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Reliable Theoretical Procedures for Calculating the Rate of Methyl Radical Addition to Carbon−Carbon Double and Triple Bonds[†]

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Geometries, frequency factors, barriers, and reaction enthalpies have been calculated at a variety of levels of theory for methyl radical addition to $CH_2{=}CH_2$, $CH_2{=}CHCH_3$, $CH{\equiv}CH$ and $CH{\equiv}CCH_3$, with a view to selecting reliable computational procedures for studying radical addition to carbon−carbon double and triple bonds. Reaction rates for both the addition and reverse (β-scission) reactions were also calculated using various transition-state-theory-based procedures, applied at a number of theoretical levels. In general it was found that the geometries, frequency factors and temperature corrections are relatively insensitive to the level of theory, but barriers and reaction enthalpies require a careful choice of theoretical level. Nonetheless, suitable lower-cost alternatives to the high-level W1 results are provided by G3X-RAD and G3(MP2)-RAD. Although errors are somewhat increased, the RMP2/6-311+G(3df,2p) (for addition to alkenes) or B3-LYP/6-311+G(3df,2p) (for addition to alkynes) levels of theory also provide a reasonable approximation to the high-level methods. The CBS-QB3 procedure also produces very good reaction enthalpies, but shows a systematic error in the reaction barriers. It appears that the correction for spin contamination in the addition transition structures may be overestimated in standard CBS-QB3 and better results are obtained if the spin-correction term is omitted (U−CBS-QB3).

1. Introduction

The addition of carbon-centered radicals to carbon−carbon multiple bonds is of fundamental importance in chemistry as a bond-forming reaction, and ab initio molecular orbital calculations have a vital role to play in elucidating mechanistic information on these important reactions.[1] Traditionally such reactions have been considered difficult to study theoretically, due to problems such as spin-contamination. However, with the advent of high-level composite procedures (such as the G3,[2] G3-RAD,[3] CBS,[4] and W*n*[5] families of methods), combined with rapid and continuing increases in computer power, "chemical accuracy" is at last becoming feasible.

In recent years, we have extensively assessed the performance of computational methods for calculating the barriers, enthalpies and frequencies for radical addition to C═C double bonds.[6−9] In general, it was found that reasonably accurate geometries and frequencies (and hence frequency factors) could be obtained at relatively low levels of theory such as B3-LYP/6-31G(d); however, high levels of theory are required for the accurate calculation of energies. One intriguing observation has been that the high-level G3-type and W1-type methods tend to produce reaction barriers that are in close agreement with one another, but are systematically higher (by around 8 kJ mol^{-1}) than those produced using the CBS-type methods.[9] Interestingly, the barriers obtained using the G3-type and W1-type methods are found generally to be close to the available gas-phase experimental data, while the CBS-type results are generally close to adjusted solution-phase data. All of these methods use additivity and/or extrapolation procedures to approximate a CCSD(T) calculation on a large (or infinite) basis set, so it is difficult to say definitively whether the G3/W1 or the CBS-type procedures should be viewed as being more reliable for the study of radical addition to C═C bonds. Formally, W1 might be expected to be the most accurate of these methods but a systematic reexamination of this problem is desirable.

Another outstanding issue in the assessment of computational methods for radical addition to multiple bonds is whether the same methods that are suitable for the study of radical addition to C═C double bonds are also applicable to the study of radical addition to C≡C triple bonds. Radical addition to C≡C bonds has received much less attention than radical addition to C═C bonds, either experimentally or theoretically, and yet it opens up considerable new chemistry and poses some intriguing questions. For example, methyl radical addition to alkynes is slower than the corresponding addition to alkenes, despite the greater exothermicity in the former case.[1,10] We recently used the curve-crossing model to examine this problem,[11] in a study in which barriers and enthalpies were calculated using the high-level W1h method, while geometries and frequencies were calculated with QCISD/6-31G(d). While this represents a very high level of theory, it is important to place these results in the context of a thorough assessment study. In addition, it is important to identify suitable lower-level methods that can be used to tackle radical addition to C≡C bonds in larger systems.

The accuracy of calculated rate constants is affected not only by the level of theory, but also by the method used to calculate the rate constants. Within the context of standard transition state theory, the low frequency torsional modes can be treated more accurately as hindered internal rotations, or more approximately, using the harmonic oscillator or free rotor approximations. The

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advantage of the simplified treatments is that they do not require the calculation of the rotational potentials associated with the torsional modes. Previously we have shown that for ethyl and propyl addition to ethene, it is important to treat the low-frequency torsional modes as hindered internal rotations.[8] More recently, this conclusion has been reinforced in studies of ethylbenzyl radical addition to ethene by Van Speybroeck et al.,[12] who also demonstrated that a simple one-dimensional treatment of the uncoupled rotations was adequate.[13] Interestingly, they also showed that for the reverse (β-scission) reaction, the harmonic oscillator approximation was reasonably accurate, due to significant cancellation of error. It is of interest to explore whether this is also the case for methyl radical addition to C═C bonds, and to establish whether the proper treatment of the low-frequency torsional modes is of greater or lesser importance for the addition to the (more-rigid) alkynes.

In the present work, we report a comparative assessment of the accuracy of computational procedures for calculating geometries, frequency factors, barriers and reaction enthalpies for methyl radical addition to C═C double and C≡C triple bonds. For the most part, we focus on the prototypical systems, methyl radical addition to ethene and ethyne. However, we also include calculations on the corresponding methyl-substituted systems so as to investigate the accuracy of the methods with respect to the calculation of substituent effects. As part of this work, we reexamine the systematic difference between the G3/W1 and CBS-type procedures, with the aim of determining which are the more reliable methods for studying these systems.

2. Theoretical Procedures

Standard ab initio molecular orbital theory[14] and density functional theory[15] calculations were carried out using the GAUSSIAN 98,[16] MOLPRO 2000.6,[17] and ACESII 3.0[18] programs. Unless otherwise noted, calculations on radicals were performed with an unrestricted wave function and the "U" prefix is omitted except where desirable for emphasis. In cases where a restricted-open-shell wave function has been used, it is designated with an "R" prefix. The frozen-core approximation was used in all calculations except where full calculations were required as part of a standard composite method.

Since this work represents an assessment of procedures, a variety of levels of theory were used for the optimization of geometries and the calculation of barriers, reaction enthalpies and reaction rates. Geometries of the reactants, transition structures and products in the addition of methyl radical to $CH_2{=}CH_2$ and $CH{\equiv}CH$ were optimized using HF/6-31G(d), B3-LYP/6-31G(d), B3-LYP/6-31G(2df,p), B3-LYP/cc-pVTZ, B3-LYP/6-311+G(3df,2p), MPW1K/6-31+G(d,p), MP2/6-31G(d), QCISD/6-31G(d) and CCSD(T)/6-311G(d,p). To assess the effect of the level of theory used for geometry optimization on the resulting barriers and reaction enthalpies, single-point energy calculations were carried out on each geometry at the CCSD(T)/6-311G(d,p) level.

Barriers and enthalpies for methyl radical addition to $CH_2{=}CH_2$ and $CH{\equiv}CH$, and also their methyl-substituted analogues (i.e., $CH_2{=}CHCH_3$ and $CH{\equiv}CCH_3$), were calculated at a wide range of low to very high levels of theory. In particular, a number of high-level composite methods were used, including methods from the G3 family such as G3X[19] and G3(MP2),[20] "RAD" variants[3] of the G3 methods including G3X-RAD and G3(MP2)-RAD, the CBS-QB3[4,21] method, and the W1 and W1h variants[5] of the W1 theory of Martin et al.[22,23] In the case of the CBS calculations, results with (CBS-QB3) and without (U-CBS-QB3) the incorporation of a correction for spin contamination are presented.[4,21] For a detailed description of these procedures, the reader is referred either to the original references[3-5,19-23] or to a recent summary in which the RAD and non-RAD methods are compared.[24] In order that the effect of the level of theory on the energy could be studied independently of effects due to the geometry and zero-point vibrational energy, all calculations in the main assessment were carried out using QCISD/6-31G(d) geometries (including those at lower levels of theory). However, additional calculations using a selection of more realistic combinations of geometry level and energy level were also performed.

