

An assessment of theoretical procedures for the calculation of reliable radical stabilization energies †‡



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The performance of a variety of theoretical methods in computing stabilization energies of the substituted methyl and vinyl radicals $\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{CN}$, $\cdot\text{CH}_2\text{CH}=\text{CH}_2$, $\cdot\text{CH}_2\text{CH}=\text{O}$, $\text{CH}_2=\text{C}\cdot\text{F}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$ is examined. The influence of electron correlation (UHF, UMP2, PMP2, RMP2, UB3-LYP, UQCISD, UQCISD(T), UCCSD(T), URCCSD(T) and RRCCSD(T)) and basis set size (from 6-31G(d) to 6-311++G(3df,3pd)) on stabilization energies is evaluated, as well as the performance of compound methods such as G2, G3, CBS-Q and CBS-APNO and their variants. The results indicate that generally reliable radical stabilization energies can be obtained at modest cost using RMP2/6-311+G(2df,p)//RMP2/6-31G(d) energies. A slightly less accurate but more economical procedure is RMP2/6-311+G(d)//B3-LYP/6-31G(d). UMP2 and PMP2 are unsuitable for obtaining radical stabilization energies for spin-contaminated radicals, while UB3-LYP appears generally to overestimate stabilization energies.

Introduction

The influence of substituents X on the stability of free radicals is important in understanding chemical processes that involve such radicals as reactants, products or intermediates. There have been many experimental^{1,2} and theoretical³ studies carried out to quantify such effects through the determination of radical stabilization energies (RSEs).

The most common definition of the RSE of a substituted methyl radical $\cdot\text{CH}_2\text{X}$ is the enthalpy change in the isodesmic reaction (1). The RSE of $\cdot\text{CH}_2\text{X}$ may equivalently be con-

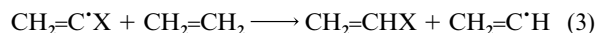


sidered to be the difference between the C–H bond dissociation energy (BDE) in methane and the C–H BDE in the substituted methane (CH_3X) (eqn. (2)). Defined in this way, a positive value

$$\text{RSE}(\cdot\text{CH}_2\text{X}) = \Delta\text{H}(1) = \text{BDE}(\text{CH}_4) - \text{BDE}(\text{CH}_3\text{X}) \quad (2)$$

for the RSE indicates that the radical $\cdot\text{CH}_2\text{X}$ is stabilized relative to $\cdot\text{CH}_3$, resulting in a smaller C–H BDE in CH_3X than in CH_4 .

In the same way that the RSE of a substituted methyl radical can be defined by the isodesmic reaction (1), the RSE of a substituted vinyl radical ($\text{CH}_2=\text{C}\cdot\text{X}$) can be calculated as the enthalpy change for reaction (3). The RSE of a substituted



vinyl radical is equivalently given by the difference between the C–H BDE of ethylene and the C–H BDE of the substituted ethylene (eqn. (4)).

$$\text{RSE}(\text{CH}_2=\text{C}\cdot\text{X}) = \Delta\text{H}(3) = \text{BDE}(\text{CH}_2=\text{CH}_2) - \text{BDE}(\text{CH}_2=\text{CHX}) \quad (4)$$

It is often assumed when using isodesmic reactions to calculate RSEs that errors in bond energies will cancel, even when low levels of theory are used. However, one aspect not taken into consideration by this argument is the effect of spin-contamination in an underlying unrestricted Hartree–Fock (UHF) wave function. If the radicals on both sides of eqns. (1) and (3) have similar amounts of spin-contamination, the assumption of cancellation of errors may be reasonable, and the RSE values thus obtained may be adequate. However, spin-contamination may be much more severe in the substituted free radicals in reactions (1) and (3), and therefore its effects will not cancel. Methods which are known to perform poorly for spin-contaminated radicals will therefore yield RSE values that are suspect.⁴

In the present study, we examine systematically the performance of a variety of levels of theory including variants of several compound methods (G2,⁵ G3,^{6,7} CBS-Q⁸ and CBS-APNO⁸) for calculating RSE values of small organic radicals. The six organic radicals treated in this study are $\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{CN}$, $\cdot\text{CH}_2\text{CH}=\text{CH}_2$, $\cdot\text{CH}_2\text{CH}=\text{O}$, $\text{CH}_2=\text{C}\cdot\text{F}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$, and were chosen because they exhibit differing degrees of spin-contamination, with $\langle S^2 \rangle$ values in the reference UHF/6-31G(d) wave functions of approximately 0.76, 0.92, 0.97, 0.94, 0.97 and 1.49, respectively. We examined the geometries, zero-point vibrational energies and heats of formation for four of these radicals ($\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{CN}$, $\text{CH}_2=\text{C}\cdot\text{F}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$) in a previous study⁹ and these are therefore discussed only briefly in the present paper. A preliminary account of our results for the cyanovinyl radical has been reported elsewhere.¹⁰

Computational methods

Ab initio molecular orbital calculations¹¹ were performed using the GAUSSIAN94,¹² GAUSSIAN98,¹³ ACESII¹⁴ and MOLPRO96¹⁵ computer programs. The effect of the level of theory on geometries, zero-point vibrational energies, heats of formation and radical stabilization energies has been examined. The theoretical methods include HF, MP2, B3-LYP, QCISD, QCISD(T) and CCSD(T), with basis sets ranging from 6-31G(d) to 6-311++G(3df,3pd). A number of compound

† Dedicated to the memory of Bob Squires, a good friend and a gifted scientist.

‡ Tables S1–S9 are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p2/1999/2305>, otherwise available from BLDSC (SUPPL. NO. 57647, pp. 20) or the RSC Library. See Instructions for Authors available via the RSC web page (<http://www.rsc.org/authors>).

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methods, including variants of the G2,⁵ G3⁶ and CBS⁸ procedures, have also been examined. Except where indicated, unrestricted open-shell wave functions (e.g. UHF, UMP2, UQCISD) and the frozen-core (fc) approximation were utilized, and the 'U' is generally dropped for simplicity. Electron correlation involving all electrons is denoted fu. Spin-projected open-shell calculations are designated with a 'P' prefix, as for PMP2. Restricted open-shell calculations are signified with an 'R' prefix, as for RMP2.¹⁶ The coupled-cluster methods of MOLPRO 96¹⁵ examined in this study are the URCCSD(T) procedure (which involves an unrestricted CCSD(T) calculation performed with a restricted open-shell HF reference wave function), and the RRCCSD(T) technique (which involves a partially spin-restricted CCSD(T) calculation carried out with a restricted open-shell HF reference wave function). Zero-point vibrational energies (ZPEs) were obtained using standard or optimized¹⁷ scaling factors, as specified. The atomization method outlined by Nicolaides *et al.*¹⁸ has been used to convert molecular energies to heats of formation at 0 K ($\Delta_f H_0$). Experimental $\Delta_f H_0$ values for the atoms have been taken from a database compiled by Lias *et al.*¹⁹ Radical stabilization energies were calculated as enthalpy changes for reactions (1) and (3), including scaled B3-LYP/6-31G(d) ZPEs unless otherwise noted.

