted methanes (CH_3X), can be found in Tables S1, S2 and S3 of the Supporting Information, while relevant total energies are listed in Table S4.

3. Results and Discussion

A. Radical Geometries. Before discussing the calculated bond dissociation energies and radical stabilization energies associated with the substituted methyl radicals, it is useful to examine the broad features of the geometries of the radicals concerned.

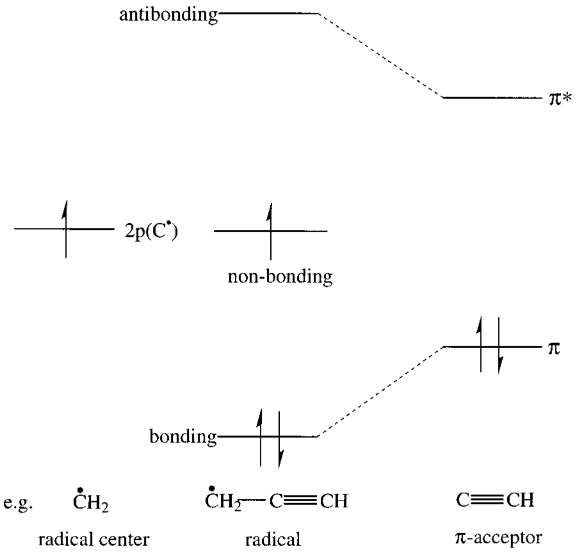

Figure 1. Orbital interaction diagram showing the net two-electron stabilization resulting from the interaction between the orbitals of a π-acceptor group and the unpaired electron at a carbon radical center.

Radicals with π-acceptor substituents (BH_2, $CH{=}CH_2$, $C{\equiv}CH$, C_6H_5, CHO, COOH, $COOCH_3$, CN and NO_2) all have planar radical centers, while radicals possessing lone pair substituents (NH_2, OH, OCH_3, F, PH_2, SH, Cl, Br and $OCOCH_3$) all have pyramidal (nonplanar) radical centers. These observations can be rationalized by noting that a radical is likely to adopt the geometry that maximizes stabilizing interactions between the formally singly occupied orbital corresponding to the unpaired electron at the radical center (and loosely referred to as the 2p(C$^{\bullet}$) orbital[18]) and the orbitals of the substituent, as detailed below.

Figure 1 displays the orbital interaction diagram showing the interaction between the 2p(C$^{\bullet}$) orbital and the π and π* orbitals of an unsaturated π-acceptor substituent.[19] These orbitals can interact, producing a stabilized doubly occupied bonding orbital, a singly occupied nonbonding orbital and a vacant antibonding orbital. The net result is a stabilizing two-electron bonding interaction in the substituted methyl radical, which will be favored by the greater overlap available in a planar structure.

The molecular orbital diagram for the interaction of a heteroatomic lone-pair-donor group with a carbon radical center is depicted in Figure 2.[19] In this case, the important orbital coupling is between the 2p(C$^{\bullet}$) orbital and a nonbonding orbital on the heteroatom corresponding to a lone pair. Pyramidalization of the radical center lowers the 2p(C$^{\bullet}$) orbital energy, which decreases the energy gap between this orbital and the lone pair orbital and thus increases the stabilization energy. However, this puckering also decreases the overlap between 2p(C$^{\bullet}$) and the heteroatom lone pair. It has been argued[19] that there is an optimum value of the overlap for stabilization of a methyl radical center by an adjacent heteroatomic lone-pair-donor group. Overlap values greater than this optimum lead to decreased stabilization. The observed pyramidal structures represent a balance between these various effects. The orientation of the 2p(C$^{\bullet}$) orbital and the heteroatom substituent is such that the 2p(C$^{\bullet}$) orbital and one of the lone pairs on the heteroatom are approximately in an antiperiplanar orientation relative to one another.