Frequency factors (at 298 K) for methyl radical addition to $CH_2{=}CH_2$, $CH_2{=}CHCH_3$, $CH{\equiv}CH$ and $CH{\equiv}CCH_3$ were calculated using standard transition state theory, via three different methods, corresponding to the treatment of the low-frequency torsional modes with either the harmonic oscillator, hindered rotor, or free rotor models. For the hindered rotor model, the partition functions and associated thermodynamic properties were obtained from the rotational potentials associated with all the torsional modes via standard methods as follows. For those modes having rotational potentials that could be described by a simple cosine function, the tables of Pitzer and co-workers[25,26] were used. For the more complex modes, the rotational potentials were fitted with a Fourier series of up to 18 terms, and the corresponding energy levels were then found by numerically solving the one-dimensional Schrödinger equation for a rigid rotor using a Fortran program described previously.[8,27] As in the case of the geometry optimizations, frequency factors were calculated at a variety of levels of theory. To simplify the assessment, at any given level of theory, the *same* level was used to optimize the geometries, calculate the vibrational frequencies and obtain the rotational potentials of the low-frequency torsional modes.

In calculating the frequency factors (and also the zero-point vibrational energies and the temperature dependence of the vibrational enthalpy), the frequencies obtained at each level of theory were scaled using their appropriate scale factors.[19,28,29] For B3-LYP/6-311+G(3df,2p), scale factors do not appear to have been reported in the literature and so the scale factor for B3-LYP/cc-pVTZ was used instead.[22] It should be noted that for this level, and also for MPW1K/6-31+G(d,p), the zero-point vibrational energy scale factor was also used for the calculation of vibrational entropies and enthalpies. In addition, no literature scale factor was found for CCSD(T)/6-311G(d,p), and a scale factor of 1 was assumed.

3. Results and Discussion

Geometries. Geometries of the reactants, products and transition structures in methyl radical addition to ethene and ethyne were optimized at a variety of levels of theory, ranging from low levels such as HF/6-31G(d) and B3-LYP/6-31G(d), to high levels such as QCISD/6-31G(d) and CCSD(T)/6-311G(d,p). Geometries, in the form of GAUSSIAN archive entries, for all species at all levels of theory examined are presented in Table S1 of the Supporting Information, while key geometrical parameters for the transition structures are shown in Table 1. Figure 1 displays the main features of the transition structures (**1** and **2**) in methyl radical addition to ethene and ethyne, respectively, and also defines the various symbols used in Table 1.

In general, the geometries are relatively insensitive to the level of theory. Even in the transition structures, the key geometrical parameters at the low levels of theory are generally within 0.1 Å (for the forming C−C bonds, r_1), 0.02 Å (for the breaking

TABLE 1. Effect of Level of Theory on the Key Geometrical Parameters in the Transition Structures (1 and 2) for Methyl Radical Addition to $CH_2{=}CH_2$ and $HC{\equiv}CH$[a]

Level of Theory	r_1	r_2	A_1	A_2	A_3	A_4
$\bullet CH_3 + CH_2{=}CH_2$ (**1**)						
HF/6-31G(d)	2.246	1.382	144.6	109.1	21.8	174.3
B3-LYP/6-31G(d)	2.364	1.356	150.9	110.0	15.2	176.6
B3-LYP/6-31G(2df,p)	2.344	1.353	150.8	110.1	15.3	176.7
B3-LYP/cc-pVTZ	2.320	1.352	150.9	109.9	16.3	176.7
B3-LYP/6-311+G(3df,2p)	2.320	1.353	151.3	109.1	16.1	176.7
MPW1K/6-31+G(d,p)	2.337	1.350	152.8	109.3	14.6	177.0
MP2/6-31G(d)	2.261	1.344	147.1	109.6	16.8	175.9
QCISD/6-31G(d)	2.272	1.367	147.5	109.5	18.9	175.0
CCSD(T)/6-311G(d,p)	2.289	1.368	148.9	109.1	17.8	174.9
$\bullet CH_3 + CH{\equiv}CH$ (**2**)						
HF/6-31G(d)	2.327	1.239	149.3	117.0	31.8	156.9
B3-LYP/6-31G(d)	2.358	1.223	152.6	115.3	24.6	166.6
B3-LYP/6-31G(2df,p)	2.325	1.219	152.0	115.1	24.3	167.5
B3-LYP/cc-pVTZ	2.301	1.216	152.3	115.2	25.1	168.0
B3-LYP/6-311+G(3df,2p)	2.300	1.216	152.7	115.0	25.1	168.0
MPW1K/6-31+G(d,p)	2.302	1.218	153.3	114.5	23.9	168.7
MP2/6-31G(d)	2.145	1.204	144.8	114.9	25.7	169.2
QCISD/6-31G(d)	2.248	1.237	148.9	116.5	29.6	161.7
CCSD(T)/6-311G(d,p)	2.241	1.235	149.5	115.2	27.5	164.4

[a] Geometrical parameters (Å or degrees) are defined in Figure 1.

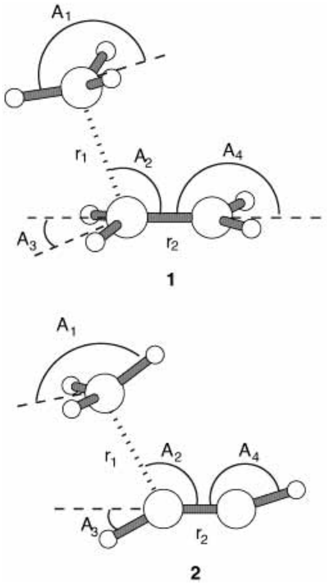

Figure 1. Schematic representation of transition structures (**1** and **2**) for methyl radical addition to $CH_2{=}CH_2$ and $CH{\equiv}CH$, respectively. Calculated values for the relevant bond lengths (r_1 and r_2) and angles (A_1-A_4) are provided in Table 1.

multiple bonds, r_2) or 5° (for the various angles) of the results at the highest level. The largest errors occur for the transition structure for addition to ethyne at the HF/6-31G(d) and MP2/6-31G(d) levels. Specifically, the distortion from linearity of the substrate at both the attacked (A_3) and distal (A_4) carbons is considerably overestimated by HF/6-31G(d), while the forming (r_1) and breaking (r_2) bond lengths are considerably underestimated by MP2/6-31G(d). It is possible that the additional spin contamination in this system (compared with ethene addition) is adversely affecting the geometry optimizations at these levels. Thus the transition structure for addition to ethyne has an $\langle S^2 \rangle$ value of 1.12 at MP2/6-31G(d), while that for addition to ethene has a lower value of 1.02. We note that the product radical for addition to ethyne is also more spin contaminated than the corresponding product for addition to ethene, with $\langle S^2 \rangle$ values of 0.99 and 0.76, respectively. It can also be seen from Table 1 that the various hybrid DFT methods have longer forming bonds and shorter breaking bonds than those found for the higher-level QCISD and CCSD(T) procedures. This tendency of hybrid DFT methods to find earlier transition structures in radical addition to multiple bonds has previously been noted for addition to C═S bonds;[30] however, in the present cases the effect is considerably smaller.