In order to assess the performance of the various levels of theory for the calculation of RSE values, it is necessary either to compare the results with reliable experimental data or with the results of a benchmark theoretical procedure. Reliable experimental data for free radicals are difficult to obtain, so the assessment of theoretical methods in the present paper has been achieved by comparing the results with those of a theoretical technique based on extrapolation schemes developed by Martin which calculate thermochemical properties of molecules very accurately.²⁰ The Martin extrapolation procedures use basis sets of systematically increasing highest angular momentum quantum number (Dunning's correlation-consistent basis sets, cc-pVnZ where *n* is T, Q or 5). The CCSD(T) energy of a species at the infinite-basis-set limit is then obtained by an asymptotic extrapolation.

The particular modification of the Martin extrapolation schemes used as a benchmark in the present study and in our previous study of free radical heats of formation⁹ is denoted Martin-3. It involves a geometry optimization at the CCSD(T) level with the cc-pVTZ basis set. A single-point energy calculation is also performed on the CCSD(T)/cc-pVTZ geometry at the CCSD(T)/cc-pVQZ level. The CCSD(T) energies computed with the cc-pVTZ and cc-pVQZ basis sets are extrapolated to the infinite-basis-set limit. Corrections to this extrapolated energy are then made for the effects of core-correlation, zero-point energy, spin-orbit coupling (in atoms) and the number of triple bonds present. A full description of this modified Martin method can be found in a previous publication.⁹

For $\cdot\text{CH}_2\text{F}$ and $\cdot\text{CH}_2\text{CN}$, RSE values were also computed using a modification of the Martin-3 method in which the two energies used in the extrapolation equation are single-point energies obtained with basis sets augmented with diffuse functions on all atoms (aug-cc-pVTZ and aug-cc-pVQZ). This procedure is denoted aug-Martin-3.

Two variations of the CBS family of procedures⁸ were also examined, CBS-Q and CBS-APNO. These two methods attempt to obtain the energy of a species at the QCISD(T) level with an infinite basis set. The main feature in each is an extrapolation of the total energy to the infinite basis set limit using pair natural orbital energies at the MP2 correlation level. The major differences between the two techniques are that (a) CBS-APNO employs QCISD/6-311G(d,p) optimized geometries while CBS-Q uses MP2/6-31G† geometries, (b) CBS-APNO uses larger basis sets for the extrapolation and for the additive correlation correction, (c) CBS-APNO contains a core-correlation correction which is missing in CBS-Q (except for

sodium), and (d) CBS-Q includes a spin-correction factor for radicals that is absent in CBS-APNO. In both methods, HF ZPEs are used, with CBS-APNO employing a larger basis set.

Two modifications of the standard CBS-Q method were also considered. The CBS-RAD procedure,⁹ introduced particularly for the treatment of radicals, differs from the standard CBS-Q method⁸ in that it (a) uses a QCISD/6-31G(d) optimized geometry, (b) contains a scaled QCISD/6-31G(d) ZPE, and (c) calculates the final level of electron correlation using CCSD(T) rather than QCISD(T). The CBS-QB3 method²¹ is similar to the (B3-LYP,B3-LYP) variant of CBS-RAD.⁹ It differs from CBS-Q by (a) employing a B3-LYP/6-311G(2d,d,p) optimized geometry, (b) using a B3-LYP/6-311G(2d,d,p) ZPE (scaled by 0.99), (c) determining the ultimate electron correlation with CCSD(T) and (d) including a spin-orbit correction for atoms.

The performance of the G2 technique⁵ in calculating RSE values has also been examined. The standard G2 procedure uses an MP2(fu)/6-31G(d) optimized geometry and a scaled HF/6-31G(d) ZPE. A base energy calculated at the MP4/6-311G(d,p) level of theory is corrected to QCISD(T)/6-311+G(3df,2p) using additivity approximations at the MP2 and MP4 levels. A "higher-level correction" (HLC) is included in an attempt to correct for remaining basis set and other deficiencies.

A modification of G2 theory was also examined in this study. The G2-RAD(QCISD) method,²² also introduced particularly for the treatment of radicals, differs from standard G2 theory in that it (a) employs a QCISD/6-31G(d) optimized geometry, (b) incorporates a scaled (by 0.9806) B3-LYP/6-31G(d) ZPE,¹⁷ (c) replaces all UMP calculations for open-shell systems with RMP, (d) calculates the final level of electron correlation using the URCCSD(T) method of MOLPRO instead of with QCISD(T), and (e) uses a modified higher-level correction of 5.32 millihartrees per electron pair.²³

The performance of G3 theory⁶ was assessed. This method uses an MP2(fu)/6-31G(d) optimized geometry and a scaled HF/6-31G(d) ZPE. A base energy calculated at the MP4/6-31G(d) level of theory is corrected to the QCISD(T)(fu)/G3Large level using several additivity approximations at the MP2 and MP4 levels, in order to take account of more complete incorporation of electron correlation, core correlation and the effect of a large basis set. In addition, a spin-orbit correction is included in the energies of atomic species. A higher-level correction (HLC) is applied to attempt to correct for residual deficiencies with the method. The HLC is $-An_\beta - B(n_\alpha - n_\beta)$ for molecules and $-Cn_\alpha - D(n_\alpha - n_\beta)$ for atoms, where n_α and n_β are the number of α and β valence electrons, respectively, and $n_\alpha \geq n_\beta$. The values of the coefficients are $A = 6.39$ mhartrees, $B = 2.98$ mhartrees, $C = 6.22$ mhartrees and $D = 1.18$ mhartrees.

A variation of the G3 method was also examined. The G3//B3-LYP⁷ procedure differs from standard G3 theory in that (a) the geometry used is optimized at the B3-LYP/6-31G(d) theory level, (b) the ZPE is calculated at the B3-LYP/6-31G(d) level of theory (and scaled by 0.96), and (c) a different HLC is used because of the change in geometry and ZPE. The values of the constants for G3//B3-LYP are $A = 6.760$ mhartrees, $B = 3.233$ mhartrees, $C = 6.786$ mhartrees and $D = 1.269$ mhartrees.

The main distinguishing features of the various compound methods used in the present study are summarized in Table 1.