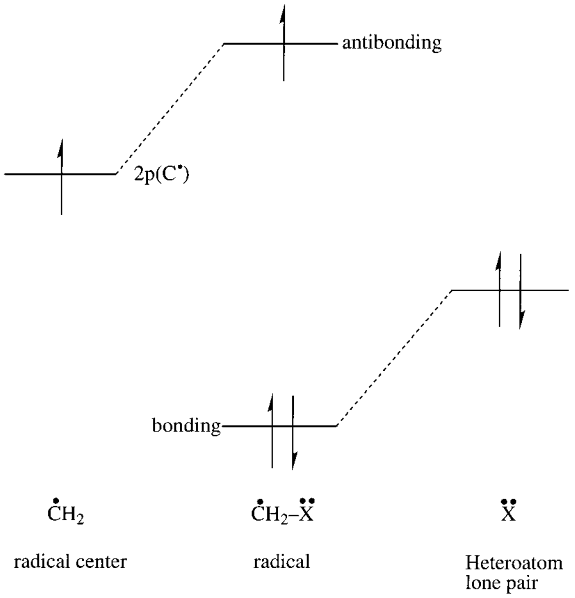

Figure 2. Orbital interaction diagram showing the three-electron interaction between the lone pair of a heteroatom and the unpaired electron at a carbon radical center.

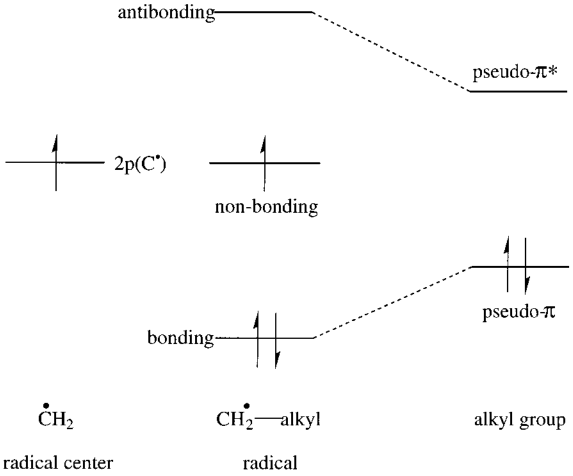

Figure 3. Orbital interaction diagram showing the net two-electron stabilization resulting from the hyperconjugative interaction between the orbitals of an alkyl group and the unpaired electron at a carbon radical center.

The alkyl and polyfluoroalkyl radicals ($^{\bullet}CH_2CH_3$, $^{\bullet}CH_2CH_2CH_3$, $^{\bullet}CH_2CF_3$ and $^{\bullet}CH_2CF_2CF_3$) have C_s symmetry, and the radical centers are slightly puckered. Figure 3 illustrates the nature of hyperconjugation taking place between a radical 2p($C^{\bullet}$) orbital and an alkyl substituent.[19] The 2p($C^{\bullet}$) orbital can interact both with pseudo π-type bonding and pseudo π^*-type antibonding orbitals on the alkyl group. As for π-acceptor substituents, this results in two electrons being located in a bonding molecular orbital and one electron being situated in a nonbonding orbital. The net effect is a two-electron bonding interaction. In the case of the ethyl radical, the 2p($C^{\bullet}$) orbital is oriented antiperiplanar to one of the β C−H bonds. For the 1-propyl radical, the minimum energy structure has the 2p($C^{\bullet}$) orbital positioned antiperiplanar to the C−CH_3 bond. The polyfluoroalkyl radicals also have the 2p($C^{\bullet}$) orbital oriented antiperiplanar to a β C−F ($^{\bullet}CH_2CF_3$) or β C−CF_3 ($^{\bullet}CH_2CF_2CF_3$) bond.

B. Bond Dissociation Energies. Bond dissociation energies for substituted methanes calculated at the UB3-LYP/6-311+G(3df,2p), RB3-LYP/6-311+G(3df,2p), RMP2/6-311+G(2df,p), G3(MP2)-RAD, CBS-RAD and W1′ levels are compared with experimental values[20,21] in Table 1. Also listed are mean deviations (MDs) and mean absolute deviations (MADs) from experimental values (e.g., MAD(Expt)) and from CBS-RAD values (e.g., MD(CBS-RAD)).

At our highest level of theory, W1′, we note general close agreement between theory and experiment, particularly for the BDEs of species that have small error bars ($<$5 kJ mol^{-1}). Slightly larger deviations (5.2−7.3 kJ mol^{-1}) are noted for $^{\bullet}CH_2SH$, $^{\bullet}CH_2C{\equiv}CH$ and $^{\bullet}CH_2CHO$, but theory and experiment still agree to within the given experimental uncertainties in these cases. Cyanomethyl and carboxymethyl radicals show the largest deviations between theory and experiment, 8.6 and 15.1 kJ mol^{-1}, respectively. The mean absolute deviation between W1′ and experiment, for those species with error bars of less than ±10 kJ mol^{-1}, is only 2.9 kJ mol^{-1}. In light of this close agreement, and noting the limitations often encountered in experimental determinations of bond dissociation energies,[1o] we have reasonable confidence in the W1′ values in the remaining cases.

