J. Phys. Chem. A **1998,** *102,* 2237−2245

Radical Addition to Alkenes: Further Assessment of Theoretical Procedures

Ming Wah Wong*,[1a] and Leo Radom*,[1b]

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, and Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Received: October 23, 1997

Ab initio molecular orbital calculations at a variety of levels of theory have been carried out for a number of prototypical radical addition reactions with a view to determining a level of theory suitable for predicting reliable barriers. Closest agreement with experimental barriers is achieved with a variant of the recently introduced CBS-RAD procedure. At this level, the mean absolute deviation from experimental barriers for methyl radical additions in solution is just 1.4 kJ mol^{-1}. A second high-level theoretical procedure examined is a variant of G2(MP2,SVP), corresponding effectively to QCISD(T)6-311+G(3df,2p) energy calculations on QCISD/6-31G(d) optimized geometries and incorporating scaled B3-LYP/6-31G(d) zero-point vibrational energy corrections. At this level, the mean absolute deviations from the experimental barriers is significantly larger at 7.7 kJ mol^{-1}, the calculated barriers being consistently too high. The effect of quadruple excitations is found to be small. The considerably less expensive B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d) procedure performs quite well, with a mean absolute deviation of about 5.6 kJ mol^{-1}. Solvent effects were estimated using the SCIPCM model. For a dielectric constant of 2 (nonpolar medium), the effect on barrier ranges from −1.1 to +1.1 kJ mol^{-1}, while for a dielectric constant of 40 (polar medium), the effects range from −3.0 to +2.8 kJ mol^{-1}.

Introduction

The addition of radicals to alkenes

$$R^{\bullet} + CH_2{=}CXY \rightarrow RCH_2{-}CXY^{\bullet} \qquad (1)$$

is of importance from both a fundamental and practical point of view.[2] Such reactions have been studied extensively both experimentally[3] and theoretically,[4−7] but the determination of accurate thermochemical and kinetic parameters is not completely straightforward and discrepancies between experimental and theoretical reaction barriers still persist. In a previous study,[6] we assessed the performance of a variety of levels of ab initio molecular orbital theory in describing radical addition reactions with a view to determining a level of theory suitable for widespread application. Since that time, more experimental data have become available[3l,m,p] which enables a more comprehensive assessment. This reveals that although the agreement between the previous theoretical treatments and the new experimental data is reasonable, there are differences that should be explored further. Such a further exploration is described in the present article. We examine levels of theory higher than those used in the previous study for geometry optimization, vibrational frequency analysis, and energy calculations. We present a more detailed study of the performance of density functional calculations, and we also investigate possible solvent effects using a continuum model.

Theoretical Procedures

Standard ab initio molecular orbital calculations[8] were carried out with the GAUSSIAN 94 suite of programs.[9] Calculations were performed with unrestricted Hartree−Fock (UHF), unrestricted (UMP2), projected (PMP2),[10] and restricted (RMP2)[11] second-order Møller−Plesset perturbation theory, quadratic configuration interaction (QCISD and QCISD(T)),[12] coupled-cluster theory (CCSD(T)),[13] and gradient-corrected nonhybrid and hybrid density functional theory (B-LYP and B3-LYP)[14] procedures. Unless explicitly noted to the contrary, open-shell systems are treated using unrestricted procedures. The U for unrestricted will occasionally be retained for emphasis but is often dropped for simplicity.

In a first series of calculations, geometries were optimized at a number of levels of theory including UHF/6-31G(d), UMP2/6-31G(d), and UQCISD/6-31G(d). Single-point energy calculations were carried out at these optimized geometries at the RMP2 and UQCISD(T) levels leading, through additivity approximations (see below), to energies effectively at the UQCISD/6-311G(d,p), UQCISD(T)/6-311G(d,p), and UQCISD(T)/6-311+G(3df,2p) levels. Zero-point vibrational energies (ZPVEs) were obtained from harmonic vibrational frequencies determined at the UHF/6-31G(d), B3-LYP/6-31G(d), and UQCISD/6-31G(d) levels using appropriate scaling factors.[15,16] Our best calculations in this series of calculations correspond to a variant of G2(MP2,SVP),[17] designated G2(MP2,SVP)(RMP2,QCISD,B3-LYP). This corresponds to a G2(MP2,SVP) calculation in which the basis set additivity is performed with RMP2 (in place of UMP2), geometries are optimized at QCISD/6-31G(d) (in place of UMP2/6-31G(d)), and ZPVEs are calculated at the scaled B3-LYP/6-31G(d) level (in place of HF/6-31G(d)). For simplicity, we will generally refer to this procedure in the text as G2(MP2,SVP).

A second series of high-level calculations uses the CBS-RAD(QCISD,B3-LYP) procedure, recently introduced as a method suitable for the calculation of reliable thermochemistry for free radicals.[18] This is a variant of the complete-basis-set CBS-Q method[19] in which the geometries are optimized at the QCISD/6-31G(d) level, zero-point energies are obtained at the B3-LYP/6-31G(d) level, and coupled-cluster theory is used in place of

S1089-5639(97)03427-0 CCC: $15.00

quadratic configuration interaction in single-point energy calculations. For simplicity, we will generally refer to CBS-RAD-(QCISD,B3-LYP) in the text as CBS-RAD.

In a third series of calculations, geometries were optimized at the B3-LYP/6-31G(d) level and single-point B3-LYP energy calculations carried out on these optimized structures with a series of basis sets up to 6-311+G(3df,2p).

Finally, solvent effects were calculated using the self-consistent isodensity polarizable continuum model (SCIPCM).[20] In this model, the solute is taken to occupy a cavity which is determined self-consistently from an isodensity surface (0.0004 au), and the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ϵ).

Results and Discussion

Experimental Comparisons. We have chosen to compare our theoretical predictions with the extensive recent experimental results from Fischer and co-workers in Zurich.[3l,m,p] Several points need to be kept in mind in making such comparisons.

In the first instance, the theoretical results refer to isolated molecules in the gas phase whereas the experiments were carried out in solution. We make some brief comments on possible solvent effects later.

Second, we note that experimental results are reported for the $Si(CH_3)_3$ substituent whereas, for computational economy, we have generally only examined the SiH_3 substituent in our calculations. However, for the $CH_3^\bullet + CH_2{=}CHX$ reaction we find barriers at the HF/6-31G(d) level of 36.9 and 38.6 kJ mol^{-1} for X = SiH_3 and $Si(CH_3)_3$, respectively, and corresponding reaction enthalpies of −113.7 and −112.4 kJ mol^{-1}. Thus, use of SiH_3 to model the $Si(CH_3)_3$ substituent appears to be a reasonable approximation, possibly underestimating the barrier and overestimating the exothermicity by 1−2 kJ mol^{-1}.

Next, we note that the calculated barriers refer to energy ($\Delta E^\ddagger$) and enthalpy ($\Delta H^\ddagger$) differences between transition structures and reactants whereas the experiments refer to Arrhenius activation energies (E_{act}). At 0 K, these three quantities are all equal (and can be denoted E_0). However, at finite temperature they differ. For bimolecular reactions, the relationship between E_{act} and $\Delta E^\ddagger$ is[21]

$$E_{act}(T) = E_0 + \Delta\Delta E^\ddagger(T) + RT \qquad (2)$$

where $\Delta\Delta E^\ddagger(T)$ is the thermal contribution to $\Delta E^\ddagger(T)$ at temperature T. In addition, for bimolecular reactions in the gas phase, $\Delta H^\ddagger = \Delta E^\ddagger - RT$ leading to

$$E_{act}(T) = E_0 + \Delta\Delta H^\ddagger(T) + 2RT \qquad (3)$$

while in condensed phases, $\Delta H^\ddagger = \Delta E^\ddagger$ leading to

$$E_{act}(T) = E_0 + \Delta\Delta H^\ddagger(T) + RT \qquad (4)$$

Finally, we note that the experimental activation energies for the methyl radical addition reactions were obtained[3p] assuming an average frequency factor of log A = 8.5. The overall uncertainty in the experimental activation energies, including this assumption, is ±4 kJ mol^{-1}.