Results and discussion

Prior to the discussion of RSE values, it is worthwhile to discuss the dependence on level of theory of the geometries, ZPEs and heats of formation of the constituent species in reactions (1) and (3), namely $\cdot\text{CH}_3$, CH_4 , $\cdot\text{CH}_2\text{X}$, CH_3X , $\text{CH}_2=\text{C}\cdot\text{H}$, $\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{C}\cdot\text{X}$ and $\text{CH}_2=\text{CHX}$. The above properties for the free radicals $\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{CN}$, $\text{CH}_2=\text{C}\cdot\text{F}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$ have been examined in detail in a previous publication,⁹ and will only

Table 1 Principal features of compound methods employed^a

Method	Geometry	ZPE	Energy
G2	UMP2(fu)/6-31G(d)	UHF/6-31G(d) ^b	Estimated UQCISD(T)/6-311+G(3df,2p) ^c
G2-RAD(QCISD)	UQCISD/6-31G(d)	B3-LYP/6-31G(d) ^d	Estimated UCCSD(T)/6-311+G(3df,2p) ^e
G3	UMP2(fu)/6-31G(d)	UHF/6-31G(d) ^b	Estimated UQCISD(T)(fu)/G3Large ^c
G3//B3-LYP	B3-LYP/6-31G(d)	B3-LYP/6-31G(d) ^f	Estimated UQCISD(T)(fu)/G3Large ^c
CBS-Q	UMP2/6-31G†	UHF/6-31G† ^g	Extrapolated UQCISD(T)
CBS-RAD	UQCISD/6-31G(d)	UQCISD/6-31G(d) ^h	Extrapolated UCCSD(T)
CBS-QB3	B3-LYP/6-311G(2d,d,p)	B3-LYP/6-311G(2d,d,p) ⁱ	Extrapolated UCCSD(T)
CBS-APNO	UQCISD/6-311G(d,p)	UHF/6-311G(d,p) ^j	Extrapolated UQCISD(T)
Martin-3	URCCSD(T)/cc-pVTZ	UQCISD/6-31G(d) ^h	Extrapolated URCCSD(T)
aug-Martin-3	URCCSD(T)/cc-pVTZ	UQCISD/6-31G(d) ^h	Extrapolated URCCSD(T) ^k

^a For full details, see text. ^b Scaled by 0.8929. ^c Uses UMP energies in the additivity schemes. ^d Scaled by 0.9806. ^e Uses RMP energies in the additivity schemes. ^f Scaled by 0.96. ^g Scaled by 0.91844. ^h Scaled by 0.9776. ⁱ Scaled by 0.99. ^j Scaled by 0.9251. ^k Basis sets augmented with diffuse functions on all atoms are used in the extrapolation scheme.

be discussed briefly in the present work where appropriate. We note again that, unless otherwise stated, calculations are based on unrestricted wave functions but the 'U' is often dropped for simplicity.

Molecular geometry

To examine the dependence of geometry on the level of theory, the geometries of CH₄, CH₃F, CH₃CN, CH₃CH=CH₂, CH₃CH=O, CH₂=CH₂, CH₂=CHF, CH₂=CHCN, [•]CH₃, [•]CH₂CH=CH₂, [•]CH₂CH=O and CH₂=C[•]H were optimized as a function of correlation method (MP2, B3-LYP or QCISD) and as a function of basis set size. Selected bond lengths and bond angles for the vinyl radical (CH₂=C[•]H) are listed in Table 2. Geometrical data for CH₃F, CH₃CN, CH₃CH=CH₂, CH₃CH=O, CH₂=CH₂, CH₂=CHF, CH₂=CHCN, [•]CH₂CH=CH₂ and [•]CH₂CH=O are given in Tables S1 to S9 in the supplementary material while corresponding data for [•]CH₂F, [•]CH₂CN, CH₂=C[•]F and CH₂=C[•]CN have been presented previously.^{9,10}

It can be seen from Table 2 that the effect of basis set size on the geometry of the vinyl radical is relatively small. The most noticeable change in geometry with basis set is a 0.008 Å contraction in the C=C bond length in going from the 6-311+G(d,p) to the 6-311++G(3df,3pd) basis set at the MP2 level. The effects of correlation on the vinyl radical geometry are greater. For example, relative to QCISD(T)/6-311G(d,p), UMP2, B3-LYP and RMP2 underestimate the C=C bond length by 0.036 Å, 0.018 Å and 0.006 Å, respectively. The experimental geometry²⁴ is close to the QCISD(T) and RMP2 geometries.

In our preliminary report on the 1-cyanovinyl radical (CH₂=C[•]CN),¹⁰ we discussed the effect of correlation level and basis set on the size of the <CCC bond angle. We noted that there is considerable variation in the calculated structures for the 1-cyanovinyl radical, ranging from bent (C_s) vinylic structures (CH₂=C[•]-C≡N) to more symmetrical (C_{2v}) allenic structures (CH₂=C=C=N[•]). Our best calculations (CCSD(T)/cc-pVTZ, with *f* functions restricted to the radical carbon atom) indicate a distinctly bent structure with <CCC = 149.1°, lying 3.4 kJ mol⁻¹ below the C_{2v} structure. UMP2 structures optimized with a variety of basis sets have <CCC bond angles in the range 135–138°, while QCISD and QCISD(T) structures have <CCC angles of 143–145°. The minimum energy RMP2/6-31G(d) geometry has a <CCC bond angle of 147.9°, but with larger basis sets RMP2 prefers a C_{2v} structure. With small basis sets B3-LYP predicts C_{2v} geometries for CH₂=C[•]CN, whereas C_s structures are calculated with larger basis sets.

In general, MP2 and B3-LYP optimized geometries for closed-shell molecules agree well with the QCISD(T) geometries. As noted in previous work, this observation contrasts with that for some of the corresponding radicals.⁹ For radicals with low spin-contamination (such as [•]CH₂F), all levels of theory examined predict adequate geometries. However, the

Table 2 Selected geometric parameters for CH₂=C[•]H calculated as a function of correlation level and basis set^a

Level of theory	r(C–H) ^b	r(C=C)	<HCC ^c
Basis set effects			
HF/6-31G(d)	1.072	1.328	134.4
HF/6-311G(d,p)	1.072	1.324	134.8
MP2/6-31G(d)	1.081	1.289	136.8
MP2/6-311G(d)	1.081	1.288	136.9
MP2/6-311G(d,p)	1.081	1.287	137.0
MP2/6-311+G(d,p)	1.081	1.289	137.4
MP2/6-311+G(df,p)	1.081	1.284	137.4
MP2/6-311+G(2df,p)	1.078	1.280	138.1
MP2/6-311++G(3df,3pd)	1.076	1.281	137.9
B3-LYP/6-31G(d)	1.083	1.310	137.5
B3-LYP/6-311G(d)	1.082	1.305	137.6
B3-LYP/6-311G(d,p)	1.080	1.305	138.4
B3-LYP/6-311+G(d,p)	1.080	1.306	138.8
QCISD/6-31G(d)	1.084	1.320	136.0
QCISD/6-311G(d,p)	1.083	1.320	136.2
QCISD(T)/6-31G(d)	1.086	1.323	136.0
QCISD(T)/6-311G(d,p)	1.085	1.323	136.2
Correlation effects			
HF/6-311G(d,p)	1.072	1.324	134.8
MP2/6-311G(d,p)	1.081	1.287	137.0
RMP2/6-311G(d,p)	1.081	1.317	136.5
B3-LYP/6-311G(d,p)	1.080	1.305	138.4
QCISD/6-311G(d,p)	1.083	1.320	136.2
QCISD(T)/6-311G(d,p)	1.085	1.323	136.2
Experiment ^{d,e}	1.080	1.316	137.3
	(0.010)	(0.006)	(4.0)

^a Bond lengths in Å, bond angles in degrees. ^b Bond length involving the radical carbon atom. ^c Bond angle involving the radical carbon atom as the central atom. ^d The experimental geometry is taken from ref. 24. ^e The figures in parentheses are experimental uncertainties.