W1′ is unfortunately not accessible for the larger systems listed in Table 1. We note, however, the excellent agreement between W1′ and CBS-RAD. The mean absolute deviation between W1′ and CBS-RAD is only 1.6 kJ mol^{-1}, while the largest absolute deviation is 3.3 kJ mol^{-1}. We therefore consider CBS-RAD a suitable secondary benchmark level for the present study. The largest deviations between CBS-RAD or W1′ and experiment occur for $^{\bullet}CH_2COOH$ and $^{\bullet}CH_2COOCH_3$. Although it is conceivable that these represent pathological cases for theory, experimental reexamination would seem desirable for these two radicals.

Interestingly, with the exception of W1′, all the other levels of theory give BDEs that are smaller than CBS-RAD values, with the result that the magnitudes of MD(CBS-RAD) and MAD(CBS-RAD) are identical in all these cases.

G3(MP2)-RAD demonstrates the smallest MAD (4.2 kJ mol^{-1}) from CBS-RAD, while bond dissociation energies determined from RMP2/6-311+G(2df,p) single-point calculations give the largest MAD(CBS-RAD) (16.7 and 16.8 kJ mol^{-1}). RB3-LYP/6-311+G(3df,2p) and UB3-LYP/6-311+G(3df,2p) give MADs between these extremes, with values of 8.6 and 14.1 kJ mol^{-1}, respectively.

Differences in the RMP2 bond dissociation energies, evaluated at RMP2 and UB3-LYP geometries, amount to less than 1 kJ mol^{-1} in all cases. It is also worth noting that geometries optimized at UB3-LYP/6-31G(d) and RB3-LYP/6-31G(d) are generally very similar.

There is an intriguing difference between the RB3-LYP and UB3-LYP BDEs (R − U) which correlates closely with the degree of spin contamination, as reflected in the $\langle S^2\rangle$ expectation values. In all cases, the RB3-LYP BDE is larger than the UB3-LYP values, corresponding to a higher total energy for the $^{\bullet}CH_2X$ radical. In the single case where $\langle S^2\rangle = 0.752$, the R − U difference is 3.1 kJ mol^{-1}. For $\langle S^2\rangle$ in the range 0.753−0.754, R − U lies between 4.0 and 4.4 kJ mol^{-1}. When $\langle S^2\rangle$ is 0.755−0.758, R − U is 4.8−5.1 kJ mol^{-1}. Finally, for $\langle S^2\rangle$ in the range 0.768−0.781, R − U lies between 7.6 and 10.1 kJ mol^{-1}.

C. Radical Stabilization Energies. As can be seen from eq 2, radical stabilization energies correspond to the difference between the calculated BDEs for methane and substituted methanes. If there is systematic cancellation of errors in the calculated BDEs, methods that perform less well in predicting

TABLE 1: Comparison of Calculated Bond Dissociation Energies with Experimental Values (0 K, kJ mol^{-1})