The experimental reaction enthalpies[3l,m,p] have been estimated using experimental data from a variety of sources. Some of the values have a significant uncertainty, and the comparisons with theoretical values should be viewed in that light. A definitive assessment of the calculation of reaction enthalpies is therefore not attempted in the present work.

TABLE 1: Calculated (B3-LYP/6-31G(d)) 298 K Temperature Corrections to Barriers, Activation Energies, and Reaction Enthalpies[a]

radical	alkene	$\Delta\Delta H^{\ddagger b}$	$\Delta\Delta H^\ddagger + RT^c$	$\Delta\Delta H^d$
$CH_3^\bullet$	$CH_2{=}CH_2$	−4.7	−2.2	−5.7
$CH_3^\bullet$	$CH_2{=}CHCH_3$	−3.8	−1.3	−5.0
$CH_3^\bullet$	$CH_2{=}CHNH_2$	−3.6	−1.2	−5.8
$CH_3^\bullet$	$CH_2{=}CHOH$	−3.8	−1.3	−5.7
$CH_3^\bullet$	$CH_2{=}CHF$	−4.0	−1.5	−5.9
$CH_3^\bullet$	$CH_2{=}CHSiH_3$	−3.7	−1.3	−5.3
$CH_3^\bullet$	$CH_2{=}CHCl$	−3.7	−1.3	−5.2
$CH_3^\bullet$	$CH_2{=}CHCHO$	−3.5	−1.0	−6.0
$CH_3^\bullet$	$CH_2{=}CHCN$	−3.4	−1.0	−5.6
$CH_3^\bullet$	$CH_2{=}CHOCH_2CH_3$	−3.6	−1.1	−5.0
$CH_3^\bullet$	$CH_2{=}CCl_2$	−2.9	−0.4	−5.4
$CH_3^\bullet$	$CH_2{=}C(CH_3)Cl$	−3.0	−0.6	−6.7
$CH_3^\bullet$	$CH_2{=}C(CH_3)CN$	−2.9	−0.4	−4.9
$CH_2OH^\bullet$	$CH_2{=}CH_2$	−3.3	−0.8	−3.1
$CH_2OH^\bullet$	$CH_2{=}CHSiH_3$	−2.1	+0.4	−2.8
$CH_2OH^\bullet$	$CH_2{=}CHCl$	−2.2	+0.3	−3.3
$CH_2OH^\bullet$	$CH_2{=}CHCHO$	−1.9	+0.6	−3.7
$CH_2OH^\bullet$	$CH_2{=}CCl_2$	−1.2	+1.3	−2.7
$CH_2OH^\bullet$	$CH_2{=}CHCN$	−2.8	−0.4	−3.3
$CH_2CN^\bullet$	$CH_2{=}CH_2$	−3.5	−1.0	−3.0
$CH_2CN^\bullet$	$CH_2{=}CHSiH_3$	−2.2	+0.3	−2.5
$CH_2CN^\bullet$	$CH_2{=}CHCl$	−2.4	+0.1	−3.1
$CH_2CN^\bullet$	$CH_2{=}CHCHO$	−2.3	+0.2	−4.6
$CH_2CN^\bullet$	$CH_2{=}CCl_2$	−1.5	+1.0	−2.6
$CH_2CN^\bullet$	$CH_2{=}CHCN$	−2.3	+0.2	−3.1

[a] Calculated from B3-LYP/6-31G(d) vibrational frequencies scaled by 0.9989. Scaling factor from ref 15. [b] Thermal contribution to the reaction barrier ($\Delta H^\ddagger$) at 298 K. [c] Thermal contribution to the activation energy (E_a) in condensed phases at 298 K (cf. eq 4). [d] Thermal contribution to the reaction enthalpy (ΔH) at 298 K.

Values for $\Delta\Delta H^\ddagger(T)$ and $\Delta\Delta H^\ddagger(T) + RT$ and for the reaction enthalpy $\Delta\Delta H(T)$ at 298 K have been obtained for all the systems under consideration in the present work using scaled B3-LYP/6-31G(d) vibrational frequencies and are presented in Table 1. These temperature corrections are then used to back-correct the experimental values[3l,m,p] of the barriers and reaction enthalpies to 0 K.

Standard Calculations. Our starting point is the standard level of theory that we have previously used in broad comparisons of barriers and reaction enthalpies for radical addition reactions.[5,6] This involves calculating geometries at the UHF/6-31G(d) level and then determining barriers and enthalpies at these geometries effectively at the QCISD/6-311G(d,p) level using the additivity approximation

$$\Delta E[\text{QCISD/6-311G(d,p)}] \approx \Delta E[\text{QCISD/6-31G(d)}] + \Delta E[\text{RMP2/6-311G(d,p)}] - \Delta E[\text{RMP2/6-31G(d)}] \qquad (5)$$

ZPVE corrections are calculated from HF/6-31G(d) vibrational frequencies scaled by 0.8929.

Table 2 presents a comparison of barriers calculated at this level with recent experimental values from the Fischer group for the addition of the $CH_3^\bullet$, $CH_2OH^\bullet$, and $CH_2CN^\bullet$ radicals to a selection of alkenes.[3l,m,p] As noted above, the experimental barriers have been corrected to 0 K using the temperature corrections of Table 1 and eq 4. The agreement between theory and experiment is generally quite pleasing, but with an overall mean absolute deviation of 8.1 kJ mol^{-1} there is room for improvement. A useful observation is that the differences between theory and experiment for the addition reactions *of a particular radical* lie within a relatively narrow range, e.g., from +7.3 to +12.7 kJ mol^{-1} for $CH_3^\bullet$ radical additions, indicating that relative values for the addition of a particular radical might be reasonably well described. However, the variation in the

TABLE 2: Comparison of Theoretical (QCISD/6-311G(d,p) + ZPVE)[a] and Experimental Barriers (kJ mol^{-1}) for the Addition of Radicals ($R^\bullet$) to Alkenes ($CH_2{=}CXY$)

		$CH_3^\bullet$		$CH_2OH^\bullet$		$CH_2CN^\bullet$	
X	Y	theory[b]	expt[c]	theory[b]	expt[d]	theory[b]	expt[e]
H	H	38.9	30.4	32.7	31.2	42.5	28.4
SiH_3	H	33.6[f]	24.7[g]	28.2[f]	25.3[g]	38.5[f]	23.8[g]
Cl	H	32.5	25.2	24.6	25.7	35.9	24.3
CHO	H	28.7	16.0	18.3	11.4	33.9	20.9
Cl	Cl	26.3[f]	18.3	21.1[f]	18.0	29.0[f]	21.9
CN	H	24.3	16.4	11.7	13.6	32.6	17.5
mean abs dev		8.9		2.9		12.6	
min dev		+7.3		−1.9		+7.1	
max dev		+12.7		+6.9		+15.1	

[a] Evaluated at UHF/6-31G(d) optimized geometries using the additivity approximation of eq 5; see text. ZPVEs calculated from UHF/6-31G(d) vibrational frequencies, scaled by 0.8929. Corresponding to 0 K. [b] From ref 5c, unless otherwise noted. [c] From ref 3p. Corrected to 0 K using the temperature corrections of Table 1 and eq 4. [d] From ref 3m. Corrected to 0 K using the temperature corrections of Table 1 and eq 4. [e] From ref 3l. Corrected to 0 K using the temperature corrections of Table 1 and eq 4. [f] Present work. [g] Experimental results are for the $(CH_3)_3Si$ substituent; see text.

differences between theory and experiment for the addition reactions *of different radicals* is large, e.g., mean absolute deviations of 8.9, 2.9, and 12.6 kJ mol^{-1} for $CH_3^\bullet$, $CH_2OH^\bullet$, and $CH_2CN^\bullet$ radical additions, respectively.

Parallel results for reaction enthalpies are shown in Table 3. The deviations between theory and experiment are smaller than those for the barriers, but in this case the differences show much greater variation, even for the addition reactions of a particular radical.