TABLE 2. Effect of Level Used for Geometry Optimization on the Barriers and Reaction Enthalpies for Methyl Radical Addition to $CH_2{=}CH_2$ and $HC{\equiv}CH$[a]

Level of Theory Used for Geometry Optimization	$CH_2{=}CH_2$ $\Delta H^{\ddagger}$	$CH_2{=}CH_2$ ΔH	$CH{\equiv}CH$ $\Delta H^{\ddagger}$	$CH{\equiv}CH$ ΔH
HF/6-31G(d)	28.9	−114.3	39.1	−124.5
B3-LYP/6-31G(d)	29.6	−112.6	37.4	−120.9
B3-LYP/6-31G(2df,p)	29.9	−112.9	38.1	−121.2
B3-LYP/cc-pVTZ	30.4	−112.9	38.9	−121.1
B3-LYP/6-311+G(3df,2p)	30.4	−112.4	39.0	−121.0
MPW1K/6-31+G(d,p)	29.9	−112.5	39.0	−120.6
MP2/6-31G(d)	32.9	−112.4	46.5	−117.3
QCISD/6-31G(d)	31.2	−112.4	41.3	−120.8
CCSD(T)/6-311G(d,p)	31.3	−112.4	41.0	−120.9

[a] All barriers and enthalpies correspond to vibrationless values (kJ mol^{-1}), calculated using CCSD(T)/6-311G(d,p) energies for geometries optimized at the levels of theory listed.

To assess the effect of the theoretical level used for geometry optimization on the calculated energies, single-point energy calculations were performed on all of the geometries at a consistent level of theory, CCSD(T)/6-311G(d,p). The resulting barriers and reaction enthalpies are shown in Table 2. It can be seen that the effects of the geometry level on the calculated barriers and enthalpies are relatively small. The largest deviation from the best results occurs when MP2/6-31G(d) is used to optimize geometries in the (more spin-contaminated) addition to ethyne. This leads to an overestimation of the barrier by 5.5 kJ mol^{-1} and the enthalpy by 3.6 kJ mol^{-1}. The other levels of theory all appear to be suitable for obtaining reasonable geometries for radical addition to double and triple bonds. In particular, use of QCISD/6-31G(d) geometries provides a very good approximation to the considerably more expensive CCSD(T)/6-311G(d,p), and would therefore be suitable as a benchmark when the CCSD(T) geometry optimizations are impractical. Of the lower levels of theory, the best performance is obtained with either the B3-LYP/6-311+G(3df,2p) or MPW1K/6-31+G(d,p) geometries, which lead to very good reaction enthalpies and errors of 2 kJ mol^{-1} or less in the barriers. Use of the small-basis-set B3-LYP geometries shows similar (very good) performance for the enthalpies, but slightly increased (by up to 1.6 kJ mol^{-1}) errors in the reaction barriers. However, the overall errors are still relatively small (up to 3.6 kJ mol^{-1}) and B3-LYP/6-31G(d) would thus be suitable as a robust low level of theory for optimizing the geometries of larger systems. The HF/6-31G(d) geometries also provide reasonable performance (also showing errors of up to 3.6 kJ mol^{-1}); however, for this method, errors of this magnitude occur in the enthalpies as well as the barriers.

Frequency Factors. Frequency factors (at 298 K) for methyl radical addition to ethene, propene, ethyne and propyne, calculated at a variety of levels of theory, are shown in Table 3. Frequency factors for the corresponding reverse reactions (i.e., β-scission of the 1-propyl, 2-butyl, 1-propenyl, and 2-butenyl radicals) are shown in Table 4. As noted above, to simplify the assessment, the same level of theory was used for optimizing the geometries, calculating the vibrational frequencies and, where relevant, obtaining the rotational potentials at each level presented in Tables 3 and 4. The frequency factors were calculated via standard transition state theory using three

TABLE 3. Effect of Level of Theory on Calculated Frequency Factors (log A/(L mol^{-1} s^{-1}), 298 K) for Methyl Radical Addition to $CH_2{=}CHR$ and $CH{\equiv}CR$ ($R = H, CH_3$)

	Treatment of Torsional Modes		
Level of Theory	Free Rotor	Hindered Rotor	Harmonic Oscillator
$\bullet CH_3 + CH_2{=}CH_2 \rightarrow CH_3{-}CH_2CH_2\bullet$			
HF/6-31G(d)	8.69	8.69	8.70
B3-LYP/6-31G(d)	8.89	8.88	8.93
B3-LYP/6-311+G(3df,2p)	8.92	8.90	8.95
MPW1K/6-31+G(d,p)	8.93	8.91	8.93
MP2/6-31G(d)	8.60	8.57	8.52
QCISD/6-31G(d)	8.72	8.69	8.67
CCSD(T)/6-311G(d,p)	8.76	8.73	8.49
Experiment[a]		8.3/9.3	
$\bullet CH_3 + CH_2{=}CHCH_3 \rightarrow CH_3{-}CH_2CHCH_3\bullet$			
B3-LYP/6-31G(d)	8.12	8.19	8.20
QCISD/6-31G(d)	8.13	8.17	8.18
Experiment[a]		7.9/9.3	
$\bullet CH_3 + CH{\equiv}CH \rightarrow CH_3{-}CH{=}CH\bullet$			
HF/6-31G(d)	9.77	9.77	10.15
B3-LYP/6-31G(d)	9.58	9.58	9.95
B3-LYP/6-311+G(3df,2p)	9.66	9.66	9.96
MPW1K/6-31+G(d,p)	9.63	9.63	9.91
MP2/6-31G(d)	8.85	8.85	9.00
QCISD/6-31G(d)	9.24	9.24	9.52
CCSD(T)/6-311G(d,p)	9.42	9.42	9.50
Experiment[a]		8.8/9.7	
$\bullet CH_3 + CH{\equiv}CCH_3 \rightarrow CH_3{-}CH{=}CCH_3\bullet$			
B3-LYP/6-31G(d)	8.85	8.85	9.85
QCISD/6-31G(d)	8.46	8.45	8.91
Experiment[a]		8.7/8.8	

[a] Taken from ref 1. The first number is the gas-phase value, while the second is the solution-phase value.

TABLE 4. Effect of Level of Theory on Calculated Frequency Factors (log A/(s^{-1}), 298 K) for β-Scission of the $CH_3CH_2CHR\bullet$ and $CH_3CH{=}CR\bullet$ ($R = H, CH_3$) Radicals

	Treatment of Torsional Modes		
Level of Theory	Free Rotor	Hindered Rotor	Harmonic Oscillator
$CH_3{-}CH_2CH_2\bullet \rightarrow \bullet CH_3 + CH_2{=}CH_2$			
HF/6-31G(d)	12.87	13.19	13.69
B3-LYP/6-31G(d)	12.96	13.24	13.77
B3-LYP/6-311+G(3df,2p)	12.94	13.21	13.62
MPW1K/6-31+G(d,p)	12.99	13.28	13.69
MP2/6-31G(d)	12.75	13.05	13.61
QCISD/6-31G(d)	12.84	13.10	13.66
$CH_3{-}CH_2CHCH_3\bullet \rightarrow \bullet CH_3 + CH_2{=}CHCH_3$			
B3-LYP/6-31G(d)	12.81	13.08	13.42
QCISD/6-31G(d)	12.89	13.14	13.64
$CH_3{-}CH{=}CH\bullet \rightarrow \bullet CH_3 + CH{\equiv}CH$			
HF/6-31G(d)	14.36	14.48	14.90
B3-LYP/6-31G(d)	14.19	14.35	14.79
B3-LYP/6-311+G(3df,2p)	14.11	14.25	14.62
MPW1K/6-31+G(d,p)	14.15	14.29	14.62
MP2/6-31G(d)	13.79	13.99	14.22
QCISD/6-31G(d)	14.04	14.17	14.53
$CH_3{-}CH{=}CCH_3\bullet \rightarrow \bullet CH_3 + CH{\equiv}CCH_3$			
B3-LYP/6-31G(d)	14.21	14.44	15.61
QCISD/6-31G(d)	14.10	14.31	14.93

different methods for treating the low frequency torsional modes. The hindered rotor values correspond to an exact (albeit one-dimensional) treatment of the rotational potentials and should be regarded as the most accurate of the three methods, while the harmonic oscillator and free rotor values should become increasingly good approximations to the hindered rotor values as the rotational barriers approach infinity and zero, respectively.