UMP2(fu)/6-31G(d) geometry used in standard G2 theory is found to differ significantly from that obtained at higher levels for radicals with significant spin-contamination (<S² greater than 0.8). The QCISD/6-31G(d) geometry is preferable for such radicals, although the considerably less expensive RMP2/6-31G(d) and B3-LYP/6-31G(d) geometries are also generally quite good.

Zero-point vibrational energy

The zero-point vibrational energy (ZPE) values for the species involved in the present study, obtained with a variety of levels of theory (and scaled accordingly),¹⁷ are listed in Table 3. The spread in calculated ZPE values for the closed-shell molecules is small, lying within a range of about 3 kJ mol⁻¹. Thus, all levels of theory in Table 3 give reasonable ZPE values for closed-shell species.

Table 3 Zero-point vibrational energies (kJ mol⁻¹) calculated with the 6-31G(d) basis set as a function of correlation level for closed-shell molecules and radicals^a

	CH ₄	CH ₃ F	CH ₃ CN	CH ₃ CH=CH ₂	CH ₃ CHO	CH ₂ =CH ₂	CH ₂ =CHF	CH ₂ =CHCN
HF ^b	112.1	99.5	114.6	200.3	140.5	128.4	111.7	128.8
HF	114.7	101.8	117.3	205.0	143.7	131.4	114.3	131.8
MP2(fu)	117.6	102.9	116.8	207.1	144.6	132.1	113.8	129.6
B3-LYP	116.4	101.7	117.5	206.2	143.7	131.9	114.0	131.2
QCISD	117.0	102.6	117.9	207.2	145.1	132.0	114.2	131.0
	[•] CH ₃	[•] CH ₂ F	[•] CH ₂ CN	[•] CH ₂ CH=CH ₂	[•] CH ₂ CHO	CH ₂ =C [•] H	CH ₂ =C [•] F	CH ₂ =C [•] CN
HF ^b	72.6	63.0	75.8	162.9	105.7	90.8	76.5	85.7
HF	74.3	64.5	77.5	166.7	108.2	92.8	78.3	87.7
MP2(fu)	77.5	65.5	84.3	172.3	111.5	98.6	83.1	103.5
B3-LYP	76.8	64.2	80.4	170.8	110.0	94.5	79.6	92.5
QCISD	77.0	65.0	80.0	170.7	110.2	95.5	80.4	94.7

^a Unless otherwise indicated, ZPEs were obtained by scaling the calculated values using optimized ZPE scaling factors from ref. 17. ^b These ZPEs were obtained after scaling by the standard G2 factor of 0.8929.

Table 4 Heats of formation (0 K, kJ mol⁻¹) for closed-shell molecules and radicals calculated using compound methods

Method	CH ₄	CH ₃ F	CH ₃ CN	CH ₃ CH=CH ₂	CH ₃ CHO	CH ₂ =CH ₂	CH ₂ =CHF	CH ₂ =CHCN
G2	-69.6	-235.9	82.7	37.3	-160.9	62.0	-138.0	198.9
G2-RAD(QCISD)	-67.5	-235.2	81.7	39.0	-160.1	62.7	-137.5	197.0
G3	-68.0	-229.9	81.3	34.7	-156.3	60.0	-136.2	193.9
G3//B3-LYP	-66.8	-228.8	79.0	35.2	-156.9	60.0	-135.8	190.7
CBS-Q	-66.0	-230.6	85.5	41.2	-155.6	65.2	-133.8	200.4
CBS-RAD	-63.2	-228.9	85.5	44.0	-152.5	66.3	-132.5	199.4
CBS-QB3	-66.1	-230.0	82.8	40.2	-155.9	64.5	-133.1	197.5
CBS-APNO	-71.0	-232.2	81.0	30.8	-159.1	59.5	-136.9	196.3
Martin-3	-67.1	-228.8	80.8	33.6 ^c	-155.3	59.5	-135.3	194.3
aug-Martin-3	-66.5	-229.7	80.3			58.9		
Experiment ^{a,b}	-66.8 (0.4)	-239.0 ^c -226.3 ^d (33.0)	81.0 (0.4)	35.4 ^c (0.4)	-160.1 ^f (1.5) -155.6 ^c (0.4)	60.7 (1.2)	-130.9 ^c (1.7)	190.6 ^c (2.9)
	[•] CH ₃	[•] CH ₂ F	[•] CH ₂ CN	[•] CH ₂ CH=CH ₂	[•] CH ₂ CHO	CH ₂ =C [•] H	CH ₂ =C [•] F	CH ₂ =C [•] CN
G2	149.6	-28.4	269.8	186.7	23.9	308.3	115.7	439.3
G2-RAD(QCISD)	152.0	-27.8	268.6	188.9	23.3	307.6	115.7	424.2
G3	144.7	-28.5	260.9	176.5	21.7	299.2	112.2	426.3
G3//B3-LYP	146.6	-28.5	259.4	179.4	20.1	298.2	112.4	421.4
CBS-Q	150.1	-27.3	264.5	180.6	24.7	304.8	112.7	418.6 ^g
CBS-RAD	153.3	-25.5	264.6	186.2	23.1	307.1	115.5	419.8 ^g
CBS-QB3	152.1	-27.0	263.1	184.1	21.5	304.9	114.7	409.0
CBS-APNO	147.0	-29.4	262.4	175.7	19.2	302.1	111.7	420.2
Martin-3	148.1	-26.5	263.0	178.0	23.3	301.8	115.2	419.4
aug-Martin-3	148.3	-28.2	262.1			301.2		
Experiment ^{a,b}	149.0 (1.0)	-29.4 ^c (8.0)	255.3 ^h (8.8)	182.7 ^f (3.0)	16.7 ⁱ (9.2)	303.8 ⁱ (3.3)		

^a From ref. 19, unless otherwise indicated. ^b The numbers in parentheses are experimental uncertainties. ^c The 0 K heats of formation for these molecules were obtained using 298 K heats of formation from ref. 19 and corrected to 0 K with a theoretical temperature correction. ^d From ref. 25. ^e Calculated using a geometry optimized at the CCSD(T) level with the cc-pVTZ basis set which has been simplified by the removal of *f* functions from carbon and *d* functions from the methyl hydrogens. ^f This 0 K heat of formation was calculated using 298 K heats of formation from ref. 26 and corrected to 0 K with a theoretical temperature correction. ^g These heats of formation are calculated for C_{2v} geometries, as the energy is lower than when a C_s geometry is used. See ref. 10. ^h The 0 K heat of formation for this radical was obtained using the 298 K heat of formation from ref. 27 and corrected to 0 K with a theoretical temperature correction. ⁱ From ref. 2.