On the basis of these results, it is clearly desirable to explore the effect of going beyond this standard level of theory.

Effect of Triple Excitations. As a first step in improving the theoretical description, we examine the effect of using QCISD(T) instead of QCISD in the calculations using a modified additivity approximation:

$$\Delta E[\text{QCISD(T)/6-311G(d,p)}] \approx \Delta E[\text{QCISD(T)/6-31G(d)}] + \Delta E[\text{RMP2/6-311G(d,p)}] - \Delta E[\text{RMP2/6-31G(d)}] \quad (6)$$

We can see (Table 4) that inclusion of triple excitations leads to a significant barrier lowering in absolute terms. However, the lowering is relatively constant at 4.1 ± 0.5 kJ mol^{-1}. This means that *relative* barriers at the QCISD and QCISD(T) levels are very similar, as we found previously.[6]

There are three examples in Table 3 showing the effect of a β-methyl substituent on the barrier. Both theory and experiment indicate that the effect is small, the theoretical effects ranging from −1.9 to −1.2 kJ mol^{-1} and the experimental effects ranging from −2.1 to 0.0 kJ mol^{-1}.

The corresponding results for reaction enthalpies (Table 5) show an effect of triple excitations that is smaller than that for the barriers; but again it is relatively constant. The exothermicities are reduced by 1.2 ± 0.5 kJ mol^{-1}. Theory indicates that the effect of methyl substitution on exothermicity is small (−0.7 to +0.7 kJ mol^{-1}) whereas the experimental estimates are much larger (−6.7 to +11.5 kJ mol^{-1}). There is also a large difference between theoretical and experimental estimates of the difference between CN and CHO substituents: 8.1 vs 21.4 kJ mol^{-1}. In general, the range of deviations between theoretical and experimental enthalpies is quite large for both QCISD and QCISD(T).

TABLE 3: Comparison of Theoretical (QCISD/6-311G(d,p) + ZPVE)[a] and Experimental Reaction Enthalpies (kJ mol^{-1}) for the Addition of Radicals ($R^\bullet$) to Alkenes ($CH_2{=}CXY$)

		$CH_3^\bullet$		$CH_2OH^\bullet$		$CH_2CN^\bullet$	
X	Y	theory[b]	expt[c]	theory[b]	expt[d]	theory[b]	expt[e]
H	H	−93.5	−92.3	−83.7	−83.4	−63.3	−65.5
SiH_3	H	−102.6[f]	−96.7[g]	−93.2[f]	−87.7[g]	−71.4[f]	−70.0[g]
Cl	H	−105.9	−100.8	−97.8	−91.2	−74.5	−73.4
CHO	H	−120.7	−112.0	−118.6	−102.8	−92.9	−83.9
Cl	Cl	−122.7[f]	−113.6	−111.2[f]	−104.8	−87.2[f]	−86.9
CN	H	−129.3	−133.4	−123.7	−124.2	−93.4	−106.4
mean abs dev		5.7		5.9		4.5	
min dev		−9.1		−15.8		−9.0	
max dev		+4.1		+0.5		+13.0	

[a] Evaluated at UHF/6-31G(d) optimized geometries using the additivity approximation of eq 5; see text. ZPVEs calculated from UHF/6-31G(d) vibrational frequencies, scaled by 0.8929. Corresponding to 0 K. [b] From ref 5c, unless otherwise noted. [c] From ref 3p. Corrected to 0 K using the temperature corrections of Table 1. [d] From ref 3m. Corrected to 0 K using the temperature corrections of Table 1. [e] From ref 3l. Corrected to 0 K using the temperature corrections of Table 1. [f] Present work. [g] Experimental results are for the $(CH_3)_3Si$ substituent; see text.

TABLE 4: Comparison of Theoretical (QCI/6-311G(d,p) + ZPVE)[a] and Experimental[b] Barriers (kJ mol^{-1}) for the Addition of Methyl Radical to Alkenes ($CH_2{=}CXY$)

X	Y	QCISD + ZPVE[a,c]	QCISD(T) + ZPVE[a,d]	B3-LYP + ZPVE[e,f]	expt[b]
OCH_2CH_3	H	40.0[f]	35.4[f]	37.7	25.9
H	H	38.9	35.2	34.7	30.4
CH_3	H	37.3[f]	33.3	34.5	29.0
SiH_3	H	33.6[f]	29.8	30.1	24.7[g]
Cl	H	32.5	28.5	29.3	25.2
Cl	CH_3	31.0[f]	26.8[f]	29.0	23.1
CHO	H	28.7	24.1	23.3	16.0
Cl	Cl	26.3[f]	22.3[f]	23.4	18.3
CN	H	24.3	20.4	19.5	16.4
CN	CH_3	23.3[f]	19.2[f]	20.3	16.4
mean abs dev		9.1	5.0	5.6	
min dev		+6.9	+2.8	+3.1	
max dev		+14.1	+9.5	+11.8	

[a] QCISD/6-311+G(3df,2p) and QCISD(T)/6-311+G(3df,2p) values obtained at UHF/6-31G(d) optimized geometries using the additivity approximations of eqs 5 or 6; see text. ZPVEs calculated from UHF/6-31G(d) vibrational frequencies, scaled by 0.8929. Corresponding to 0 K. [b] From ref 3p. Corrected to 0 K using the temperature corrections of Table l and eq 4. [c] From ref 5c, unless otherwise noted. [d] From ref 5b, unless otherwise noted. [e] B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d). ZPVEs calculated from B3-LYP/6-31G(d) vibrational frequencies, scaled by 0.9806 (see ref 15). [f] Present work. [g] Experimental results are for the $(CH_3)_3Si$ substituent; see text.

Effect of Geometry. We have explored the effect of choice of geometry on the calculated reaction barriers and enthalpies through optimizations with the 6-31G(d) basis set at the UHF, UMP2, B3-LYP, and QCISD levels followed by single-point energy calculations with QCISD(T)/6-31G(d) (Table 6). We see that the results can be extremely sensitive to choice of geometry, particularly for unsaturated substituents such as CHO and CN that are associated with large spin contamination where the barriers can be affected by as much as 14 kJ mol^{-1}. Interestingly, for the seven saturated systems, use of UHF/6-31G(d) geometries leads to an underestimation of the barriers within the narrow range of 2.6 ± 0.7 kJ mol^{-1}, use of UMP2/6-31G(d) geometries leads to an overestimation of the barriers by 2.5 ± 0.5 kJ mol^{-1}, while use of B3-LYP/6-31G(d) geometries gives the best results, underestimating the barriers by 1.8 ± 0.3 kJ mol^{-1}; results in all cases are compared with those obtained using QCISD/6-31G(d) geometries. There are

TABLE 5: Comparison of Theoretical (QCI/6-311G(d,p) + ZPVE)[a] and Experimental[b] Reaction Enthalpies (kJ mol^{-1}) for the Addition of Methyl Radical to Alkenes (CH_2═CXY)

X	Y	QCISD + ZPVE[a,c]	QCISD(T) + ZPVE[a,d]	B3-LYP + ZPVE[e,f]	expt[b]
OCH_2CH_3	H	−95.8[f]	−94.1[f]	−80.0	−101.0
H	H	−93.5	−92.3	−79.3	−92.3
CH_3	H	−93.4[f]	−92.4	−76.8	−99.0
SiH_3	H	−102.6[f]	−101.1	−88.7	−96.7[g]
Cl	H	−105.9	−105.0	−92.0	−100.8
Cl	CH_3	−105.9[f]	−105.2[f]	−89.7	−89.3
CHO	H	−120.7	−119.6	−110.1	−112.0
Cl	Cl	−122.7[f]	−122.0[f]	−107.1	−113.6
CN	H	−129.3	−127.7	−115.3	−133.4
CN	CH_3	−130.7[f]	−129.4[f]	−116.4	−122.1
mean abs dev		7.0	6.7	9.6	
min dev		−16.6	−15.9	−0.4	
max dev		+5.6	+6.9	+21.0	

[a] QCISD/6-311+G(3df,2p) and QCISD(T)/6-311+G(3df,2p) values obtained at UHF/6-31G(d) optimized geometries using the additivity approximations of eqs 5 or 6; see text. ZPVEs calculated from UHF/6-31G(d) vibrational frequencies, scaled by 0.8929. Corresponding to 0 K. [b] From ref 3p. Corrected to 0 K using the temperature corrections of Table 1. [c] From ref 5c, unless otherwise noted. [d] From ref 5b, unless otherwise noted. [e] B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d). ZPVEs calculated from B3-LYP/6-31G(d) vibrational frequencies, scaled by 0.9806 (see ref 15). [f] Present work. [g] Experimental results are for the $(CH_3)_3Si$ substituent; see text.

larger differences, however, for the unsaturated substituents, particularly for UMP2. B3-LYP geometries give results consistently closest to QCISD.