Examining first the frequency factors for the addition reactions (Table 3), it is seen that the frequency factors are relatively insensitive to both the level of theory and the method for treating the low frequency torsional modes. In general, the free rotor approximation produces frequency factors that are within 10% of the corresponding hindered rotor values. The harmonic oscillator approximation also generally provides very good results for the addition to alkenes but overestimates the frequency factors for addition to the alkynes, generally by a factor of less than 3 (depending on the system and the level of theory).[31] One particularly poor case occurs for the B3-LYP/6-31G(d) description of the addition to propyne, for which the harmonic oscillator frequency factor exceeds the corresponding hindered rotor value by an order of magnitude. This larger error arises partly because B3-LYP significantly underestimates the frequency corresponding to rotation of the attacking methyl group in the transition structure. At the (higher) QCISD/6-31G(d) level, the error in this frequency is reduced and the harmonic oscillator result is in much closer agreement with the hindered rotor result.

The success of the free rotor approximation for these reactions is not surprising, given that the rotational barriers for the modes specifically treated in the hindered rotor model (namely, the rotation of the attacking methyl group and, where relevant, the rotation of the methyl group in the substrate) are generally quite low. This is especially the case for the addition to the alkynes where the relevant rotational barriers do not exceed 1 kJ mol^{-1}. The lower rotational barriers in the addition transition structures for the alkynes also account for the poorer performance of the harmonic oscillator approximation (which of course performs best for large barriers). Even for the additions to alkynes, however, the errors in the harmonic oscillator approximation are generally lower than those observed previously for ethylbenzyl radical addition to ethene[12] and ethyl and propyl addition to ethene.[8] This is because in these previous reactions, rotations about the C−C single bonds in the attacking radicals were important (and these are of course absent in the present reactions). Indeed, it should be noted that, since errors in the partition functions for the individual low-frequency torsional modes are multiplicative, we might expect the errors in the harmonic oscillator approximation for addition of substituted radicals to alkenes and alkynes to be somewhat larger than those reported here for methyl radical addition.

The effects on the calculated frequency factors of level of theory are also relatively minor for the addition reactions, with even the poorest levels producing results within an order of magnitude of the high-level values. Not surprisingly, the levels of theory showing the poorest performance for geometry optimizations, namely HF/6-31G(d) and MP2/6-31G(d) for addition to alkynes, generally produce the worst frequency factors. However, as noted above, the B3-LYP/6-31G(d) harmonic oscillator value for addition to propyne is also poor, exceeding the corresponding QCISD/6-31G(d) value by an order of magnitude. At all other levels of theory, the frequency factors are within a factor of 2 of the corresponding highest-level values for the free rotor and hindered rotor methods, and a factor of 3 for the harmonic oscillator method. The increased sensitivity to level of theory of the harmonic oscillator method arises in the frequency corresponding to rotation of the attacking methyl group (which is not involved in the hindered rotor and free rotor calculations). The good performance of B3-LYP/6-31G(d) compared with the highest-level CCSD(T)/6-311G(d,p) free rotor and hindered rotor results is noteworthy.

It can also be seen from Table 3 that the highest-level values for the frequency factors of the four addition reactions are within a factor of 4 of the corresponding gas-phase experimental values. Interestingly, the calculated values are also within a factor of 4 of the solution-phase values, generally in the opposite direction, except for addition to propene (where the difference is an order of magnitude). However, when the experimental gas-phase and solution-phase frequency factors are themselves compared, it is seen that they differ by factors ranging from as little as 1.3, to as much as 25. The difference in gas- and solution-phase frequency factors is not surprising because the translational and external rotational contributions to the entropy of activation in solution and in the gas phase might be expected to be significantly different.[32] The variability of the gas-phase/solution-phase difference might partly reflect the difficulties in estimating Arrhenius parameters from experimental rate data.

It has been noted previously that the uncertainties in the Arrhenius parameters estimated from typical experimental data are highly correlated with one another, with a wide range of pairs of activation energies and frequency factors providing adequate fits to the same experimental rate data.[1] To address this problem, it was proposed to instead assume an average value for the frequency factor for a class of reactions, in order to calculate the Arrhenius activation energy from the experimental rate data with improved precision. Based on an analysis of the observed experimental data, values of log A = 8.5 per $CH_2=$ group and 9.2 per $CH\equiv$ group were proposed for the addition of primary radicals to alkenes and alkynes, respectively. The high-level calculated values from the present work for the parent systems are in reasonable agreement with these averages. However, substituent effects are significant and amount to a consistent reduction in log A of 0.6−0.7 in the methyl-substituted systems. The neglect of substituent effects is of course the main disadvantage of assuming a global average. Given this problem, a better method for estimating "experimental" Arrhenius activation energies (at least for gas-phase data) might be to use a reliable calculated frequency factor in conjunction with measured rate data to estimate the activation energy. In the next section, we use this approach to re-estimate experimental Arrhenius activation energies for the reactions of the present work.

For the β-scission reactions (Table 4), the calculated frequency factors are also relatively insensitive to the method used for treating the low frequency torsional modes. For all four reactions, the free rotor approximation leads to an underestimation of the frequency factor by up to a factor of 2, while the harmonic oscillator approximation generally leads to an overestimation by up to a factor of 4, except in the addition to propyne at the B3-LYP/6-31G(d) level (where, as noted above, a poor value for the frequency corresponding to rotation of the attacking methyl group in the transition structure leads to somewhat larger errors). In essence, the harmonic oscillator approximation is reasonable for most of the low frequency torsional modes in the alkyl and alkenyl reactant radicals (as these generally have relatively high barriers), while the free rotor approximation is better for the low frequency torsional modes in the transition structures (which, as noted above, have much lower rotational barriers). Clearly, a hybrid approach in which the harmonic oscillator approximation is used for high-barrier rotations, and the free rotor approximation is used for low-barrier rotations, would be attractive and should approximate the hindered rotor model quite closely. However, since the main additional computational expense of the hindered rotor method is the calculation of the rotational potentials, the hybrid technique would only be useful in cases where the separation of high-barrier and low-barrier rotations can be reliably predicted without recourse to direct calculation.

As in the case of the addition reactions, the effects of level of theory are relatively minor with even the worst levels of theory for the geometries, HF/6-31G(d) and MP2/6-31G(d), having errors of only a factor of 2 compared with the highest-level calculations. Again, the only exception to this is the harmonic oscillator result for addition to propyne at the B3-LYP/6-31G(d) level which, due to a poor value for the frequency corresponding to rotation of the attacking methyl group in the transition structure, exceeds the corresponding QCISD/6-31G(d) value by around an order of magnitude.

In summary, the frequency factors for addition of methyl radicals to both alkenes and alkynes, and the corresponding reverse reactions, can be calculated with reasonable accuracy at most low levels of theory. For example, B3-LYP/6-31G(d) generally shows errors of less than a factor of 2, and thus provides a reasonable compromise between accuracy and expense. The introduction of the free rotor and harmonic oscillator approximation does introduce further errors to the calculated frequency factors, the magnitude of which depends on the specific nature of the low frequency torsional modes in the system. In the present reactions, however, these approximations generally introduce errors of less than a factor of 4, and hence such methods would provide reasonable "order of magnitude" results.

Temperature Corrections. In calculating the Arrhenius parameters for a chemical reaction at a given temperature, it is necessary to calculate the temperature correction to the barrier ($\Delta\Delta H^{\ddagger}$). The temperature dependence of the barrier arises mainly in the vibrational contribution to the enthalpy, and as such its estimation depends on both the level of theory used in the frequency calculation and on the method for treating the low-frequency torsional modes. The temperature corrections (at 298 K) for methyl radical addition to ethene, propene, ethyne and propyne, calculated at a variety of levels of theory (and using the free rotor, hindered rotor and harmonic oscillator models), are shown in Table 5, while values for the corresponding reverse reactions are shown in Table 6.