radical	UB3-LYP// UB3-LYP[a]	$\langle S^2\rangle$[b]	RB3-LYP// RB3-LYP[c]	RMP2// UB3-LYP[d]	RMP2// RMP2[e]	G3(MP2)-RAD	CBS-RAD	W1′	expt[f]
$^{\bullet}\mathrm{CH_3}$	424.6	0.754	428.8	413.0	413.0	426.4	433.0	432.3	432.2±0.4
$^{\bullet}\mathrm{CH_2NH_2}$	369.3	0.754	373.4	367.2	367.4	382.1	384.4	383.0	384.4±8.4
$^{\bullet}\mathrm{CH_2OH}$	385.3	0.754	389.4	380.8	381.2	394.8	398.6	397.0	396.3±1.3[g]
$^{\bullet}\mathrm{CH_2OCH_3}$	384.4	0.754	388.4	382.7	383.1	395.3	398.7	397.1	395.9
$^{\bullet}\mathrm{CH_2F}$	406.9	0.753	411.1	400.0	400.6	413.9	419.1	417.5	417.4±4.0
$^{\bullet}\mathrm{CH_2CH_3}$	404.4	0.754	408.8	399.3	399.4	412.3	417.3	416.4	415.7±1.6
$^{\bullet}\mathrm{CH_2CH_2CH_3}$	407.0	0.754	411.3	403.0		413.9	419.9		416.6±2.1
$^{\bullet}\mathrm{CH_2CF_3}$	425.7	0.754	430.0	421.1	421.3	434.1	440.1		439.4±4.6
$^{\bullet}\mathrm{CH_2CF_2CF_3}$	422.6	0.754	426.9	418.4		431.3			
$^{\bullet}\mathrm{CH_2PH_2}$	392.4	0.756	397.2	392.4	392.5	403.1	405.9		
$^{\bullet}\mathrm{CH_2SH}$	380.4	0.756	385.4	378.7	378.4	390.3	393.4	391.5	386.3±8.4
$^{\bullet}\mathrm{CH_2Cl}$	398.2	0.755	403.1	392.9	393.0	405.3	410.0	409.2	411.4±2.3
$^{\bullet}\mathrm{CH_2Br}$	404.8	0.755	409.6	398.3	399.0				418.1±4.2
$^{\bullet}\mathrm{CH_2BH_2}$	379.4	0.752	382.5	373.1	373.0	386.3	391.4		
$^{\bullet}\mathrm{CH_2CH{=}CH_2}$	345.4	0.778	355.5	335.9	336.0	355.7	359.3	362.0	358.5±4.3[h]
$^{\bullet}\mathrm{CH_2C{\equiv}CH}$	358.1	0.771	366.6	362.7	362.9	373.8	377.5	378.6	371.3±12.6[i]
$^{\bullet}\mathrm{CH_2C_6H_5}$	357.3	0.781	365.4	362.8		367.5	377.8		371.1±1.7
$^{\bullet}\mathrm{CH_2CHO}$	379.4	0.768	387.0	380.7	380.6	391.4	393.0	395.6	389.5±9.2
$^{\bullet}\mathrm{CH_2COOH}$	394.5	0.758	399.5	392.8	392.7	405.2	408.4	408.6	393.5±12.1[j]
$^{\bullet}\mathrm{CH_2COOCH_3}$	394.0	0.757	398.9	392.4		404.8	407.9		384.0±12.2[k]
$^{\bullet}\mathrm{CH_2OCOCH_3}$	396.7	0.754	400.9	395.9		408.3	412.1		
$^{\bullet}\mathrm{CH_2CN}$	380.4	0.768	388.5	381.8	382.1	394.5	395.8	399.1	390.5±4.4[l]
$^{\bullet}\mathrm{CH_2NO_2}$	403.7	0.757	408.6	401.1	401.1	414.8	419.0		
MD(expt)[m,n]	−11.2		−5.5	−14.8	−15.3	−2.1	2.5	2.2	
MAD(expt)[m,n]	11.2		5.5	14.8	15.3	3.6	2.7	2.9	
MD(CBS-RAD)[m]	−14.1		−8.6	−16.7	−16.8	−4.2		0.0	
MAD(CBS-RAD)[m]	14.1		8.6	16.7	16.8	4.2		1.6	

[a] UB3-LYP/6-311+G(3df,2p)//UB3-LYP/6-31G(d). [b] Spin-squared expectation value at the UB3-LYP/6-311+G(3df,2p)//UB3-LYP/6-31G(d) level. [c] RB3-LYP/6-311+G(3df,2p)//RB3-LYP/6-31G(d). [d] RMP2/6-311+G(2df,p)//UB3-LYP/6-31G(d). [e] RMP2/6-311+G(2df,p)//RMP2/6-31G(d). [f] Calculated using experimental bond dissociation energies at 298 K for species in reaction 1 that were obtained from the *Handbook of Chemistry and Physics*[20] (and references therein), unless otherwise noted, and back-corrected to 0 K using theoretical temperature corrections (scaled by 0.9989).[12] [g] Calculated using experimental BDE for $^{\bullet}\mathrm{CH_2OH}$ reported by Dobe et al.[21a] [h] Calculated using experimental BDE for $^{\bullet}\mathrm{CH_2CHCH_2}$ reported by Seetula.[21b] [i] Calculated using experimental BDE for $^{\bullet}\mathrm{CH_2CCH}$ reported by Robinson et al.[21c] [j] Calculated using experimental BDE for $^{\bullet}\mathrm{CH_2COOH}$ reported by Wenthold and Squires.[21d] [k] Calculated using experimental BDE for $^{\bullet}\mathrm{CH_2COOCH_3}$ reported by Holmes et al.[21e] [l] Calculated using experimental heats of formation for $^{\bullet}\mathrm{CH_2CN}$ and $\mathrm{CH_3CN}$ reported by Lafleur et al.[21f] [m] MD and MAD are the mean deviation and mean absolute deviation, respectively, from experiment or CBS−RAD values. [n] For species with experimental uncertainties of less than ±10 kJ mol^{-1}.