For the reaction enthalpies (also included in Table 6), the differences between using UHF/6-31G(d) and QCISD/6-31G(d) geometries is 1.8 ± 0.4 kJ mol^{-1} for the saturated systems but is as large as 7 kJ mol^{-1} for X = CN. The differences in enthalpies calculated with UMP2/6-31G(d) and QCISD/6-31G(d) geometries is smaller at 0.4 ± 0.1 kJ mol^{-1} for the saturated systems, but for X = CN the difference becomes nearly 8 kJ mol^{-1}. B3-LYP/6-31G(d) geometries again consistently give results closest to those obtained using QCISD/6-31G(d) geometries. Interestingly, in the adverse cases the effects of choice of geometry at the UHF and UMP2 levels are very similar for the barriers and enthalpies, which means that the transition structures and products are affected similarly by changes in the choice of geometry while the reactants are affected to a different extent. This would seem a surprising result for a reaction with an early transition structure, but it is perhaps consistent with the generally observed correlation of barrier height with reaction exothermicity.[5]

Effect of Basis Set. Barriers and enthalpies calculated for the reactions of CH3$^{\bullet}$ with CH_2═CHX (X = H, Cl, and CN) for several different basis sets and levels of theory are shown in Table 7. There are quite large decreases in barriers in going from 6-31G(d) to 6-311G(d,p) (2−4 kJ mol^{-1}), but the changes beyond that are smaller (up to 2 kJ mol^{-1}). The best estimates of the QCISD(T) basis set effect in the cases available are given by RMP2 and that is why RMP2 is used in the basis set additivity approximations such as eqs 5 and 6. RMP2 indicates a decrease in barrier in going from 6-311G(d,p) to 6-311+G(3df,2p) of 1−2 kJ mol^{-1}.

Interestingly, for the reaction enthalpies, the exothermicity decreases substantially (by 6−9 kJ mol^{-1}) in going from 6-311G(d,p) to 6-311+G(2d,p) but increases (by 3−6 kJ mol^{-1}) in going further from 6-311+G(2d,p) to 6-311+G(3df,2p). The overall effect is a decrease by about 2−4 kJ mol^{-1} in going from 6-311G(d,p) to 6-311+G(3df,2p).

Effect of Zero-Point Vibrational Energies. Zero-point vibrational energies for species relevant to the reaction of $CH_3^{\bullet}$ with CH_2═CH_2, as calculated at the HF, B3-LYP, and QCISD levels with the 6-31G(d) basis set, are shown in Table 8. We note to begin that the ZPVE has the effect of increasing the barrier and decreasing the reaction exothermicity so that overestimation of the ZPVE will lead to a larger barrier but a smaller exothermicity. HF/6-31G(d) ZPVEs are reported both for the standard scale factor of 0.8929 used in our previous work and with a scale factor of 0.9135 more appropriate for ZPVEs.[15] The scale factors of 0.9806 for B3-LYP/6-31G(d) and 0.9776 for QCISD/6-31G(d) are the recommended values for ZPVE calculations.[15] The ZPVE contribution to the barrier increases by about 1 kJ mol^{-1} in going from HF/6-31G(d) to B3-LYP/6-31G(d) and by another 1 kJ mol^{-1} in going to QCISD/6-31G(d). The ZPVE contribution to the reaction enthalpy decreases by about 1 kJ mol^{-1} in going from HF to B3-LYP but increases by about 1 kJ mol^{-1} in going from HF to QCISD.

A wider range of comparisons of HF and B3-LYP ZPVE contributions to barriers and enthalpies for reactions of $CH_3^{\bullet}$ with CH_2═CHX and for the reactions of $CH_2OH^{\bullet}$ and $CH_2CN^{\bullet}$ with CH_2═CH_2 is presented in Table 9. The differences are generally not large. Use of B3-LYP ZPVEs would generally lead to an increase in barrier and exothermicity of about 1 kJ mol^{-1}, but there are cases, particularly with the unsaturated substituents, where the effects are larger or smaller or even of the opposite sign. Because B3-LYP has been found to be particularly suitable for ZPVE calculations,[22] we adopt this procedure in our higher-level calculations described below.

Higher-Level (G2(MP2,SVP)) Theoretical Barriers and Enthalpies. Higher level estimates of the barriers and reaction enthalpies for the reactions of $CH_3^{\bullet}$ with CH_2═CHX and for the reactions of $CH_2OH^{\bullet}$ and $CH_2CN^{\bullet}$ with CH_2═CH_2 are presented in Table 10. On the basis of the analysis in preceding sections, we used geometries optimized at the QCISD/6-31G(d) level, and ZPVE corrections were calculated using scaled

TABLE 6: Effect of Geometry on Calculated Barriers and Reaction Enthalpies (kJ mol^{-1})

	barrier[a]				enthalpy[a]			
X	UHF[b]	UMP2[b]	UB3-LYP	QCISD[b]	UHF[b]	UMP2[b]	UB3-LYP	QCISD
H	31.7	35.9	31.9	33.8	−114.4	−112.4	−112.8	−112.7
CH_3	30.7	35.1	31.3	32.9	−115.6	−113.7	−112.7	−114.1
NH_2	29.2	34.7	31.1	32.5	−125.6	−123.2	−123.8	−123.6
OH	32.2	37.4	33.8	35.2	−117.6	−115.2	−114.3	−115.6
F	31.8	37.4	32.6	34.4	−120.4	−117.9	−118.0	−118.2
SiH_3	25.6	30.1	26.1	27.8	−124.8	−122.9	−123.3	−123.3
Cl	25.5	30.3	25.9	27.9	−129.5	−127.3	−127.2	−127.7
CN	16.7	30.7	19.3	22.5	−151.4	−136.7	−144.5	−144.6
CHO	18.8	31.3	20.4	23.5	−151.3	−139.5	−142.5	−146.0

[a] QCISD(T)/6-31G(d) values calculated at the specified geometries without ZPVEs. [b] Level of geometry optimization; 6-31G(d) basis set used throughout.

TABLE 7: Effect of Basis Set on Calculated Barriers and Reaction Enthalpies for the Reaction of $CH_3^\bullet$ with $CH_2{=}CHX$ (kJ mol^{-1})[a]