As in the case of the frequency factors, the temperature corrections are relatively insensitive to both the level of theory and method for treating the low-frequency torsional modes. For the addition to alkenes, and the corresponding reverse reactions, the temperature corrections vary by less than 2 kJ mol^{-1} (which corresponds to a variation in the reaction rate of less than a factor of 2). For the alkynes, the errors incurred in using a low level of theory and/or the harmonic oscillator model are somewhat larger, especially for the HF and MP2 levels. However, using the low-level B3-LYP/6-31G(d) method in conjunction with the harmonic oscillator model leads to errors of 1.4−1.6 kJ mol^{-1} for the (forward and reverse) reactions of ethyne, and 2.6−3.0 kJ mol^{-1} for the reactions of propyne, compared with the corresponding benchmark calculations. In the latter case, the additional error arises because of the poor value (at the B3-LYP level) for the frequency corresponding to rotation of the attacking methyl group in the transition structure, as already noted. Even in this worst case, however, the error in the resulting rate calculation is still only a factor of 3.4 at room temperature. Furthermore the error in the temperature correction

TABLE 5. Effect of Level of Theory on Calculated Thermal Corrections to the Barriers (kJ mol^{-1}, 298 K) for Methyl Radical Addition to $CH_2{=}CHR$ and $CH{\equiv}CR$ (R = H, CH_3)

	Treatment of Torsional Modes		
Level of Theory	Free Rotor	Hindered Rotor	Harmonic Oscillator
$\bullet CH_3 + CH_2{=}CH_2 \rightarrow CH_3{-}CH_2CH_2\bullet$			
HF/6-31G(d)	−5.88	−5.86	−5.18
B3-LYP/6-31G(d)	−5.44	−5.17	−4.71
B3-LYP/6-311+G(3df,2p)	−5.34	−5.04	−4.62
MPW1K/6-31+G(d,p)	−5.38	−5.05	−4.69
MP2/6-31G(d)	−6.25	−5.82	−5.65
QCISD/6-31G(d)	−5.90	−5.50	−5.26
CCSD(T)/6-311G(d,p)	−5.82	−5.41	−5.54
$\bullet CH_3 + CH_2{=}CHCH_3 \rightarrow CH_3{-}CH_2CHCH_3\bullet$			
B3-LYP/6-31G(d)	−5.19	−4.63	−4.23
QCISD/6-31G(d)	−5.15	−4.65	−4.26
$\bullet CH_3 + CH{\equiv}CH \rightarrow CH_3{-}CH{=}CH\bullet$			
HF/6-31G(d)	−4.60	−4.56	−3.60
B3-LYP/6-31G(d)	−5.29	−5.26	−4.31
B3-LYP/6-311+G(3df,2p)	−4.97	−4.93	−4.02
MPW1K/6-31+G(d,p)	−5.09	−5.04	−4.16
MP2/6-31G(d)	−7.60	−7.49	−6.77
QCISD/6-31G(d)	−6.36	−6.31	−5.43
CCSD(T)/6-311G(d,p)	−5.75	−5.68	−4.98
$\bullet CH_3 + CH{\equiv}CCH_3 \rightarrow CH_3{-}CH{=}CCH_3\bullet$			
B3-LYP/6-31G(d)	−4.84	−4.72	−2.79
QCISD/6-31G(d)	−5.99	−5.82	−4.18

TABLE 6. Effect of Level of Theory on Calculated Thermal Corrections to the Barriers (kJ mol^{-1}, 298 K) for *β*-Scission of the $CH_3CH_2CHR\bullet$ and $CH_3CH{=}CR\bullet$ (R = H, CH_3) Radicals

	Treatment of Torsional Modes		
Level of Theory	Free Rotor	Hindered Rotor	Harmonic Oscillator
$CH_3{-}CH_2CH_2\bullet \rightarrow \bullet CH_3 + CH_2{=}CH_2$			
HF/6-31G(d)	0.68	0.43	0.79
B3-LYP/6-31G(d)	0.89	0.83	0.99
B3-LYP/6-311+G(3df,2p)	0.83	0.61	0.75
MPW1K/6-31+G(d,p)	0.94	0.81	0.91
MP2/6-31G(d)	0.35	0.50	0.57
QCISD/6-31G(d)	0.59	0.65	0.74
$CH_3{-}CH_2CHCH_3\bullet \rightarrow \bullet CH_3 + CH_2{=}CHCH_3$			
B3-LYP/6-31G(d)	1.03	0.51	0.58
QCISD/6-31G(d)	1.24	0.82	0.98
$CH_3{-}CH{=}CH\bullet \rightarrow \bullet CH_3 + CH{\equiv}CH$			
HF/6-31G(d)	2.98	2.53	3.59
B3-LYP/6-31G(d)	2.45	2.02	3.20
B3-LYP/6-311+G(3df,2p)	2.20	1.77	2.87
MPW1K/6-31+G(d,p)	2.33	1.91	2.96
MP2/6-31G(d)	1.33	1.03	2.00
QCISD/6-31G(d)	2.08	1.65	2.72
$CH_3{-}CH{=}CCH_3\bullet \rightarrow \bullet CH_3 + CH{\equiv}CCH_3$			
B3-LYP/6-31G(d)	2.08	1.16	3.47
QCISD/6-31G(d)	1.78	0.92	2.88

acts in the opposite direction to that of the frequency factors, and hence some degree of cancellation occurs.

Barriers and Enthalpies. Barriers and enthalpies for methyl radical addition to ethene, propene, ethyne and propyne at 0 K are shown in Tables 7 and 8, respectively. Of the methods chosen, the highest level of theory is the W1 theory (or its W1h variant[5]) of Martin et al.,[22,23] which attempts to produce coupled cluster energies [URCCSD(T)] with an infinite basis set via extrapolation procedures. This is generally regarded as an accurate procedure, having an estimated uncertainty (based on comparison with a test set of experimental heats of formation for 55 stable molecules[5]) of just 2.5 kJ mol^{-1}. In the present work, we treat this as our benchmark procedure. The other composite methods in Tables 7 and 8 also approximate UCCSD(T) or URCCSD(T) (or equivalently, QCISD(T)) energies with a large or infinite basis set, using extrapolation and/or additivity corrections carried out at the MP2 and/or MP4 levels of theory (rather than with coupled cluster methods, as in W1). These lower-level composite methods are therefore considerably less expensive than W1, and we include them in the study with a view to selecting a reliable alternative to W1 for larger systems. Finally, we consider various lower-level direct energy calculations with a view to identifying a reasonable procedure for the study of very large systems. In what follows, we first compare the results at the highest level of theory with the available experimental values, and then assess in turn the alternative composite procedures and the lower-level direct theoretical methods.

Comparison with Experiment. Experimental values for the barriers and enthalpies for methyl radical addition to ethene, propene, ethyne and propyne are included in Tables 7 and 8, respectively. The experimental reaction enthalpies were calculated from (gas-phase) experimental heats of formation at 298 K for the reactants and products in the various reactions, taken from ref 33 for the radicals ($CH_3\bullet$, $CH_3CH_2CH_2\bullet$ and $CH_3CH{=}CH\bullet$) and from ref 34 for all the other species. The resulting 298 K reaction enthalpies were then back corrected to 0 K and then to vibrationless values by subtracting the calculated QCISD/6-31G(d) temperature corrections (ΔΔH) and zero-point vibrational energy (ZPVE). The experimental values for the barriers were taken from the compilation in ref 1. Since these correspond to Arrhenius activation energies (E_a) at 298 K, they have been back-corrected to vibrationless barriers ($\Delta E^{\ddagger}_{e}$) using the following equation:[35,36]

$$\Delta E^{\ddagger}_{e} = E_a - mRT - \Delta\Delta H^{\ddagger} - ZPVE \qquad (1)$$

As foreshadowed in the previous section, we include two sets of experimental barriers in Table 7, the original reported values, and those recalculated from the experimental rates using our calculated (gas-phase) frequency factors. In this way, we hope to address the problem of estimating accurate and precise Arrhenius barriers from experimental rate constant data.