BDEs may still produce acceptable stabilization energies. Table 2 presents calculated and experimental RSEs.

As noted earlier, W1′ gives very accurate BDEs and this is further reflected in the RSEs calculated at this level. The MAD from experiment for W1′ is 3.1 kJ mol^{-1}. The W1′ RSEs tend to be slightly lower than those determined from experimental data (MD(Expt) = −2.2 kJ mol^{-1}).

At the CBS-RAD level, the MAD from experiment is only 2.4 kJ mol^{-1}. Here once again, CBS-RAD tends to give slightly lower RSEs than experiment (MD(Expt) = −1.9 kJ mol^{-1}).

G3(MP2)-RAD compares well with CBS-RAD (MAD(CBS-RAD) = 2.9 kJ mol^{-1}). It can be seen from Table 2 that G3(MP2)-RAD systematically underestimates CBS-RAD stabilization energies, with MD(CBS-RAD) = −2.5 kJ mol^{-1}. This appears to be due to the slightly larger deviation in the BDE for methane (6.6 kJ mol^{-1}) than for the substituted methanes (∼4.1 kJ mol^{-1}).

Because of a systematic cancellation of errors in the BDEs, RMP2/6-311+G(2df,p) single-point calculations also perform quite acceptably in predicting RSEs (MAD(CBS-RAD) = 3.8 kJ mol^{-1}). The slightly greater underestimation of the BDE for methane (20.0 kJ mol^{-1}) than for the substituted methanes (∼16.5 kJ mol^{-1}) leads to systematically low RSEs (MD(CBS-RAD) = −3.4 kJ mol^{-1}).

RB3-LYP/6-311+G(3df,2p), (MAD(CBS-RAD) = 4.7 kJ mol^{-1}), performs slightly less well than RMP2 for stabilization energies, while UB3-LYP/6-311+G(3df,2p) shows the largest MAD (6.0 kJ mol^{-1}) from CBS-RAD. Interestingly, RB3-LYP and UB3-LYP both tend to overestimate the CBS-RAD RSEs (MD(CBS-RAD) = 4.6 and 5.9 kJ mol^{-1} respectively). This can be attributed to the fact that both levels underestimate the BDEs for the substituted methanes (∼8.8 and 14.3 kJ mol^{-1}) to a greater extent than for methane (4.2 and 8.4 kJ mol^{-1}, respectively).

The results in Table 2 indicate that unsaturated π-acceptor substituents (such as C≡N, C≡CH, CH═CH$_2$, CHO and C$_6$H$_5$) all produce significant radical stabilization. This is a consequence of π resonance involving the interaction of the radical 2p(C$^{\bullet}$) orbital with the occupied π and empty π^* orbitals of the π-acceptor substituent, as discussed above (Figure 1).[19] The net result is a two-electron bonding stabilization. Of the π-acceptor groups, vinyl (CH═CH$_2$) is calculated to yield the highest RSE with a value of greater than 70 kJ mol^{-1}, while the $^{\bullet}\mathrm{CH_2C{\equiv}CH}$ and $^{\bullet}\mathrm{CH_2C_6H_5}$ radicals are predicted to have stabilization energies of about 50−60 kJ mol^{-1}. The relatively high RSE value for the $^{\bullet}\mathrm{CH_2BH_2}$ radical (42 kJ mol^{-1}) is due to a stabilizing one-electron interaction between the radical carbon 2p(C$^{\bullet}$) orbital and the formally unoccupied p-type orbital on the boron atom.

It is also clear that lone-pair-donor substituents (NH$_2$, OH, OCH$_3$, F, PH$_2$, SH, Cl and Br) all stabilize a methyl radical center. This stabilization can be explained by the molecular orbital diagram in Figure 2.[19] The overall result of interaction between the radical 2p(C$^{\bullet}$) orbital and the lone pair orbital of the heteroatom is a net one-electron stabilization, the magnitude of which is related to the energy separation of the interacting