method	6-31G(d)	6-311G(d,p)	6-311+G(d,p)	6-311+G(2d,p)	6-311+G(2df,p)	6-311+G(3df,2p)
			Barrier			
X = H						
UMP2	60.7	57.3	58.6	57.1	57.4	57.5
PMP2	22.4	20.1	22.0	20.5	20.8	20.9
RMP2	39.7	35.4	36.7	34.7	34.5	34.4
QCISD	36.8	34.2	35.5	34.2		
QCISD(T)	33.8	30.3	31.5	29.8		
X = Cl						
UMP2	57.1	53.9	55.1	54.2	54.2	53.9
PMP2	18.5	15.8	17.2	16.2	16.2	15.9
RMP2	32.8	28.7	29.7	28.1	27.5	27.1
QCISD	31.0	28.1				
QCISD(T)	27.9	24.0				
X = CN						
UMP2	83.7	81.6	81.6	80.3	79.4	79.6
PMP2	16.7	15.3	16.3	14.9	15.3	15.3
RMP2	24.1	21.7	22.4	20.5	19.8	19.8
QCISD	24.5	22.9				
QCISD(T)	22.5	20.2				
			Enthalpy			
X = H						
UMP2	−122.4	−120.7	−117.5	−113.4	−115.4	−116.4
PMP2	−122.8	−121.2	−118.0	−113.8	−115.8	−116.9
RMP2	−123.2	−121.3	−118.1	−113.9	−115.9	−117.0
QCISD	−114.3	−113.2	−110.0	−106.6		
QCISD(T)	−112.7	−112.4	−110.2	−105.6		
X = Cl						
UMP2	−133.9	−133.2	−129.7	−124.4	−127.5	−130.1
PMP2	−134.7	−134.2	−130.8	−125.8	−128.9	−131.6
RMP2	−135.8	−134.6	−131.0	−125.7	−128.9	−131.4
QCISD	−129.1	−129.3				
QCISD(T)	−127.7	−128.9				
X = CN						
UMP2	−103.1	−100.7	−98.2	−94.2	−98.0	−98.7
PMP2	−144.1	−141.9	−139.0	−134.9	−137.6	−138.4
RMP2	−153.0	−150.2	−147.2	−143.6	−147.1	−147.9
QCISD	−148.0	−145.8				
QCISD(T)	−144.6	−143.1				

[a] Based on QCISD/6-31G(d) geometries throughout, without ZPVEs.

TABLE 8: Comparison of Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) Relevant to the Addition of Methyl Radical to Ethylene[a]

species	HF[b]	HF[c]	B3-LYP[c]	QCISD[c]
$CH_3^\bullet$	72.6	74.3	76.8	77.0
$CH_2{=}CH_2$	128.4	131.4	131.9	132.0
TS	209.0	213.9	217.8	219.4
$CH_3CH_2CH_2^\bullet$	221.2	226.3	228.5	230.9
barrier[d]	8.0	8.2	9.1	10.3
enthalpy[d]	20.3	20.7	19.8	21.8

[a] 6-31G(d) basis set used throughout. [b] ZPVE scaled by "standard" factor of 0.8929. [c] ZPVEs scaled by 0.9135 (HF), 0.9806 (B3-LYP), and 0.9776 (QCISD), respectively. Scaling factors from ref 15. [d] ZPVE contribution to the barrier or reaction enthalpy.

TABLE 9: Zero-Point Vibrational Energy Corrections[a] (kJ mol^{-1}) for Barriers and Reaction Enthalpies for $CH_3^\bullet$ + $CH_2{=}CHX$ and for $CH_2OH^\bullet$ + $CH_2{=}CH_2$ and $CH_2CN^\bullet$ + $CH_2{=}CH_2$

	barrier			enthalpy		
X	HF[b]	B3-LYP[b]	diff	HF[b]	B3-LYP[b]	diff
H	8.2	9.1	0.9	20.7	19.8	−0.9
CH_3	7.7	8.2	0.5	21.3	20.4	−0.9
NH_2	7.9	8.1	0.2	24.4	23.0	−1.4
OH	7.5	8.3	0.8	24.0	22.7	−1.3
F	7.5	8.5	1.0	24.7	23.2	−1.5
SiH_3	8.4	8.5	0.1	22.4	21.7	−0.7
Cl	7.7	8.3	0.6	23.7	21.9	−1.8
CN	5.6	7.8	2.2	20.3	22.1	1.8
CHO	6.1	7.9	1.8	22.8	23.0	0.2
$CH_2OH^\bullet$ [c]	3.4	6.2	2.8	12.8	12.9	0.1
$CH_2CN^\bullet$ [d]	6.3	7.9	1.6	17.2	15.0	−2.2

[a] 6-31G(d) basis set used throughout. [b] ZPVEs scaled by 0.9135 (HF/6-31G(d)) and 0.9806 (B3-LYP/6-31G(d)). Scaling factors from ref 15. [c] $CH_2OH^\bullet$ + $CH_2{=}CH_2$. [d] $CH_2CN^\bullet$ + $CH_2{=}CH_2$.

B3-LYP/6-31G(d) vibrational frequencies. Single-point energies were obtained at the QCISD(T)/6-311+G(3df,2p) level using the additivity approximation:

$$\begin{aligned}\Delta E[\text{QCISD(T)/6-311+G(3df,2p)}] \approx{}& \\ \Delta E[\text{QCISD(T)/6-3G(d)}] +{}& \\ \Delta E[\text{RMP2/6-311+G(3df,2p)}] - \Delta E[\text{RMP2/6-31G(d)}]& \quad (7)\end{aligned}$$

This corresponds to the G2(MP2,SVP) procedure except that (a) RMP2 rather than UMP2 is used in the basis set additivity approximation, (b) QCISD/6-31G(d) geometries are used in place of UMP2/6-31G(d) geometries, and (c) scaled B3-LYP/6-31G(d) ZPVEs are used in place of scaled HF/6-31G(d) ZPVEs. This method can formally be designated G2(MP2,SVP)-(RMP2,QCISD,B3-LYP).

For the methyl radical additions, the deviations from experimental barriers lie within the narrow range of +5.3 to +10.9 kJ mol^{-1}, but there is still a significant mean absolute deviation of 7.7 kJ mol^{-1}. The differences between the theoretical and experimental barriers are comparable for the reaction of CH_2-

TABLE 10: G2(MP2,SVP)(RMP2,QCISD,B3-LYP) Barriers and Reaction Enthalpies for $CH_3^{\bullet} + CH_2{=}CHX$ and for $CH_2OH^{\bullet} + CH_2{=}CH_2$ and $CH_2CN^{\bullet} + CH_2{=}CH_2$ (kJ mol^{-1})[a]

	barrier		enthalpy	
X	theory	expt[b]	theory	expt[b]
F	38.3		−87.0	
OH	38.1		−87.0	
H	37.7	30.4	−86.7	−92.3
CH_3	35.9	29.0	−86.7	−99.0
NH_2	35.3		−93.6	
SiH_3	30.9	24.7[c]	−96.3	−96.7[c]
Cl	30.5	25.2	−101.5	−100.8
CHO	26.9	16.0	−116.2	−112.0
CN	25.9	16.4	−117.5	−133.4
mean abs dev	7.7		6.5	
min dev	+5.3		−4.2	
max dev	+10.9		+15.9	
$CH_2OH^{\bullet}$ [d]	32.7	31.2	−79.1	−83.4
$CH_2CN^{\bullet}$ [e]	36.6	28.4	−64.2	−65.5

[a] Obtained from QCISD(T)/6-311+G(3df,2p) energies (derived using eq 6) calculated at QCISD/6-31G(d) optimized geometries with scaled B3-LYP/6-31G(d) ZPVEs. Corresponding to 0 K. [b] Experimental results from refs 3l,m,p. Corrected to 0 K using the temperature corrections of Table 1. [c] Experimental results are for the $(CH_3)_3Si$ substituent; see text. [d] $CH_2OH^{\bullet} + CH_2{=}CH_2$. [e] $CH_2CN^{\bullet} + CH_2{=}CH_2$.