Comparing first the calculated W1h reaction enthalpies with the corresponding gas-phase experimental values in Table 8, we see that the calculated values all fall within the uncertainty of the experimental values. This reinforces the idea that the W1 methods are capable of achieving "chemical accuracy" for the relative energies of stable molecules.

However, when we compare the W1h and experimental barriers (Table 7), the deviations are substantial. In the case of the solution-phase values, these differences may be the result of solvent effects. This is because the calculated rate constants are based on the theory of ideal gases and therefore do not take into account the partition functions corresponding to the motion of the solvent or of the solvent interacting with the solute.[37] These effects can be very significant, and lead to experimental solution-phase rate constants for the addition of carbon-centered radicals to unsaturated compounds exceeding the corresponding gas-phase values by at least an order of magnitude at room temperature.[1] While it is possible in principle to calculate solvent effects by incorporating solvent molecules directly into the

TABLE 7. Effect of Level of Theory on the Barriers (kJ mol^{-1}) for Methyl Radical Addition to CH≡CR and CH_2=CHR (R = H, CH_3)[a]

Level of Theory	CH_2=CH_2	CH_2=$CHCH_3$	CH≡CH	CH≡CCH_3
B3-LYP/6-311+G(d,p)	24.3	24.8	30.2	30.4
B3-LYP/6-311+G(3df,2p)	25.0	25.7	30.2	30.7
RB3-LYP/6-311+G(d,p)	30.3	30.6	35.6	35.5
RB3-LYP/6-311+G(3df,2p)	30.9	31.3	35.5	35.7
RMP2/6311+G(d,p)	36.7	34.5	41.6	39.3
RMP2/6311+G(3df,2p)	34.4	32.7	39.1	37.2
MPW1K/6-311+G(d,p)	23.0	24.0	32.4	33.4
MPW1K/6-311+G(3df,2p)	23.5	24.7	32.4	33.6
G3(MP2)-RAD	28.2	27.5	35.2	34.5
G3X-RAD	28.0	27.2	35.6	35.1
G3(MP2)	30.6	30.0	35.2	34.6
G3X	28.7	28.0	35.0	34.6
CBS-QB3	21.5	20.4	29.8	28.6
U−CBS-QB3[b]	27.6	26.4	38.0	35.9
W1h	27.5	27.0	36.0	35.1
W1[c]	27.5	—	36.2	—
Experiment Gas-Phase[d]	21.0/23.2	20.0/21.5	22.4/25.0	26.8/25.4
Experiment Solution-Phase[d]	21.6/18.1	22.6/16.2	24.5/21.9	21.1/19.1

[a] Vibrationless values, calculated using QCISD/6-31G(d) geometries, unless otherwise noted. [b] CBS-QB3 without the spin-correction term. [c] CCSD(T)/6-311G(d,p) geometries. [d] Experimental values are taken from ref 1, and back-corrected to 0 K and then to vibrationless values using our calculated (QCISD/6-31G(d)) values for the ZPVE and temperature correction to the enthalpy ($\Delta\Delta H^{\ddagger}$), as follows: $\Delta E_e^{\ddagger} = E_a - 2RT - ZPVE - \Delta\Delta H^{\ddagger}$. Two "experimental" estimates are provided for each Arrhenius energy. The first entry corresponds to the value reported in the original work, and the second to a reanalysis of the rate data using calculated (QCISD/6-31G(d)) values for Arrhenius frequency factors for the respective reactions (see text).

TABLE 8. Effect of Level of Theory on the Reaction Enthalpies (kJ mol^{-1}) for Methyl Radical Addition to CH≡CR and CH_2=CHR (R = H, CH_3)[a]

Level of Theory	CH_2=CH_2	CH_2=$CHCH_3$	CH≡CH	CH≡CCH_3
B3-LYP/6-311+G(d,p)	−101.4	−102.0	−122.7	−121.1
B3-LYP/6-311+G(3df,2p)	−99.1	−99.7	−122.5	−120.3
RB3-LYP/6-311+G(d,p)	−101.2	−101.8	−122.6	−120.9
RB3-LYP/6-311+G(3df,2p)	−99.0	−99.6	−122.6	−120.3
RMP2/6-311+G(d,p)	−118.1	−115.9	−110.7	−112.1
RMP2/6-311+G(3df,2p)	−117.0	−115.2	−112.2	−111.8
MPW1K/6-311+G(d,p)	−133.9	−133.4	−153.1	−149.7
MPW1K/6-311+G(3df,2p)	−131.9	−131.4	−152.6	−148.7
G3(MP2)-RAD	−105.5	−105.7	−120.9	−120.3
G3X-RAD	−109.8	−110.1	−122.1	−121.2
G3(MP2)	−105.5	−105.9	−121.4	−121.0
G3X	−107.5	−107.8	−122.0	−121.6
CBS-QB3	−110.8	−112.3	−125.8	−126.6
U−CBS-QB3[b]	−110.8	−112.2	−121.0	−122.3
W1h[c]	−112.3	−112.8	−123.9	−124.4
Experiment[d]	−114.5 ± 3	−115.1 ± 3	−127.4 ± 7	-

[a] Vibrationless values calculated using QCISD/6-31G(d) geometries, unless otherwise noted. [b] CBS-QB3 without the spin-correction term. [c] CCSD(T)/6-311G(d,p) geometries. [d] Calculated using experimental heats of formation at 298 K taken from ref 33 for the radicals (CH_3•, $CH_3CH_2CH_2$• and CH_3CH=CH•) and from ref 34 for all other species. The resulting 298 K reaction enthalpies were back-corrected to 0 K and then to vibrationless values by subtracting the calculated QCISD/6-31G(d) temperature corrections and zero-point vibrational energy.

quantum chemical calculation (using for example a cluster-continuum model[38]), such calculations are beyond the scope of the present study, and we instead concentrate on the gas-phase experimental data.

The gas-phase experimental barriers (after adjustment to vibrationless values) are lower than the corresponding W1h values by approximately 5 kJ mol^{-1} for the additions to alkenes, and 10 kJ mol^{-1} for the additions to alkynes. These differences may in part reflect the greater uncertainty in the theoretical barriers. It is certainly true that the calculation of reaction barriers generally represents a more theoretically demanding problem, as it involves the calculation of transition structures that have partially formed bonds and (in the case of unrestricted treatments) spin-contaminated wave functions. However, for the addition reactions, the earliness of the transition structures assists the calculations through the possibility of substantial cancellation of error. This can be seen in the generally better performance of the low levels of theory for barriers (Table 7) compared with enthalpies (Table 8). Hence, while additional errors in the calculation of the reaction barriers cannot be ruled out, it seems reasonable to suppose that part of the large difference between the experimental and calculated barriers arises instead in the greater uncertainty in experimental measurements of barriers for radical addition reactions (compared with heats of formation of stable molecules). For the present systems, the gas-phase experimental data were obtained prior to the development of techniques (such as laser flash photolysis) capable of measuring the rates of radical addition reactions directly, and a reinvestigation using contemporary procedures would therefore be desirable. The differences between theory and experiment may also reflect shortcomings in standard transition state theory though we do not believe that this is particularly important in the current instances.