For radicals with low spin-contamination ([•]CH₃ and [•]CH₂F), all theoretical levels again predict similar ZPE values (Table 3). However, for radicals with significant spin-contamination ([•]CH₂CN, [•]CH₂CH=CH₂, [•]CH₂CH=O, CH₂=C[•]H, CH₂=C[•]F and CH₂=C[•]CN), the differences in calculated ZPE values are greater. B3-LYP yields ZPE values that agree well with QCISD in all cases. HF generally underestimates the ZPE values of spin-contaminated radicals (by up to 7 kJ mol⁻¹), while MP2 tends to overestimate the ZPE values in such cases (by 9 kJ mol⁻¹ for the CH₂=C[•]CN radical). A relatively efficient level of

theory for obtaining reliable ZPE values for the closed-shell molecules and the radicals in the isodesmic reactions (1) and (3) is B3-LYP/6-31G(d).

Heats of formation

The heats of formation of the species in this study, calculated with the standard G2,⁵ G3,⁶ CBS-Q⁸ and CBS-APNO⁸ methods, and variations of these methods, are given in Table 4. Heats of formation calculated with the Martin-3 extrapolation

Table 5 Radical stabilization energies (0 K, kJ mol⁻¹) computed using compound methods^a

Method	[•] CH ₂ F	[•] CH ₂ CN	[•] CH ₂ CH=CH ₂	[•] CH ₂ CHO	CH ₂ =C [•] F	CH ₂ =C [•] CN
G2	11.7	32.2	69.8	34.4	-7.4	6.1
G2-RAD(QCISD)	12.0	32.6	69.6	36.0	-8.3	17.7
G3	11.4	33.1	70.9	34.7	-9.3	6.7
G3//B3-LYP	13.1	33.0	69.2	36.4	-10.0	7.5
CBS-Q	12.8	37.2	76.7	35.9	-6.9	21.4 ^b
CBS-RAD	13.1	37.6	74.3	40.9	-7.3	20.4 ^b
CBS-QB3	15.2	37.9	74.2	40.8	-7.4	28.7
CBS-APNO	15.2	36.6	73.0	39.6	-6.1	18.7
Martin-3	12.9	33.0	70.8	36.6	-8.2	17.1
aug-Martin-3	13.3	32.9				

^a Calculated using reactions 1 and 3 from the text. ^b The RSE value has been calculated using a C_{2v} geometry for CH₂=C[•]CN since this structure leads to a total energy with the particular compound method lower than when a C_s geometry is used. See ref. 10.

procedure are given for reference, along with aug-Martin-3 and experimental^{19,26,27} Δ_fH₀ values, where available. The best theoretical benchmark heats of formation are those calculated with the aug-Martin-3 procedure, but where these are unavailable, Martin-3 becomes the preferred benchmark method. The differences between Martin-3 and aug-Martin-3 Δ_fH₀ values are no more than 2 kJ mol⁻¹. Significantly, results at the G3 (or G3//B3-LYP in the case of CH₂=C[•]CN), CBS-APNO and Martin-3 levels lie close to one another in all cases. Considering all the theoretical results in Table 4, we note that the largest spread in the theoretical heats of formation for the closed-shell molecules occurs for CH₃CH=CH₂, the values covering a 13 kJ mol⁻¹ range. For radicals, the largest spread among the calculated values occurs for the highly spin-contaminated CH₂=C[•]CN (21 kJ mol⁻¹).

All the calculated heats of formation in Table 4 lie within 10 kJ mol⁻¹ of the best available experimental values, except for the [•]CH₂CN radical at some levels of theory. The consistent calculated results for this radical suggest that the experimental heat of formation for [•]CH₂CN may be underestimated by up to 8 kJ mol⁻¹. The experimental heat of formation for [•]CH₂CH=O also appears to be too low on the basis of the theoretical values, while that for CH₂=CHF looks to be not sufficiently negative.

The G2-RAD(QCISD) method generally predicts heats of formation for closed-shell molecules and radicals that are not significantly different from those of standard G2 theory (Table 4). However, for the CH₂=C[•]CN radical, the G2-RAD(QCISD) procedure calculates a much better Δ_fH₀ value than G2. The difference of 15.1 kJ mol⁻¹ between the G2 and G2-RAD(QCISD) heats of formation for CH₂=C[•]CN is mainly due to the effects of geometry (+14.0 kJ mol⁻¹), correlation method (+4.1 kJ mol⁻¹), ZPE (-6.8 kJ mol⁻¹) and higher-level correction (HLC) (+4.1 kJ mol⁻¹). The HLC in G2-RAD(QCISD) is modified from the standard HLC in order to compensate for the use of modified scaled ZPEs, so it is not surprising that the differences in ZPE and HLC largely cancel one another. Both the G3 and G3//B3-LYP methods generally calculate Δ_fH₀ values for closed-shell molecules and radicals that are in good agreement with the Martin results. G3//B3-LYP predicts a better heat of formation for CH₂=C[•]CN than does G3. CBS-RAD and CBS-QB3 yield heats of formation for closed-shell molecules that are close to those obtained with standard CBS-Q. For most radicals, CBS-QB3 performs somewhat better than CBS-RAD. However, for CH₂=C[•]CN, CBS-QB3 predicts a heat of formation that is 11 kJ mol⁻¹ lower than the CBS-RAD value. This discrepancy may be attributed largely to the fact that the C–CN bond lengths in the two geometries used differ by 0.055 Å. CBS-RAD yields slightly better Δ_fH₀ values than G2-RAD(QCISD) for the cyano-containing radicals ([•]CH₂CN and CH₂=C[•]CN). The CBS-APNO procedure calculates Δ_fH₀ values that are in good general agreement with the Martin results.

Radical stabilization energies

Compound methods. Radical stabilization energies that have been determined using the compound methods are presented in Table 5. The best benchmark RSE values in Table 5 are again the aug-Martin-3 results. However, it can be seen from a comparison of the Martin-3 and aug-Martin-3 RSE values for [•]CH₂F and [•]CH₂CN that the addition of diffuse functions does not have a large effect on the calculated RSEs. Therefore, the Martin-3 RSE values are also considered adequate for general use as benchmarks.