TABLE 2: Comparison of Radical Stabilization Energies of Substituted Methyl Radicals with Experimental Values (0 K, kJ mol^{-1})[a]

radical	UB3-LYP//UB3-LYP[b]	RB3-LYP//RB3-LYP[c]	RMP2//UB3-LYP[d]	RMP2//RMP2[e]	G3(MP2)-RAD	CBS-RAD	W1′	expt[f]
$^\bullet CH_2NH_2$	55.3	55.4	45.8	45.7	44.2	48.6	49.3	47.8 ± 8.8
$^\bullet CH_2OH$	39.4	39.4	32.2	31.8	31.6	34.4	35.3	35.9 ± 1.7[g]
$^\bullet CH_2OCH_3$	40.2	40.4	30.3	29.9	31.0	34.3	35.2	36.3
$^\bullet CH_2F$	17.7	17.7	13.0	12.4	12.4	13.9	14.8	14.8 ± 5
$^\bullet CH_2CH_3$	20.2	20.0	13.7	13.7	14.1	15.7	15.9	16.5 ± 2.0
$^\bullet CH_2CH_2CH_3$	17.6	17.5	10.0		12.5	13.1		15.6 ± 2.5
$^\bullet CH_2CF_3$	−1.1	−1.2	−8.1	−8.3	−7.7	−7.2		−7.2 ± 5.0
$^\bullet CH_2CF_2CF_3$	2.0	1.9	−5.4		−4.9			
$^\bullet CH_2PH_2$	32.3	31.6	20.6	20.5	23.3	27.1		
$^\bullet CH_2SH$	44.1	43.4	34.3	34.6	36.1	39.6	40.9	45.9 ± 8.8
$^\bullet CH_2Cl$	26.4	25.7	20.1	20.0	21.1	23.0	23.1	20.8 ± 2.7
$^\bullet CH_2Br$	19.8	19.2	14.7	14.1				14.1 ± 4.6
$^\bullet CH_2BH_2$	45.2	46.3	39.9	40.0	40.1	41.6		
$^\bullet CH_2CH{=}CH_2$	79.2	73.3	77.1	77.0	70.7	73.7	70.4	73.7 ± 4.7[h]
$^\bullet CH_2C{\equiv}CH$	66.6	62.2	50.3	50.1	52.6	55.5	53.7	60.9 ± 13[i]
$^\bullet CH_2C_6H_5$	67.3	63.4	50.2		58.9	55.1		61.1 ± 2.1
$^\bullet CH_2CHO$	45.2	41.8	32.3	32.4	34.9	40.0	36.7	42.7 ± 9.6
$^\bullet CH_2COOH$	30.1	29.3	20.2	20.3	21.2	24.6	23.8	38.7 ± 12.5[j]
$^\bullet CH_2COOCH_3$	30.6	29.9	20.6		21.5	25.1		48.2 ± 12.6[k]
$^\bullet CH_2OCOCH_3$	27.9	27.9	17.1		18.1	20.9		
$^\bullet CH_2CN$	44.3	40.3	31.2	30.9	31.9	37.2	33.2	41.7 ± 4.8[l]
$^\bullet CH_2NO_2$	20.9	20.2	11.9	11.9	11.6	14.0		
MD(expt)[m,n]	4.0	2.3	−4.8	−4.2	−4.1	−1.9	−2.2	
MAD(expt)[m,n]	4.2	3.2	5.4	4.9	4.1	2.4	3.1	
MD(CBS-RAD)[m]	5.9	4.6	−3.4	−3.4	−2.5		−0.7	
MAD(CBS-RAD)[m]	6.0	4.7	3.8	3.8	2.9		1.5	

[a] The RSEs were calculated as the enthalpy change for reaction 1. [b] UB3-LYP/6-311+G(3df,2p)//UB3-LYP/6-31G(d). [c] RB3-LYP/6-311+G(3df,2p)//RB3-LYP/6-31G(d). [d] RMP2/6-311+G(2df,p)//UB3-LYP/6-31G(d). [e] RMP2/6-311+G(2df,p)//RMP2/6-31G(d). [f] Calculated using experimental bond dissociation energies at 298 K for species in reaction 2 that were obtained from the *Handbook of Chemistry and Physics*[20] (and references therein), unless otherwise noted, and back-corrected to 0 K using theoretical temperature corrections (scaled by 0.9989).[12] [g] Calculated using experimental BDE for $^\bullet CH_2OH$ reported by Dobe et al.[21a] [h] Calculated using experimental BDE for $^\bullet CH_2CHCH_2$ reported by Seetula.[21b] [i] Calculated using experimental BDE for $^\bullet CH_2CCH$ reported by Robinson et al.[21c] [j] Calculated using experimental BDE for $^\bullet CH_2COOH$ reported by Wenthold and Squires.[21d] [k] Calculated using experimental BDE for $^\bullet CH_2COOCH_3$ reported by Holmes et al.[21e] [l] Calculated using experimental heats of formation for $^\bullet CH_2CN$ and CH_3CN reported by Lafleur et al.[21f] [m] MD and MAD are the mean deviation and mean absolute deviation, respectively, from experiment or CBS−RAD values. [n] For species with experimental uncertainties of less than ±10 kJ mol^{-1}.