TABLE 11: Analysis of G2(MP2,SVP)(RMP2,QCISD,B3-LYP) Barrier Calculations

alkene	$CH_2{=}CH_2$			$CH_2{=}CHCN$
radical	$CH_3^{\bullet}$	$CH_2OH^{\bullet}$	$CH_2CN^{\bullet}$	$CH_3^{\bullet}$
standard[a]	38.9	32.7	42.5	24.3
triples[b]	−3.7	−4.6	−5.3	−3.9
geometry[c]	+1.7	+2.4	+1.1	+5.8
basis set[d]	−1.0	−0.7	−3.3	−1.9
ZPVE[e]	+1.1	+2.9	+1.8	+2.3
G2(MP2,SVP)[f]	37.7	32.7	36.6	25.9
expt[g]	30.4	31.2	28.4	16.4
dev[h]	+7.3	+1.5	+8.2	+9.5

[a] QCISD/6-311G(d,p) energy calculations evaluated at UHF/6-31G(d) optimized geometries using the additivity approximation of eq 5 with ZPVEs calculated from UHF/6-31G(d) vibrational frequencies scaled by 0.8929. Corresponding to 0 K. [b] Estimated as the difference between QCISD(T)/6-31G(d) and QCISD/6-31G(d) values. [c] Estimated as the difference between QCISD(T)/6-31G(d) values calculated at QCISD/6-31G(d) and UHF/6-31G(d) optimized geometries. [d] Estimated as the difference between RMP2/6-311+G(3df,2p) and RMP2/6-311G(d,p) values. [e] Estimated as the difference between scaled B3-LYP/6-31G(d) and scaled UHF/6-31G(d) values. [f] G2(MP2,SVP)-(RMP2,QCISD,B3-LYP) values obtained from QCISD(T)/6-311+G(3df,2p) energy calculations evaluated at QCISD/6-31G(d) optimized geometries using the additivity approximation of eq 7 with ZPVEs calculated from B3-LYP/6-31G(d) vibrational frequencies scaled by 0.9806, i.e., G2(MP2,SVP)(RMP2,QCISD,B3-LYP). [g] Experimental results from refs 3l,m,p. Corrected to 0 K using the temperature corrections of Table 1 and eq 4. [h] Deviation between G2(MP2,SVP) and experimental values.

TABLE 12: Analysis of G2(MP2,SVP)(RMP2,QCISD,B3-LYP) Reaction Enthalpy Calculations

alkene	$CH_2{=}CH_2$			$CH_2{=}CHCN$
radical	$CH_3^{\bullet}$	$CH_2OH^{\bullet}$	$CH_2CN^{\bullet}$	$CH_3^{\bullet}$
standard[a]	−93.5	−83.7	−63.3	−129.3
triples[b]	+1.2	+1.2	+0.7	+1.6
geometry[c]	+2.1	+1.6	−2.0	+6.8
basis set[d]	+4.3	+1.5	+2.0	+2.3
ZPVE[e]	−0.5	+0.3	−1.8	+2.2
G2(MP2,SVP)[f]	−86.7	−79.1	−64.2	−117.5
expt[g]	−92.3	−83.4	−65.5	−133.4
dev[h]	+5.6	+4.3	+1.3	+15.9

[a] QCISD/6-311G(d,p) energy calculations evaluated at UHF/6-31G(d) optimized geometries using the additivity approximation of eq 5 with ZPVEs calculated from UHF/6-31G(d) vibrational frequencies scaled by 0.8929. Corresponding to 0 K. [b] Estimated as the difference between QCISD(T)/6-31G(d) and QCISD/6-31G(d) values. [c] Estimated as the difference between QCISD(T)/6-31G(d) values calculated at QCISD/6-31G(d) and UHF/6-31G(d) optimized geometries. [d] Estimated as the difference between RMP2/6-311+G(3df,2p) and RMP2/6-311G(d,p) values. [e] Estimated as the difference between scaled B3-LYP/6-31G(d) and scaled UHF/6-31G(d) values. [f] G2(MP2,SVP)-(RMP2,QCISD,B3-LYP) values obtained from QCISD(T)/6-311+G(3df,2p) energy calculations evaluated at QCISD/6-31G(d) optimized geometries using the additivity approximation of eq 7 with ZPVEs calculated from B3-LYP/6-31G(d) vibrational frequencies scaled by 0.9806, i.e., G2(MP2,SVP)(RMP2,QCISD,B3-LYP). [g] Experimental results from refs 3l,m,p. Corrected to 0 K using the temperature corrections of Table 1. [h] Deviation between G2(MP2,SVP) and experimental values.

$CN^{\bullet}$ with $CH_2{=}CH_2$ but somewhat smaller for the reaction of $CH_2OH^{\bullet}$ with $CH_2{=}CH_2$.

The differences between theoretical and experimental reaction enthalpies are more variable, but because the experimental estimates are largely obtained using additivity rules, the significance of this comparison is less clear.

Analysis of G2(MP2,SVP)(RMP2,QCISD,B3-LYP) Barrier and Enthalpy Calculations. It is useful to analyze some of the factors that influence the calculated G2(MP2,SVP)-(RMP2,QCISD,B3-LYP) barrier heights and reaction enthalpies for radical addition reactions. This is done in Tables 11 (barriers) and 12 (enthalpies) by examining the changes in going from our standard QCISD/6-311G(d,p)//HF/6-31G(d) calculations to the higher-level QCISD(T)/6-311+G(3df,2p)//QCISD/6-31G(d) calculations. It can be seen that triple excitations, improved geometries, use of a larger basis set, and improved zero-point vibrational energies all contribute significantly to the overall change. Some of the improvements have a negative sign and therefore lead to closer agreement with experiment whereas those with a positive sign increase the discrepancy with experiment.

Effect of Quadruple Excitations. Because the inclusion of triple excitations leads to significant barrier lowerings (Tables 4 and 11), it is important to also examine the effect of quadruple excitations. We therefore calculated barriers and reaction enthalpies for the $CH_3^{\bullet} + CH_2{=}CH_2$ reaction at the QCISD, QCISD(T), and QCISD(TQ) levels with the 6-31G(d) basis set on UHF/6-31G(d) optimized geometries. The barrier values are, respectively, 35.5, 31.7, and 31.0 kJ mol^{-1} while the reaction enthalpies are −115.6, −114.2, and −114.2 kJ mol^{-1} (without ZPVE corrections). Thus it can be seen that, while there is a significant change that accompanies the inclusion of triple excitations, there is not much further change when quadruple excitations are included as well.

Complete Basis Set Calculations. Barriers and reaction enthalpies calculated at the CBS-RAD level[18] are presented in Table 13. The agreement between the calculated barriers at 0 K and the experimental solution-phase values is quite remarkable. For the methyl addition reactions, the mean absolute deviation is just 1.4 kJ mol^{-1}, with deviations ranging from −3.1 to −0.4 kJ mol^{-1}. The agreement is also very good for the additions to ethylene of $CH_2OH^{\bullet}$ and $CH_2CN^{\bullet}$, with discrepancies of less than 4 kJ mol^{-1}.

The differences between the CBS-RAD results and the G2-(MP2,SVP) results of Table 10 can be largely traced to the spin-correction term incorporated in CBS-RAD that attempts to correct for the effects of spin contamination (see Table S2 of Supporting Information). Before spin correction, the CBS-RAD

TABLE 13: CBS-RAD(QCISD,B3-LYP) Barriers and Enthalpies for $CH_3^{\bullet} + CH_2{=}CHX$ and for $CH_2OH^{\bullet} + CH_2{=}CH_2$ and $CH_2CN^{\bullet} + CH_2{=}CH_2$ (kJ mol^{-1})[a]

	barrier		enthalpy	
X	theory	expt[b]	theory	expt[b]
F	29.9		−93.0	
OH	30.0		−92.5	
H	30.0	30.4	−91.7	−92.3
CH_3	28.1	29.0	−93.0	−99.0
NH_2	27.2		−100.6	
SiH_3	23.4	24.7[c]	−100.7	−96.7[c]
Cl	22.1	25.2	−108.0	−100.8
CHO	15.4	16.0	−125.4	−112.0
CN	14.4	16.4	−128.4	−133.4
mean abs dev	1.4		6.0	
min dev	−3.1		−13.4	
max dev	−0.4		+6.0	
$CH_2OH^{\bullet}$[d]	27.6	31.2	−82.8	−83.4
$CH_2CN^{\bullet}$[e]	29.0	28.4	−68.7	−65.5

[a] Calculated at QCISD/6-31G(d) optimized geometries with scaled B3-LYP/6-31G(d) ZPVEs. Corresponding to 0 K. [b] Experimental results from refs 3l,m,p. Corrected to 0 K using the temperature corrections of Table 1. [c] Experimental results are for the $(CH_3)_3Si$ substituent; see text. [d] $CH_2OH^{\bullet} + CH_2{=}CH_2$. [e] $CH_2CN^{\bullet} + CH_2{=}CH_2$.

barriers for methyl radical additions are all just 2.0 ± 0.5 kJ mol^{-1} lower than the G2(MP2,SVP) values. The spin-correction term is −5.8 ± 0.3 kJ mol^{-1} except for the CHO (−9.2 kJ mol^{-1}) and CN (−10.0 kJ mol^{-1}) substituents.