In general, the G2, G3, CBS-Q and CBS-APNO standard methods, as well as their modifications, give RSE values within 6 kJ mol⁻¹ of the Martin values, indicating a reasonable cancellation of errors in isodesmic reactions (1) and (3). The G2 and G3 methods tend to slightly underestimate the RSEs relative to the Martin-3 values, whereas the CBS methods tend to overestimate the RSEs. For the G3 and CBS procedures, this can largely be attributed to the small deviations from Martin-3 for the methane bond dissociation energy, while for the G2 methods the overestimation of the methane BDE carries over to the other systems leading generally to a good cancellation of errors. The only exceptions occur for CH₂=C[•]CN, where the G2 and G3 theories underestimate the stabilization by 9–11 kJ mol⁻¹ relative to Martin-3. G2-RAD(QCISD) offers improvement in this case and gives RSE values that are consistently in good agreement with the benchmark results (within 2 kJ mol⁻¹). Except for CH₂=C[•]CN, the G3 methods calculate stabilization energies that are within 2 kJ mol⁻¹ of the Martin values. The CBS-RAD procedure calculates RSE values for the [•]CH₂F and CH₂=C[•]F radicals that agree well with the Martin results. However, the results for the other four radicals are slightly too high. RSE values predicted by CBS-QB3 are very similar to the CBS-RAD results, except for CH₂=C[•]CN where the RSE appears to be somewhat too high.

Direct methods. The compound methods discussed above are generally computationally too demanding for the calculation of RSE values of larger radicals. It is therefore important to examine the performance of methods that might be more generally applicable. Table 6 lists RSE values for the radicals that have been computed with a variety of electron correlation treatments and basis sets. In all cases, the energies used to calculate the RSE values were corrected with scaled B3-LYP/6-31G(d) ZPEs. The Martin-3 benchmark RSE values are included for comparison purposes. The fluoromethyl, cyanomethyl, allyl, formylmethyl and cyanovinyl radicals are predicted to be stabilized at all levels of theory other than UMP2 for cyanomethyl radical, and UMP2 and PMP2 for the cyanovinyl radical. The fluorovinyl radical is computed to be slightly destabilized at all levels of theory.

We have classified the calculations according to the treatment used for the free radicals involved in reactions (1) and (3):

Table 6 Radical stabilization energies (0 K, kJ mol⁻¹) computed as a function of correlation level and basis set^{a,b}

Method	[•] CH ₂ F	[•] CH ₂ CN	[•] CH ₂ CH=CH ₂	[•] CH ₂ CHO	CH ₂ =C [•] F	CH ₂ =C [•] CN
UHF						
6-31G(d)	7.6	38.3	81.9	48.2	-10.9	32.4
6-311G(d,p)	3.9	33.8	78.1	43.1	-13.2	28.6
6-311+G(d,p)// ^c	1.9	31.9	76.6	41.0	-13.7	28.5
6-311+G(2df,p)// ^c	3.5	31.7	75.6		-12.0	27.1
6-311+G(3df,2p)// ^c	3.7	31.7	75.8	38.7	-12.2	26.8
UMP2						
6-31G(d)	16.9	-8.3	44.3	2.8	-3.5	-46.1
6-311G(d)	16.3	-8.7	41.9		-3.2	-43.4
6-311G(d,p)	16.4	-7.5	41.9	3.0	-4.0	-42.8
6-311+G(d,p)	11.7	-9.9	41.4		-7.8	-44.3
6-311+G(df,p)	14.5	-8.4	42.2	2.8	-5.3	-43.0
6-311+G(2df,p)	13.0	-5.7	44.8		-7.5	-41.1
6-311++G(3df,3pd)	12.2	-6.3	44.0	4.4	-7.5	-41.1
PMP2^d						
6-31G(d)//	16.0	20.1	77.4	27.1	-6.4	17.4
6-311+G(d,p)//	11.2	18.6	72.9	25.9	-9.1	15.2
6-311+G(2df,p)//	12.1	22.3	76.0	28.4	-9.0	16.9
6-311+G(3df,2p)//	12.0	22.2	76.0	28.7	-8.8	14.7
PMP2^e						
6-31G(d)//	16.0	18.5	76.1	26.4	-6.1	-10.2
6-311+G(d,p)//	11.2	17.0	71.8	25.3	-8.9	-11.6
6-311+G(2df,p)//	12.1	20.7	74.8	27.8	-8.8	-11.7
6-311+G(3df,2p)//	12.0	20.6	74.8	28.1	-8.6	-12.3
RMP2						
6-31G(d)	17.5	33.0	73.7	34.1	-3.5	16.9
6-31+G(d)// ^f	7.9	29.0	72.7	31.5	-8.3	14.9
6-311+G(d)// ^f	11.0	27.7	72.8	30.0	-7.3	15.3
6-311+G(d)// ^g	11.3	28.0	72.9	29.8	-7.1	14.1
6-311+G(d,p)// ^f	11.6	28.2	72.4	29.5	-7.2	16.2
6-311+G(2df,p)// ^f	12.4	30.9	77.0	32.4	-7.5	21.4 ^h
6-311+G(3df,2p)// ^f	12.3	30.8	77.3	32.4	-7.3	19.5 ^h
B3-LYP						
6-31G(d)	25.4	49.6	82.1	50.6	-1.4	37.8
6-311G(d)	22.3	46.7	80.3		-3.2	35.6
6-311G(d,p)	22.0	46.3	79.9	46.6	-4.8	34.5
6-311+G(d,p)	16.3	43.3	78.3		-8.1	33.4
6-311+G(d,p)// ^g	16.6	43.3	78.7	44.8	-7.9	33.4
6-311+G(2df,p)// ^g	17.7	44.2	78.7		-6.7	34.5
6-311+G(3df,2p)// ^g	17.9	44.5	78.8	45.4	-6.9	33.7
QCISD						
6-31G(d)	17.0	35.1	67.6	37.3	-4.9	11.5
6-311G(d,p)	15.2	32.7	65.8	34.1	-5.5	11.8
6-311+G(d,p)// ⁱ	10.9	30.0	65.1	33.1	-8.4	11.1
6-311+G(2df,p)// ⁱ	11.9	31.9	67.9	35.4	-8.9	12.3
QCISD(T)						
6-31G(d)	17.1	34.6	66.9	37.4	-4.5	12.2
6-311G(d,p)// ⁱ	16.2	32.2	64.9	33.3	-4.6	12.4
6-311+G(d,p)// ⁱ	11.8	29.5	64.3	32.4	-7.4	11.7
6-311+G(2df,p)// ⁱ	13.0	32.2	67.8	35.3	-7.9	13.7
UCCSD(T)						
6-31G(d)// ⁱ	16.8	33.4	66.2	36.5	-4.8	12.1
6-311G(d,p)// ⁱ	15.7	30.7	64.1	32.3	-4.9	11.1
6-311+G(d,p)// ⁱ	11.4	28.4	63.5	31.3	-7.7	11.1
6-311+G(2df,p)// ⁱ	12.6	31.0	66.9	34.2	-8.2	12.8
URCCSD(T)						
6-31G(d)// ⁱ	16.8	34.6	67.7	37.2	-4.8	16.8
6-311G(d,p)// ⁱ	15.8	32.2	65.6	33.6	-4.9	16.9
6-311+G(d,p)// ⁱ	11.5	29.9	65.0	32.6	-7.6	16.1
6-311+G(2df,p)// ⁱ	12.7	32.5	68.5	35.5	-8.1	17.9

Table 6 (Contd.)