Comparison of the High-Level Composite Methods. Examining first the barriers for addition to alkenes and alkynes (Table 7), the following observations may be made. First, results

TABLE 9. Calculated Values of Forward (log k/(L mol^{-1} s^{-1}) and Reverse (log k/(s^{-1})) Rate Constants at 298 K for Methyl Radical Addition to Ethene and Ethyne

	Forward Reaction (Addition)		Reverse Reaction (β-Scission)	
Level of Theory[a]	CH_2═CH_2	CH≡CH	CH_2═CH_2	CH≡CH
RB3-LYP/6-311+G(3df,2p) //B3 (HO)	2.08	2.44	−7.49	−10.70
RMP2/6-311+G(3df,2p) //B3 (HO)	1.93	2.41	−10.80	−9.11
G3(MP2)-RAD //B3 (HO)	2.51	2.65	−8.26	−10.23
G3(MP2)-RAD //B3 (HR)	2.54	2.46	−8.76	−10.47
G3X-RAD //QCI (HR)	2.06	1.29	−9.57	−11.15
W1h //QCI (HR)	2.14	1.23	−9.94	−11.53
Gas-Phase Experiment[b]	2.9	3.1		

[a] The abbreviations //B3 and //QCI refer to the use of B3-LYP/6-31G(d) or QCISD/6-31G(d), respectively, for both geometry optimizations and frequency factor calculations, while HO and HR refer to the use of the harmonic oscillator or hindered rotor models in calculating the frequency factors and temperature corrections to the activation energies. [b] Taken from ref 1.

obtained with the W1h method (which differs from W1 by using nonaugmented basis functions on both hydrogen and carbon) is in excellent agreement with the W1 results, and therefore should provide suitable benchmark values for the larger systems in the present work. Second, we note that the considerably less expensive G3X-RAD and G3(MP2)-RAD composite methods give results within 1 kJ mol^{-1} of the W1/W1h values. The standard G3 methods, G3X and G3(MP2), are also in very good agreement with W1, though the errors are slightly increased for G3(MP2) (to 3 kJ mol^{-1}) for the addition to alkenes. Finally, the barriers calculated with the CBS-QB3 procedure are lower than those obtained from the W1- and G3-type methods by 6−7 kJ mol^{-1}.

As we noted earlier, this systematic difference between the barriers calculated with the CBS procedures and the G3, G3-RAD, and W1 families of methods has been observed previously for radical addition to C═C bonds.[9] We have also reported a similar systematic difference for methyl radical addition to C═S double bonds,[30] and for bond dissociation energies (BDEs) and radical stabilization energies (RSEs) associated with substituted amino radicals (•NHX).[39] In this previous work,[30,39] we observed that the difference was approximately equal to the value of the spin-correction term in the CBS-type methods. In the present systems we note that this is again the case, with the CBS barriers without spin correction (denoted U−CBS-QB3) showing close agreement with the results of other composite methods (see Table 7). It therefore seems likely the spin-correction term in the CBS-type methods is overestimating the errors due to spin contamination in radical addition transition structures, and hence the empirical pre-factor in this term might require some adjustment for such systems.

Examining next the reaction enthalpies for radical addition to alkenes and alkynes (Table 8), we find that the differences between the alternative composite methods are somewhat larger, due perhaps to reduced cancellation of error. G3X-RAD nonetheless provides close agreement with the corresponding W1/W1h values (within 2−3 kJ mol^{-1}), though the cheaper G3(MP2)-RAD method shows deviations of up to 7 kJ mol^{-1}. The standard G3 methods also show larger deviations, especially for addition to the alkenes, for which G3X shows an error of approximately 5 kJ mol^{-1} and G3(MP2) shows an error of approximately 7 kJ mol^{-1}. Interestingly, the deviations from W1h for the CBS-QB3 and U−CBS-QB3 enthalpies for methyl addition to alkynes are virtually equal and opposite at approximately 2−3 kJ mol^{-1}, and hence it is difficult to establish on the basis of these results whether the spin-correction term is overestimating the effects of spin contamination in the reaction enthalpies.

In summary, the G3X-RAD method provides close agreement with the considerably more expensive W1 level of theory for the calculation of both the barriers and reaction enthalpies in radical addition to alkenes and alkynes. This method should therefore provide suitable benchmark values for larger systems. The lower-level RAD variant of G3, G3(MP2)-RAD, and also the standard G3 methods, show somewhat larger errors, especially for the reaction enthalpies. However, all provide results within 7 kJ mol^{-1} of the high-level values. The spin-correction term in the CBS-QB3 method appears to be introducing a systematic error to the addition barriers, and better results are obtained without its inclusion (U−CBS-QB3). For the reaction enthalpies, standard CBS-QB3 provides good agreement with W1, but the spin-correction term is somewhat smaller in these cases so it is a less demanding test. Formulation of a restricted version of CBS-QB3, namely R−CBS-QB3, which avoids the use of the spin-correction term, would be desirable.

Lower-Level Methods. Barriers and reaction enthalpies obtained using a variety of direct single-point energy calculations are included in Tables 7 and 8, respectively, with a view to selecting a suitable low-cost procedure for the study of larger systems. Examining first the barriers, we note that the large-basis-set calculations with each method produce absolute barriers within 7 kJ mol^{-1} of the W1h results. In the case of the reaction enthalpies, however, the absolute errors are substantially larger due to reduced cancellation of errors. In general, both UB3-LYP and RB3-LYP overestimate the reaction enthalpy for addition to alkenes by approximately 13 kJ mol^{-1}, but produce results for the addition to alkynes within 4 kJ mol^{-1} of W1h. In contrast, RMP2 produces reasonable results for the alkenes (with errors up to 5 kJ mol^{-1}), but overestimates the enthalpy for addition to alkynes by around 13 kJ mol^{-1}. The MPW1K method underestimates the enthalpy both for addition to alkenes and to alkynes, by approximately 20 kJ mol^{-1} and 30 kJ mol^{-1}, respectively. All four methods show large errors (5−19 kJ mol^{-1}) for the relative enthalpies for addition to double and triple bonds, which is not surprising, given their differing performance for addition to alkenes and alkynes. Finally it should be noted that the low-level methods all agree with the W1h result that the effect of a methyl substituent on both the barrier and enthalpy for radical addition to alkenes and alkynes is very small, though in some cases the sign of the calculated effect is the opposite of that predicted by W1h.

None of the low-cost methods above appears to be suitable for comparing the *enthalpies* of radical addition to double and triple bonds. For a study of this type, a composite method such as G3X-RAD (or at least G3(MP2)-RAD) is recommended. Interestingly, most of the methods examined give reasonable values for the relative *barriers* for methyl radical addition to double and triple bonds. However, the difficulties encountered with reaction enthalpies means that barriers for the reverse β-scission reaction are poor in several cases.

If we examine radical addition to C═C double bonds and to C≡C triple bonds as independent problems, the results are more encouraging. For addition to C═C double bonds, a method such as RMP2/6-311+G(3df,2p), which produces enthalpies within 5 kJ mol^{-1} of the W1h values and barriers within 7 kJ mol^{-1}, would be suitable for large systems. Interestingly, this method also shows reasonable performance for radical addition to C═S double bonds.[30] For addition to C≡C triple bonds, the UB3-LYP/6-311+G(3df,2p) or RB3-LYP/6-311+G(3df,2p) methods appear to be suitable, both producing enthalpies within 4 kJ mol^{-1} of the W1h values and barriers within 6 kJ mol^{-1}. Of these two alternative methods, RB3-LYP/6-311+G(3df,2p) is slightly superior, showing errors in the reaction barriers of less than 1 kJ mol^{-1}.

Reaction Rates. Having examined the individual performance of the methods in calculating the geometries, frequency factors, temperature corrections and barriers, it is of interest to examine the overall accuracy of various combinations of procedures in the calculation of rate constants. In Table 9, we show the rate constants (at 298 K) for both the forward (addition) and reverse (β-scission) reactions, obtained using barriers and frequency factors at combinations of levels of theory that might typically be used in practice. In calculating the rate constants, the W1h//QCISD/6-31G(d) barriers provide our benchmark values, while the G3X-RAD//QCISD/6-31G(d) barriers provide an excellent lower-cost alternative. In both these cases, the barriers are combined with high-level frequency factors, namely QCISD/6-31G(d) in conjunction with the hindered rotor model. A method suitable for larger systems would involve G3(MP2)-RAD calculations on the cheaper B3-LYP/6-31G(d) geometries for the barriers, and for these calculations we present rate constants obtained using both the harmonic oscillator and hindered rotor models at the B3-LYP/6-31G(d) level for the frequency factors. Finally, methods suitable for very large systems would involve RMP2/6-311+G(3df,2p) or RB3-LYP/6-311+G(3df,2p) barriers obtained using the B3-LYP/6-31G(d) geometries, and for these we present rate constants calculated using the harmonic oscillator B3-LYP/6-31G(d) frequency factors. A larger set of combinations of procedures for the addition and β-scission reactions is provided in Tables S7 and S8 of the Supporting Information.