The results in this study extend our findings concerning the good performance of CBS-RAD in describing radical thermochemistry[18] to the calculation of reaction barriers. More extensive comparisons are nevertheless desirable to examine further the generality of these observations. It would seem unlikely that the present mean absolute deviation of less than 2 kJ mol^{-1} can be sustained over a wider comparison set (in that the performance of CBS-RAD should be comparable to that of CBS-Q for closed-shell molecules), but the excellent results for the present systems is certainly encouraging.

The agreement between theoretical and experimental reaction enthalpies is less good. The discrepancies continue to show wide variation, casting doubt on some of the experimental values.

The contribution of the spin-correction term to the reaction enthalpy is close to zero for all of the methyl radical additions except again for the CHO (−3.7 kJ mol^{-1}) and CN (−4.8 kJ mol^{-1}) substituents (see Table S2).

Density Functional Calculations. We have previously reported a limited assessment of the performance of density functional theory (DFT) for the calculation of the barriers and reaction enthalpies for radical addition reactions.[6] The B-LYP/6-31G(d) level was found to grossly underestimate the activation barriers. A recent study,[4m] however, has shown that considerably improved results may be obtained using a hybrid functional (e.g., B3-LYP) in conjunction with a large basis. We have therefore included a more detailed examination in the present study.

Results for the addition of methyl radical to ethylene with a variety of basis sets and the B-LYP and B3-LYP functionals are presented in Table 14. It can be seen that the effect of basis set is greater than that for conventional ab initio procedures (Table 7) and it is also in the opposite direction. In particular, the inclusion of diffuse sp functions on heavy atoms and the inclusion of p polarization functions on hydrogen are very important for both the calculated barriers and enthalpies. Such a sensitivity to basis set is rather unusual for density functional theory calculations. For both B-LYP and B3-LYP, the barriers with the 6-311+G(d,p) basis set lie within 1 kJ mol^{-1} of the 6-311+G(3df,2p) values. For reaction enthalpies, the difference between 6-311+G(d,p) and 6-311+G(3df,2p) values is slightly greater at 2−3 kJ mol^{-1}. These results suggest that the 6-311+G(d,p) basis set might be suitable for DFT calculations on larger systems in cases where 6-311+G(3df,2p) is too computationally demanding.

TABLE 14: Effect of Basis Set on DFT Barriers and Reaction Enthalpies (kJ mol^{-1}) for $CH_3^{\bullet} + CH_2{=}CH_2$[a]

basis set	B-LYP barrier[b]	B3-LYP barrier[c]	B-LYP enthalpy[b]	B3-LYP enthalpy[c]
6-31G(d)	13.2	18.3	−107.2	−119.8
6-31+G(d)	19.1	23.6	−95.3	−109.1
6-311G(d)	16.1	20.8	−98.1	−111.5
6-311G(d,p)	16.7	22.4	−92.9	−105.4
6-311+G(d)	18.6	22.9	−94.3	−108.2
6-311+G(d,p)	20.3	25.0	−87.8	−101.5
6-311+G(2df,p)	20.1	25.4	−86.8	−99.7
6-311+G(3df,2p)	20.7	25.6	−85.5	−99.0

[a] Without ZPVE corrections. [b] Based on B-LYP/6-31G(d) geometries. [c] Based on B3-LYP/6-31G(d) geometries.

B3-LYP calculations were carried out for the set of addition reactions of $CH_3^{\bullet}$ to $CH_2{=}CHX$ and of $CH_2OH^{\bullet}$ and $CH_2CN^{\bullet}$ to $CH_2{=}CH_2$ shown in Table 15. This wider set of results confirms that the 6-311+G(d,p) barriers are within 1−2 kJ mol^{-1} of the 6-311+G(3df,2p) values and that the 6-311+G(d,p) reaction enthalpies are within 2−3 kJ mol^{-1} of the 6-311+G(3df,2p) values. The agreement between B3-LYP/6-311+G(3df,2p) and experimental barriers is quite good, with discrepancies for methyl radical additions lying in the range +3.1 to +7.3 kJ mol^{-1}, giving a mean absolute deviation of 5.0 kJ mol^{-1}. For the still wider set of barrier comparisons included in Table 4, the mean absolute deviation is 5.6 kJ mol^{-1}. The agreement between B3-LYP/6-311+G(3df,2p) and experimental reaction enthalpies (Table 5 and Table 15) is less satisfactory. The discrepancies in Table 15 lie between 1.9 and 18.1 kJ mol^{-1}, with a mean deviation of 12.0 kJ mol^{-1}.

The performance of B3-LYP/6-311+G(3df,2p) in predicting the barriers of these radical addition reactions (Table 15) can be seen to be not as good as that of CBS-RAD (Table 13) but slightly better than that of G2(MP2,SVP) (Table 10). It is not clear whether this latter result is fortuitous and whether it will be maintained over a wider comparison set. However, it is certainly true that the B3-LYP/6-311+G(d,p) and B3-LYP/6-311+G(3df,2p) calculations are much less expensive than the higher-level ab initio calculations, and so the very good performance in the current comparisons is very encouraging.

Correlations. It is instructive to examine correlations between the barriers and reaction enthalpies calculated at our three principal levels of theory: G2(MP2,SVP)(RMP2,QCISD,-B3-LYP), CBS-RAD(QCISD,B3-LYP), and B3-LYP/6-311+G-(3df,2p)//B3-LYP/6-31G(d). Correlation coefficients (quoted as R^2 values) obtained from data for the methyl radical additions to alkenes in Tables 10, 13, and 15 are listed in Table 16.

The correlation coefficients are all very good (greater than 0.90), showing that relative enthalpies and barriers at the three levels of theory are in close agreement. In addition, at all three levels of theory, there is a strong correlation between the calculated barrier and reaction enthalpy, with correlation coefficients (R^2) in the 0.93−0.99 range. This correlation appears somewhat stronger than that derived from experimental data.[3p,r]

Solvent Effects. As noted earlier, our calculations refer to isolated molecules in the gas phase whereas the experiments were carried out in solution, specifically 1,1,2-trichloro-1,2,2-

TABLE 15: Effect of Basis Set on B3-LYP Barriers and Reaction Enthalpies (kJ mol^{-1}) for $CH_3^{\bullet}$ + CH_2═CHX[a]

X	6-31G(d)	6-311G(d,p)	6-311+G(d,p)	6-311+G(3df,2p)	6-311+G(3df,2p)[b]	expt[c]
			Barrier			
F	19.1	22.5	24.7	25.7	34.2	
OH	20.0	23.1	25.6	26.5	34.9	
H	18.3	22.4	25.0	25.6	34.7	30.4
CH_3	18.8	22.5	25.5	26.3	34.5	29.0
NH_2	16.9	19.7	23.0	23.7	31.8	
SiH_3	14.7	18.8	21.4	21.7	30.1	24.7[d]
Cl	13.9	17.9	20.0	21.0	29.3	25.2
CHO	6.4	12.0	13.7	15.4	23.3	16.0
CN	5.4	9.1	11.2	11.8	19.5	16.4
$CH_2OH^{\bullet}$	19.5	23.9	27.9	29.1	35.4	31.2
$CH_2CN^{\bullet}$	24.4	30.1	31.7	32.5	40.4	28.4
			Enthalpy			
F	−123.4	−109.5	−105.3	−102.3	−79.1	
OH	−118.0	−104.0	−100.2	−97.3	−74.5	
H	−119.8	−105.4	−101.5	−99.0	−79.3	−92.3
CH_3	−118.7	−104.3	−99.7	−97.2	−76.8	−99.0
NH_2	−127.1	−112.8	−109.3	−106.2	−83.2	
SiH_3	−130.1	−116.6	−112.6	−110.4	−88.7	−96.7[d]
Cl	−134.2	−120.0	−115.8	−113.9	−92.0	−100.8
CHO	−154.2	−139.3	−135.8	−133.1	−110.1	−112.0
CN	−158.1	−143.6	−139.6	−137.4	−115.3	−133.4
$CH_2OH^{\bullet}$	−92.3	−78.7	−76.7	−73.1	−60.3	−83.4
$CH_2CN^{\bullet}$	−72.0	−59.8	−58.0	−55.2	−40.2	−65.5

[a] Based on B3-LYP/6-31G(d) geometries, without ZPVEs unless otherwise noted. [b] Including zero-point vibrational energies (calculated at the B3-LYP/6-31G(d) level) scaled by 0.9806 (ref 15). Corresponding to 0 K. [c] From refs 3l,m,p. Corrected to 0 K using the temperature corrections of Table 1. [d] Experimental results are for the $(CH_3)_3Si$ substituent; see text.