Method	$\cdot\text{CH}_2\text{F}$	$\cdot\text{CH}_2\text{CN}$	$\cdot\text{CH}_2\text{CH}=\text{CH}_2$	$\cdot\text{CH}_2\text{CHO}$	$\text{CH}_2=\text{C}\cdot\text{F}$	$\text{CH}_2=\text{C}\cdot\text{CN}$
RRCCSD(T)						
6-31G(d)// ⁱ	16.6	33.0	65.1	35.2	-5.0	15.4
6-311G(d,p)// ⁱ	15.5	30.5	63.0	31.4	-5.2	15.5
6-311+G(d,p)// ⁱ	11.1	28.2	62.5	30.5	-8.0	14.7
6-311+G(2df,p)// ⁱ	12.3	30.5	65.9	33.3	-8.5	16.3
Martin-3						
	12.9	33.0	70.8	36.6	-8.2	17.1

^a Calculated using reactions (1) and (3) from the text. ^b All levels of theory (except for Martin-3) have been corrected with scaled B3-LYP/6-31G(d) ZPE values. ^c The single-point energies were calculated at the HF/6-31G(d) geometries. ^d The single-point energies were calculated with the leading (quartet) component of the spin-contamination annihilated. The geometries used were UMP2/6-31G(d) except for $\text{CH}_2=\text{C}\cdot\text{CN}$ where the C_{2v} B3-LYP/6-31G(d) geometry is used since this structure gives a lower total energy. See ref. 10. ^e The single-point energies were calculated with the first four components of the spin-contamination annihilated. The geometries used were UMP2/6-31G(d) except for $\text{CH}_2=\text{C}\cdot\text{CN}$ where the QCISD/6-31G(d) geometry was used as this gives a lower energy. See ref. 10. ^f The single-point energies were calculated at the RMP2/6-31G(d) geometries. ^g The single-point energies were calculated at the B3-LYP/6-31G(d) geometries. ^h The RSE values were computed using the C_{2v} B3-LYP/6-31G(d) geometry of $\text{CH}_2=\text{C}\cdot\text{CN}$ as this gives a lower energy. See ref. 10. ⁱ The single-point computation was performed on the QCISD/6-31G(d) geometry.

A) UHF. The results in Table 6 show that the UHF/6-31G(d) level of theory predicts RSE values in reasonable agreement with the Martin results, except for the allyl, formylmethyl and cyanovinyl radicals. In the case of the cyano-containing radicals ($\cdot\text{CH}_2\text{CN}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$), as well as for $\cdot\text{CH}_2\text{CH}=\text{CH}_2$ and $\cdot\text{CH}_2\text{CH}=\text{O}$, increasing the basis set size improves the agreement of the results with Martin-3, whereas for the fluorine-containing radicals, the discrepancy with Martin-3 increases as the basis set gets larger. All the UHF/6-311+G(3df,2p) RSEs agree with the Martin-3 values to within 10 kJ mol⁻¹, but in two cases the discrepancy is greater than 9 kJ mol⁻¹.

B) UMP2. One conclusion that is clear from Table 6 is that for both of the cyano-containing radicals ($\cdot\text{CH}_2\text{CN}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$), as well as for the allyl and formylmethyl radicals, the UMP2 level of correlation predicts RSE values that are significantly different from those of the benchmark. In the case of $\cdot\text{CH}_2\text{CN}$ and $\text{CH}_2=\text{C}\cdot\text{CN}$, not only are the magnitudes of the RSEs incorrect, but the signs are wrong. UMP2 likewise considerably underestimates the stabilization of the allyl and formylmethyl radicals. Computing the RSE values with very large basis sets does not greatly improve the agreement with the Martin-3 results. The failure of UMP2 to predict adequate stabilization energies may be attributed to the fact that it copes poorly with spin-contamination in radicals. This conclusion is supported by the fact that the deviation from Martin-3 values generally increases with greater radical spin-contamination. The difference between the UMP2 and Martin-3 RSE values for the cyanovinyl radical is about 60 kJ mol⁻¹.

C) PMP2. When the 6-31G(d) basis set is used, PMP2 with only the leading component of the spin-contamination annihilated leads to RSE values that agree well with Martin-3, except for $\cdot\text{CH}_2\text{CN}$ and $\cdot\text{CH}_2\text{CH}=\text{O}$ (Table 6). Increasing the basis set size slightly improves the agreement with Martin-3 for both $\cdot\text{CH}_2\text{CN}$ and $\cdot\text{CH}_2\text{CH}=\text{O}$, but the changes with basis set are relatively small. More complete annihilation of the spin-contamination actually increases the deviation of the results from Martin-3 in the case of the cyano-containing radicals, particularly for $\text{CH}_2=\text{C}\cdot\text{CN}$ which is calculated to be destabilized. The PMP2 results are found to differ considerably from RMP2 (see below) in situations involving strongly spin-contaminated radicals.

D) RMP2. Stabilization energies calculated using RMP2 energies are in good general agreement with Martin-3. At the RMP2/6-31G(d) level, the largest deviations from Martin-3 RSE values are 4–5 kJ mol⁻¹ for the $\cdot\text{CH}_2\text{F}$ and $\text{CH}_2=\text{C}\cdot\text{F}$ radicals. Addition of diffuse functions to heavy atoms (the 6-31+G(d) basis set) results in a decrease in calculated RSE values, particularly for the fluorine-containing radicals. Computing RSEs with single-point energies using still larger basis sets improves agreement with the Martin-3 result for the $\cdot\text{CH}_2\text{F}$

radical. The RSEs have essentially converged with the 6-311+G(2df,p) basis set. The changes observed in increasing the basis set size further to 6-311+G(3df,2p) are less than 1 kJ mol⁻¹, except for $\text{CH}_2=\text{C}\cdot\text{CN}$ (where there is a 1.9 kJ mol⁻¹ change). The cyanovinyl radical is calculated to have a lower energy with the C_{2v} B3-LYP/6-31G(d) geometry than with the C_s RMP2/6-31G(d) geometry for RMP2 calculations with the 6-311+G(2df,p) and 6-311+G(3df,2p) basis sets.¹⁰ With the 6-311+G(2df,p) basis set, the largest deviation from the Martin-3 RSE values is 6.2 kJ mol⁻¹ for the $\cdot\text{CH}_2\text{CH}=\text{CH}_2$ radical. The smaller 6-311+G(d) basis set which would be applicable to larger systems gives results to within 7 kJ mol⁻¹ of the Martin-3 values for the radicals studied. Thus RMP2 appears to be attractive for calculating radical stabilization energies.