orbitals. The difference in energy between the 2p(C$^\bullet$) orbital and the heteroatom lone pair orbital increases across the first row of the periodic table (going from NH_2 to OH to F), which is reflected in decreasing stabilization energies. It should be noted that heteroatom substituents also destabilize a radical center through their σ-accepting character. For first-row substituents, the order of increasing σ-accepting ability is $NH_2 <$ OH $<$ F, which is the reverse of the order of lone-pair-donating abilities. Therefore, the σ-accepting and lone-pair-donation effects reinforce one another. For the first-row heteroatoms, we can see that $^\bullet CH_2NH_2$, which has the smallest orbital energy gap and the least electronegative substituent, produces the largest RSE value of nearly 50 kJ mol^{-1}. Less effective π overlap may be responsible for the reduced RSE values for corresponding second-row systems (e.g., $^\bullet CH_2PH_2$).

A methyl substituent is predicted to give rise to slight radical stabilization. This occurs as a result of hyperconjugation in which the radical 2p(C$^\bullet$) orbital interacts with an occupied π-type and a vacant π*-type orbital of the methyl group, as discussed above (Figure 3).[19] This orbital interaction is similar to that occurring between a 2p(C$^\bullet$) orbital and a π-acceptor substituent, but the resulting stabilization is smaller because the energy difference between the orbitals is larger. Hyperconjugation due to the methyl substituent involves the three β C−H bonds. The ethyl group also stabilizes a methyl radical, this time due to hyperconjugation involving the β C−H and C−CH_3 bonds. The stabilization provided by the ethyl group is slightly less than that afforded by the methyl group.

All substituents other than CF_3 and CF_2CF_3 are calculated to stabilize methyl radicals (Table 2). The slight destabilization caused by polyfluoroalkyl substitution is presumably due to the dominance of the electron-withdrawing fluorine atoms acting on the electron-deficient radical center. This electron-withdrawal effect apparently exceeds any stabilizing hyperconjugative interaction between the 2p(C$^\bullet$) orbital and the β C−F bonds. The CF_3 substituent is slightly more destabilizing than is CF_2CF_3, the three β C−F bonds apparently outweighing the two β C−F bonds and one β C−CF_3 bond.

D. Comparison with Other Studies. Theoretical investigations of stabilization effects include that of Pasto et al.,[2e] who performed a study of RSEs at the UHF and ROHF levels with the 4-31G+d basis set (+d indicates the addition of a d-function on second-row atoms). These results are generally lower than our RB3-LYP and CBS-RAD RSEs. Higher RSEs are normally obtained with the inclusion of electron correlation, as indicated by the results of Delbecq (CI/STO-3G),[2c] and Coolidge and Borden (UMP4/6-31G(d)),[2f] whose values are generally similar to our CBS-RAD stabilization energies except for systems displaying considerable spin contamination. Lehd and Jensen[2j] evaluate stabilization energies at the AUMP4/6-31G(d) level of theory. Their results are also generally similar to our CBS-RAD RSEs, with the exception of $^\bullet CH_2{-}CH{=}CH_2$, $^\bullet CH_2CN$ and $^\bullet CH_2BH_2$, for which they predict significantly different (by 9.1−21.0 kJ mol^{-1}) values. In some of their work, Leroy et al.[2d] have used an alternative definition for stabilization energy, defined in terms of the atomization energies and standard bond energies. This is a general definition applicable to both open- and closed-shell species but does not appear to offer any advantages in the present case over the use of the enthalpy change for the isodesmic reaction 3. While the values from this work are not directly comparable to our RSEs, they generally indicate the same trends in substituent effects. One notable exception is the Cl substituent, which Leroy et al.[2d] predict provides almost no stabilization, whereas all of our calculations indicate significant stabilization.

The RSEs of Jursic and Timberlake,[2n] as well as Brinck et al.,[2u] determined at the UB3-LYP/6-311+G(2d,2p) level, are in close agreement with our UB3-LYP values. Brinck et al.[2u] also report UB3-LYP/6-31G(d,p) RSEs that are generally slightly higher than our larger basis set UB3-LYP single-point calculations. Their modified G2 (specifically G2MS)[22] results, however, are generally in reasonable agreement with our stabilization energies. Korth and Sicking[2q] report PUMP2(full)/6-31G(d,p) and UB3-LYP/6-31G(d,p) results, some of which differ significantly from our values. In particular, the stabilization due to the NH_2 substituent is greatly overestimated, while for CN the PUMP2 value is significantly lower.