TABLE 16: Calculated Correlation Coefficients[a]

property[b,c,d]	property[b,c,d]	correlation coefficient
G2 barrier	DFT barrier	0.906
G2 barrier	CBS barrier	0.974
DFT barrier	CBS barrier	0.961
G2 enthalpy	DFT enthalpy	0.981
G2 enthalpy	CBS enthalpy	0.994
DFT enthalpy	CBS enthalpy	0.979
G2 barrier	G2 enthalpy	0.925
DFT barrier	DFT enthalpy	0.985
CBS barrier	CBS enthalpy	0.965

[a] Correlation coefficients (R^2) between properties calculated at various levels of theory, based on the barriers and reaction enthalpies for methyl radical additions to alkenes for the set of 9 substituents shown in Tables 10, 13, and 15. [b] G2 refers to G2(MP2,SVP)(RMP2,QCISD,B3-LYP) values; see text and Table 10. [c] CBS refers to CBS-RAD(QCISD,B3-LYP) values; see text and Table 13. [d] DFT refers to B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d) values with scaled B3-LYP/6-31G(d) ZPVEs; see text and Table 15.

trifluoroethane ($\epsilon = 2.4$, $CH_3^{\bullet}$ additions), methanol ($\epsilon = 32.6$, $CH_2OH^{\bullet}$ additions), or acetonitrile ($\epsilon = 37.5$, $CH_2CN^{\bullet}$ additions). We have estimated the effect of solvent with B3-LYP/6-311+G(d,p)//HF/6-31G(d) calculations using the SCIPCM model and dielectric constants (ϵ) of 2 (representing a nonpolar solvent) and 40 (representing a polar solvent) for a selection of radical addition reactions (Table 17).

The predicted effect of solvent is generally not large but is always in the direction of increasing the barrier for additions of radicals bearing saturated substituents to alkenes bearing saturated substituents but decreasing the barriers in unsaturated cases. For $\epsilon = 2$, the increases for saturated substituents range from +0.5 to +1.1 kJ mol^{-1} whereas the reductions for the unsaturated systems range from −0.2 to −1.1 kJ mol^{-1}. For $\epsilon = 40$, the effects are +1.1 to +2.8 kJ mol^{-1} and −0.6 to −3.0 kJ mol^{-1}, respectively. The large predicted lowering (by 4.7 kJ mol^{-1}) by solvent ($\epsilon = 40$) of the barrier for $CH_2OH^{\bullet}$ + CH_2═CHCN relative to $CH_2OH^{\bullet}$ + CH_2═CH_2 is consistent with the significant polar character predicted for the transition structure for the $CH_2OH^{\bullet}$ + CH_2═CHCN reaction.[5c]

TABLE 17: Effect of Solvent on Calculated Barriers and Enthalpies (kJ mol^{-1})[a]

X	barrier $\epsilon = 2$[b]	barrier $\epsilon = 40$[c]	enthalpy $\epsilon = 2$[b]	enthalpy $\epsilon = 40$[c]
H	0.7	1.7	1.2	3.2
CH_3	0.7	1.6	1.3	2.9
NH_2	1.1	2.8	2.2	5.9
OH	0.7	1.6	1.1	2.8
F	0.5	1.4	0.9	2.4
Cl	0.6	1.5	1.2	3.2
SiH_3	0.5	1.1	1.0	2.7
CN	−0.2	−0.6	1.2	3.0
CHO	−1.1	−3.0	1.3	2.8
CH_2OH[d]	1.1	2.4	2.0	4.9
CH_2CN[d]	−0.6	−1.5	−0.3	−0.4
CH_2OH[e]	−0.8	−2.3	2.2	5.3
CH_2CN[e]	−0.1	−0.9	−0.5	−1.9

[a] Calculated at the B3-LYP/6-311+G(d,p)//HF/6-31G(d) level using the SCIPCM model. [b] Difference between $\epsilon = 2$ (representing a nonpolar solvent) and $\epsilon = 1$ (gas phase) values. [c] Difference between $\epsilon = 40$ (representing a polar solvent) and $\epsilon = 1$ (gas phase) values. [d] Addition to CH_2═CH_2. [e] Addition to CH_2═CHCN.

The effect of solvent (with $\epsilon = 40$) on reaction enthalpy lies between +2.4 and +4.3 kJ mol^{-1} for methyl radical additions except +5.9 kJ mol^{-1} for X = NH_2. Larger effects are seen for the $CH_2OH^{\bullet}$ additions. For $\epsilon = 2$ the solvent effect is reduced by about 60%.

Concluding Remarks

Several important points emerge from this study. (1) Use of QCISD/6-31G(d) or B3-LYP/6-31G(d) geometries is preferable to UHF/6-31G(d) or UMP2/6-31G(d) geometries. (2) Use of (scaled) QCISD/6-31G(d) or B3-LYP/6-31G(d) ZPVEs is preferable to UHF/6-31G(d) or UMP2/6-31G(d) ZPVEs. (3) Calculations at the QCISD(T)/6-311+G(3df,2p) level (obtained through additivity) on QCISD(T)/6-31G(d) geometries and with B3-LYP/6-31G(d) ZPVEs (i.e., G2(MP2,SVP)(RMP2,QCISD,B3-LYP)) give barriers for radical addition reactions to alkenes that are consistently higher than values obtained from solution-phase experimental data. The mean absolute deviation for methyl radical additions is 7.7 kJ mol^{-1}. (4) Calculations at the B3-LYP/6-311+G(3df,2p) level with B3-LYP/6-31G(d) geometries and ZPVEs yield barriers in slightly better agreement with experiment, with a mean absolute deviation from the experimental values for methyl radical additions in solution of 5.6 kJ mol^{-1}. (5) B3-LYP/6-311+G(d,p) performs only slightly worse than B3-LYP/6-311+G(3df,2p) and could be suitable for examining barriers in radical additions for large systems. (6) Closest agreement with experiment is obtained with the CBS-RAD(QCISD,B3-LYP) method. This gives barriers for methyl radical additions with a mean absolute deviation from experiment of just 1.4 kJ mol^{-1}. (7) The effect of solvent on the calculated barriers for radical addition reactions, estimated using the SCIPCM method, range from −1.1 to +1.1 kJ mol^{-1} for a dielectric constant of 2 (representing a nonpolar solvent) and from −3.0 to +2.8 kJ mol^{-1} for a dielectric constant of 40 (representing a polar solvent).

Acknowledgment. The generous allocation of time on the Fujitsu VPP300 supercomputer of the Australian National University Supercomputer Facility and helpful comments and a preprint of ref 3r from Professor Hanns Fischer are gratefully acknowledged.

Supporting Information Available: Zero-point vibrational energies for $CH_3 + CH_2{=}CHX$ additions (Table S1) and magnitude of spin-correction contributions to calculated CBS-RAD(QCISD,B3-LYP) barriers and enthalpies for $CH_3^{\bullet} + CH_2{=}CHX$ and for $CH_2OH^{\bullet} + CH_2{=}CH_2$ and $CH_2CN^{\bullet} + CH_2{=}CH_2$ (Table S2) (3 pages). See any current masthead page for ordering and Internet access instructions.

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