E) B3-LYP. The B3-LYP density functional procedure yields RSE values that are generally 5–20 kJ mol⁻¹ higher than the Martin-3 results. Increasing the basis set size improves the agreement of the results with Martin-3, but the RSE values are still significantly higher than the Martin values. The largest differences are found for the two cyano-substituted radicals.

F) QCISD and QCISD(T). Table 6 shows that energies calculated with the QCISD and QCISD(T) methods and a variety of basis sets yield good RSE values. Once a sufficiently large basis set is used at the QCISD(T) level, the calculated RSEs for $\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{CN}$ and $\text{CH}_2=\text{C}\cdot\text{F}$ lie within 1 kJ mol⁻¹ of the Martin-3 values, within 2 kJ mol⁻¹ for $\cdot\text{CH}_2\text{CH}=\text{O}$, within 3 kJ mol⁻¹ for $\cdot\text{CH}_2\text{CH}=\text{CH}_2$, and within 4 kJ mol⁻¹ for the cyanovinyl radical. It should be noted, however, that the large basis set single-point QCISD(T) energy calculations are computationally quite expensive for large molecules.

G) UCCSD(T), URCCSD(T) and RRCCSD(T). The various coupled-cluster methods generally predict RSE values that agree well with Martin-3 results (Table 6). The three procedures calculate very similar stabilization energies for the $\cdot\text{CH}_2\text{F}$, $\cdot\text{CH}_2\text{CN}$, $\cdot\text{CH}_2\text{CH}=\text{CH}_2$, $\cdot\text{CH}_2\text{CH}=\text{O}$ and $\text{CH}_2=\text{C}\cdot\text{F}$ radicals. For the $\text{CH}_2=\text{C}\cdot\text{CN}$ radical, the URCCSD(T) and RRCCSD(T) methods calculate RSEs that are slightly closer to Martin-3 than those predicted using the UCCSD(T) procedure, a result that is not unexpected given that Martin-3 is based on URCCSD(T).

Recommended procedures

Of the compound methods examined in the present study, the Martin-3 and aug-Martin-3 procedures are considered the most accurate but they are also computationally the most expensive and thus cannot be routinely applied to larger free radicals. G2-RAD(QCISD) appears to yield very good RSE values, but the method will also be computationally quite demanding for larger systems. The CBS-RAD method does not perform quite as well

Table 7 Radical stabilization energies (0 K, kJ mol⁻¹) calculated using RMP2/6-311+G(2df,p) energies at various geometries^a

Geometry	[•] CH ₂ F	[•] CH ₂ CN	[•] CH ₂ CH=CH ₂	[•] CH ₂ CHO	CH ₂ =C [•] F	CH ₂ =C [•] CN
UHF/6-31G(d)	12.8	34.1	77.3	34.3	-5.9	23.1
B3-LYP/6-31G(d)	13.0	31.2	77.1	32.3	-7.4	21.4
RMP2/6-31G(d)	12.4	30.9	77.0	32.4	-7.5	18.7
Martin-3	12.9	33.0	70.8	36.6	-8.2	17.1

^a All results other than Martin-3 have been corrected with scaled B3-LYP/6-31G(d) ZPE values.

as G2-RAD(QCISD) but is somewhat less computationally intensive. CBS-QB3 calculates good stabilization energies apart from the cyanovinyl radical. G3 theory generally predicts reasonable RSE values, though the CH₂=C[•]CN results are less good.

A good compromise between accuracy and expense is provided by RMP2. It is apparent from the results in Table 6 that RMP2 single-point energies obtained with sufficiently large basis sets lead to RSE values that are in generally good agreement with the Martin-3 results. In particular, it should be noted that the calculated RSE values appear to have converged at the 6-311+G(2df,p) basis set. The RMP2/6-311+G(2df,p) single-point computations for radicals are significantly less computationally demanding than the compound methods listed in Table 5 (e.g. Martin-3, G2-RAD(QCISD), G3, CBS-RAD and CBS-QB3) and thus represent an attractive level of theory for calculating RSEs.

In order to probe further the use of RMP2 in obtaining RSEs for larger radicals, stabilization energies were evaluated with RMP2/6-311+G(2df,p) single-point calculations on B3-LYP/6-31G(d) and HF/6-31G(d) geometries (Table 7). When the B3-LYP/6-31G(d) geometries are used, the largest deviation from the Martin-3 RSE values is 6.3 kJ mol⁻¹ for the [•]CH₂CH=CH₂ radical. In the case of HF/6-31G(d) geometries, the largest deviation from the Martin-3 values is 6.5 kJ mol⁻¹ for the [•]CH₂CH=CH₂ radical. This indicates that it may also be possible to obtain good RSE values by using RMP2/6-311+G(2df,p) single-point energies on B3-LYP/6-31G(d) or HF/6-31G(d) geometries.

If slightly reduced accuracy is acceptable, then RSE values can be calculated using RMP2/6-311+G(d)//B3-LYP/6-31G(d) energies. It can be seen from Table 6 that results at this level lie within 7 kJ mol⁻¹ of the Martin-3 values.

Summary

Taken together with the results of our previous work,⁹ there are several important general points that emerge from the present study:

(1) As expected, the standard G2 geometry (MP2(fu)/6-31G(d)) is generally adequate for closed-shell molecules. However, for spin-contaminated radicals, UMP2 geometries may differ significantly from those obtained at higher levels of theory. RMP2/6-31G(d) and B3-LYP/6-31G(d) represent a reasonable compromise to the computationally more expensive UQCISD/6-31G(d) geometries.

(2) All levels of theory examined predict good ZPE values for closed-shell molecules. However, UHF and UMP2 ZPE values can be inadequate for spin-contaminated radicals. B3-LYP/6-31G(d) yields good ZPE values for both radicals and closed-shell molecules.

(3) The UMP2 level of electron correlation should generally be avoided for the calculation of RSE values. The failure of UMP2 arises as a result of significant spin-contamination in some of the radicals, leading to incomplete cancellation of errors in the reactions that define the stabilization energies. PMP2, although better than UMP2, is also not recommended for the calculation of RSE values. The B3-LYP density functional method tends to somewhat overestimate RSE values.

(4) All the compound methods examined (G2, G3 and CBS and modifications of these) lead generally to RSE values that are in reasonable accord with benchmark values.

(5) RMP2/6-311+G(2df,p) single-point calculations on RMP2/6-31G(d) or B3-LYP/6-31G(d) geometries give RSEs that are generally in good agreement with the benchmark Martin-3 values. This level of theory is less computationally demanding than the G2, G3 and CBS methods and is recommended for general use. A slightly less accurate but more economical procedure for calculating RSE values involves using RMP2/6-311+G(d)//B3-LYP/6-31G(d) energies and this is recommended for the treatment of larger systems.

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