Recently, Vreven and Morokuma[2v] reported theoretical bond dissociation energies at a range of levels of theory (UHF and B3-LYP through to UCCSD(T) and G2MS) for application in IMOMO methods. Stabilization energies calculated from their BDEs for ethyl radical are generally in good agreement with our results. For the benzyl radical, however, they note that the unrestricted methods display considerable spin contamination and as such give results significantly different from experiment. The values that they obtain with restricted-open-shell and higher-level methods (CCSD, CCSD(T) and G2MS) are generally in accord with the present work.

The direct gas-phase thermochemical data in Tables 1 and 2 generally agree well with our calculated RSEs, as discussed above. Previous indirect experimental studies of the RSE values of substituted methyl radicals include that of McKean,[1k] in which stabilization energies were correlated with CH stretching frequencies. These are not directly comparable to our RSEs but generally demonstrate similar trends. Exceptions to this are the OH, OCH_3 and NH_2 substituents, for which McKean predicts almost no stabilization, in contrast to the present study that indicates that these groups produce significant stabilization. RSE values listed by Bordwell and Zhang[1m] tend to be somewhat higher than those obtained here, especially for the NH_2 substituent, which is predicted to yield roughly twice the stabilization calculated in the present study.

4. Concluding Remarks

We have assessed the performance of a series of theoretical methods, for the calculation of bond dissociation energies and radical stabilization energies, against benchmark W1′ and CBS-RAD values. The W1′ method is the most accurate of the theoretical procedures used in the present study. CBS-RAD gives results close to W1′ and is therefore used as a secondary benchmark.

We find that, for bond dissociation energies, G3(MP2)-RAD most closely approximates CBS-RAD with a mean absolute deviation of 4.2 kJ mol^{-1}. RB3-LYP/6-311+G(3df,2p), UB3-LYP/6-311+G(3df,2p) and RMP2/6-311+G(2df,p) single-point energies perform less well with MADs of 8.6, 14.1 and 16.7 kJ mol^{-1}, respectively. All of these levels systematically underestimate the CBS-RAD bond dissociation energies (MDs of -4.2 to -16.7 kJ mol^{-1}).

For the calculation of radical stabilization energies, we find that G3(MP2)-RAD also compares well with CBS-RAD (MAD 2.9 kJ mol^{-1}). As a result of a systematic cancellation of errors, RMP2/6-311+G(2df,p) and RB3-LYP/6-311+G(3df,2p) single-point calculations also give satisfactory performance for RSEs, with MADs of 3.8 and 4.7 kJ mol^{-1}, respectively. UB3-LYP/6-311+G(3df,2p) performs slightly less well with an MAD of 6.0 kJ mol^{-1}.

Most of the substituents examined in the present study stabilize a methyl radical center. The only exceptions are the perfluoroalkyl substituents, CF_3 and CF_2CF_3. These two substituents destabilize radicals because of the electronegative inductive effect of the fluorine atoms which draw electron density away from the electron-deficient radical center.

All other substituents are predicted to stabilize a methyl radical. This can be rationalized in terms of the ability of these substituents to delocalize the unpaired electron. Alkyl substituents (CH_3 and CH_2CH_3) delocalize the odd electron by the process of hyperconjugation involving groups that are β to the radical center. π-acceptor substituents (BH_2, $CH{=}CH_2$, $C{\equiv}CH$, C_6H_5, CHO, COOH, $COOCH_3$ and CN) all stabilize a methyl radical center significantly by permitting delocalization of the unpaired electron into the π-system. Lone-pair-donor substituents stabilize methyl radicals through a three-electron bonding interaction between the radical $2p(C^\bullet)$ orbital and a nonbonding pair of electrons on the heteroatom.

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Supporting Information Available: Tables S1, S2 and S3 contain the GAUSSIAN archive entries for the RMP2/6-31G(d), RB3-LYP/6-31G(d) and UB3-LYP/6-31G(d) optimized geometries of the substituted methyl radicals ($^\bullet CH_2X$) and substituted methanes (CH_3X) considered in this study. Table S4 contains the total energies that lead to the BDEs and RSEs of Tables 1 and 2, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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