Experimental gas-phase rate constants, where available, have been included in Table 9 for the sake of comparison. As might have been anticipated from the preceding comparisons of the theoretical and experimental Arrhenius parameters, there is significant disagreement between the high-level W1h//QCISD/6-31G(d) results and the experimental rate constants, especially for the addition to ethyne. Experimental reinvestigation of these systems in the gas-phase using contemporary procedures would be desirable. For the remainder of this discussion, we will compare the lower levels of theory with the W1h calculations, which we will consider as our benchmark.

We note first that there is very good agreement between the G3X-RAD and W1h results, but somewhat larger differences for the lower levels of theory. For G3(MP2)-RAD//B3-LYP/6-31G(d), the combination of relatively small errors in the geometries, frequency factors, temperature corrections and barriers leads to errors of around an order of magnitude for the rate constants for addition to ethyne, and for β-scission of both the propyl radical and the propenyl radical. These errors are slightly increased when the harmonic oscillator approximation is used. However, it is noteworthy that the G3(MP2)-RAD//B3-LYP/6-31G(d) procedure provides very good rate constants for addition to ethene for both the hindered rotor and harmonic oscillator models. Thus, this relatively inexpensive high-level procedure may be suitable for the more general study of radical addition to alkenes.

The lowest levels of theory, RMP2/6-311+G(3df,2p)//B3-LYP/6-31G(d) and RB3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G(d), perform reasonably well for the addition rate constants, showing an accuracy comparable to the more expensive G3(MP2)-RAD procedure. This may partly be due to significant cancellation of errors in the early transition structures for these reactions. However, as might be expected from the earlier discussion of reaction enthalpies, larger errors arise at the lower levels of theory for the reverse reactions. In particular, RB3-LYP/6-311+G(3df,2p) performs quite poorly for the β-scission of the propyl radical (giving methyl radical plus ethene), showing errors of more than 2 orders of magnitude in the reaction rates. RMP2/6-311+G(3df,2p) performs significantly better, providing rates within 1 order of magnitude of the high-level values. Interestingly, for the β-scission of the propenyl radical (giving methyl radical plus ethyne), the situation is reversed. In this case, RMP2/6-311+G(3df,2p) shows errors of more than 2 orders of magnitude, while RB3-LYP/6-311+G(3df,2p) provides rate constants within 1 order of magnitude. Thus, as noted above, RMP2/6-311+G(3df,2p) shows the best low-cost performance for radical addition to alkenes, while RB3-LYP/6-311+G(3df,2p) is better for studying radical addition to alkynes.

4. Conclusions

Based on the above assessment of procedures for calculating the geometries, frequency factors, barriers and enthalpies for methyl radical addition to ethene, propene, ethyne and propyne, the following conclusions may be drawn.

(1) Calculated geometries, frequency factors and temperature corrections are relatively insensitive to level of theory. In particular, QCISD/6-31G(d) provides a very good approximation to the higher-level CCSD(T)/6-311G(d,p) results, while B3-LYP/6-31G(d) calculations provide a reasonable low-cost alternative for larger systems. As observed previously, (U)MP2/6-31G(d) calculations should be avoided for spin-contaminated systems.

(2) In calculating the frequency factors for the four reactions, both the free rotor and harmonic oscillator approximations provide reasonable “order of magnitude” approximations to the more accurate hindered rotor treatment in these prototype systems. However, one might expect the errors in these approximations to increase for the reactions of substituted radicals, and a careful hindered rotor treatment of the low-frequency modes —even if applied at a low level of theory such as B3-LYP/6-31G(d)— might be advisable in these cases.

(3) At the highest level of theory, W1h//QCISD/6-31G(d), the reaction enthalpies for the four reactions show very good agreement with the available experimental data. However, the barriers for addition to alkenes and alkynes differ from the available gas-phase data by approximately 5 and 10 kJ mol^{-1}, respectively. While the errors in the calculations may be somewhat more than normal for the (more theoretically demanding) calculation of barriers, a gas-phase experimental investigation of these systems using modern techniques would be desirable.

(4) Barriers and enthalpies are very sensitive to the level of theory selected. However, suitable lower cost alternatives to W1 theory are available. In particular, G3X-RAD shows excellent agreement with W1 (within 3 kJ mol^{-1}) for both barriers and enthalpies, while the cheaper G3(MP2)-RAD method shows very good agreement for barriers and only slightly increased (to 7 kJ mol^{-1}) errors for enthalpies. CBS-QB3 systematically

underestimates the barriers (by 6−7 kJ mol^{-1}) but provides reasonable estimates of the reaction enthalpies. When composite methods cannot be afforded, the use of RMP2/6-311+G(3df,2p) single-point energies appears to be suitable for addition to C═C double bonds (giving results within 7 kJ mol^{-1} of W1h), while RB3-LYP/6-311+G(3df,2p) appears to be suitable for addition to C≡C triple bonds (giving results within 4 kJ mol^{-1} of W1h).

(5) The systematic difference between the barriers for radical addition reactions that are calculated using CBS-QB3, and those calculated with G3- or W1-type methods, appears to be attributable to the spin-correction term in standard CBS-QB3. This term appears to be overestimating the effects of spin contamination in the radical addition transition structures, and its (empirically optimized) pre-factor may require some adjustment for these systems. Better results are obtained when the spin-correction term is omitted (U−CBS-QB3). Formulation of a restricted version of CBS-QB3 (R−CBS-QB3) would be desirable.

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Supporting Information Available: Table S1 contains GAUSSIAN archive entries showing optimized geometries for all species considered in the present work at various levels of theory. Corresponding total energies at several levels of theory are contained in Tables S2-S5, while total entropies are included in Table S6, and selected rate coefficients in Tables S7-S8. This material is available free of charge via the Internet at http://pubs.acs.org

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(35) We have previously (in ref 7) suggested that the solution-phase experimental barriers could be back corrected to their equivalent gas-phase values using the formula: $\Delta E^{\ddagger}_0 = E_a - RT - \Delta\Delta H^{\ddagger}$. This is based on the idea that in an incompressible fluid, $\Delta H^{\ddagger} = \Delta E^{\ddagger}$. However, to apply this correction, it is necessary to calculate $\Delta\Delta H^{\ddagger}$ for the solution phase. Previously, we used the gas-phase formulae to calculate this quantity. However, this ignores the additional contribution from the derivatives of the partition functions that correspond to the motion of the solvent and also the interaction of the solvent with the solute. These errors could be substantial and render it difficult to predict accurate solution-phase activation energies from such gas-phase calculations. Given this problem, in the present work we apply the gas-phase correction in its entirety to the solution-phase values in order to preserve the experimental gas-phase/solution-phase difference, which we will discuss separately.

(36) There is often some confusion surrounding the relationship between the Arrhenius activation energy (E_a), the internal energy of activation (usually denoted $\Delta E^{\ddagger}$ or $\Delta U^{\ddagger}$) and the enthalpy of activation ($\Delta H^{\ddagger}$). At 0 K, these quantities are identical ($E_{a\,0} = \Delta E^{\ddagger}_0 = \Delta H^{\ddagger}_0$), but at nonzero temperatures, these quantities can differ by various multiples of RT. For a gas-phase reaction of molecularity m, the following relation holds: $E_{a\,T} = \Delta E^{\ddagger}_T + RT = \Delta H^{\ddagger}_T + mRT$. Thus, to convert Arrhenius activation energies to vibrationless barriers at 0 K, we must subtract the quantity mRT (as well as the ZPVE and the enthalpic temperature correction to the barrier, $\Delta\Delta H^{\ddagger}$). For further details, see for example: Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, New Jersey, 1989.

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