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Thermochemical Kinetics for Multireference Systems: Addition Reactions of Ozone

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The 1,3-dipolar cycloadditions of ozone to ethyne and ethene provide extreme examples of multireference singlet-state chemistry, and they are examined here to test the applicability of several approaches to thermochemical kinetics of systems with large static correlation. Four different multireference diagnostics are applied to measure the multireference characters of the reactants, products, and transition states; all diagnostics indicate significant multireference character in the reactant portion of the potential energy surfaces. We make a more complete estimation of the effect of quadruple excitations than was previously available, and we use this with CCSDT/CBS estimation of Wheeler et al. (Wheeler, S. E.; Ess, D. H.; Houk, K. N. *J. Phys. Chem. A* 2008, 112, 1798.) to make new best estimates of the van der Waals association energy, the barrier height, and the reaction energy to form the cycloadduct for both reactions. Comparing with these best estimates, we present comprehensive mean unsigned errors for a variety of coupled cluster, multilevel, and density functional methods. Several computational aspects of multireference reactions are considered: (i) the applicability of multilevel theory, (ii) the convergence of coupled cluster theory for reaction barrier heights, (iii) the applicability of completely renormalized coupled cluster methods to multireference systems, (iv) the treatment by density functional theory, (v) the multireference perturbation theory for multireference reactions, and (vi) the relative accuracy of scaling-type multilevel methods as compared with additive ones. It is found that scaling-type multilevel methods do not perform better than the additive-type multilevel methods. Among the 48 tested density functionals, only M05 reproduces the best estimates within their uncertainty. Multireference perturbation theory based on the complete-active-space reference wave functions constructed using a small number of reaction-specific active orbitals gives accurate forward barrier heights; however, it significantly underestimates reaction energies.

1. Introduction

Modern wave function theory (WFT) of thermochemistry and thermochemical kinetics is based on including electron correlation to a high level, and popular methods for doing this are essentially all post-Hartree–Fock methods; that is, they add electron correlation to a single-configuration (Hartree–Fock) reference state.¹ For this reason they are often labeled by the shorthand phrase “single-reference methods.” The methods that are most popular are those that can be reduced to a routine that does not require individual judgment; Wheeler et al.² have called these “black box” methods. When Hartree–Fock theory does not provide a good starting point, post-Hartree–Fock methods have larger errors; such cases are called multireference systems because they are better treated by multiconfiguration reference states, such as multiconfiguration self-consistent-field^{3–7} (MC-SCF) wave functions. Multireference effects are also known under other names such as near-degeneracy effects and static correlation energy. Post-MCSCF methods, which may also be called multireference methods, are available,^{8–13} but their greater complexity means that they usually treat dynamical electron correlation energy to a lower order (e.g., only double excitations out of the reference function). Even more problematic is that they require considerable human judgment,^{14,15} which has

prevented their incorporation into black box routines. A variant approach, which holds promise, but which has received only limited systematic exploration so far, is to base correlated wave functions on Kohn–Sham or hybrid Kohn–Sham orbitals.^{16–19}

The most systematic routines for electronic structure theory are called theoretical model chemistries.^{1,20–22} Theoretical model chemistries are also called “methods” or “models”, and they are precisely defined for any process. The most straightforward methods correspond to a choice of wave function level combined with a basis set or a choice of density functional approximation combined with a basis set. Complete definition of a method also requires specification of how relativistic effects and core correlation are handled and whether geometries are consistently optimized or treated by another method.

A class of methods that may be called multilevel correlation single-reference methods has been very successful for both energies of reaction (as required to calculate heats of formation) and barrier heights. These theories involve adding the effects of various high-level correlation effects.^{1,16} For most systems, the highest accuracy for a given computational expense is obtained by adding empirical terms, called the high-level correction^{1,23–27} or the size-consistent empirical correction,^{28–31} to high-level post-Hartree–Fock calculations. Wheeler et al.² applied some of these methods (CBS-QBS,²³ CBS-APNO,²⁸ G3,²⁴ G3//B3LYP,²⁵ G3(MP2)//B3LYP,²⁵ G4,²⁶ G4(MP3),²⁷ and G4(MP2)²⁷) to 1,3-dipolar cycloadditions of ozone to ethyne and ethene and found somewhat erratic results with calculated

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potential energy barriers for C_2H_2 in the wide range of 3.0–11.1 kcal/mol and those for C_2H_4 in the wide range of –1.6 to +4.1 kcal/mol. They concluded that results from these approaches must be closely scrutinized and not assumed to be of benchmark quality. We agree; these methods should be validated for various kinds of systems, processes, and properties to learn their expected accuracy for various kinds of predictions. Whereas extensive validation studies are available for heats of formation^{26,32,33} and reaction barrier in systems with low-to-moderate multireference character,³⁴ further tests are needed for barrier heights in systems with large static correlation energy.

Ozone is a notorious example^{31,35–37} of a multireference system (although, formally, ozone is a closed-shell singlet, the diradical character has been estimated to be about 33%^{2,38–40}), and single-reference methods were not designed to treat that kind of system. For example, Ljubic and Sabljic⁴¹ applied multireference second-order perturbation theory with a cc-pVTZ basis set to the addition of ozone to ethene and obtained a barrier of –2.3 kcal/mol, which differs appreciably from the single-reference second-order perturbation theory value (with the most similar basis set) of –5.2 kcal/mol reported by Wheeler et al.² (The potential energy value of –2.3 becomes positive when the change in zero-point energy is added; the potential energy value was obtained from the Supporting Information.²)

In the present article we use the two addition reactions of ozone as representative cases for exploring the treatment of singlet-state reactions with high multireference character. In particular, we consider (i) the convergence of coupled cluster (CC) theory (in particular, CC theory with single and double excitations, denoted CCSD, and with single, double, and triple excitations, denoted CCSDT) and coupled cluster theory (CCSD or CCSDT) with various quasiperturbative correction schemes for triple or triple and quadruple excitations, for multireference energy of reactions and barrier heights, (ii) the applicability of completely renormalized (CR) coupled cluster (CR-CC) theory to multireference systems, (iii) the applicability of single-reference multilevel methods to multireference systems, (iv) the treatment of multireference reactions by density functional theory (DFT), and (v) multireference perturbation theory for multireference reactions. We next introduce these five topics.

(i) The most straightforward approach to accurate calculations is single-level single-reference WFT in which post-Hartree–Fock calculations are carried out with a high level of electron correlation and a large one-electron basis set. Most modern high-level calculations start with a CCSD step. The most affordable benchmark level built on CCSD is called CCSD(T), which involves a particular quasiperturbative treatment⁴² of connected triple excitations. When affordable, one can also consider CCSDT, which denotes a fully coupled CC treatment of single, double, and triple excitations. When both the level and the basis set are pushed toward convergence, this is called the focal point method.⁴³ The convergence of the electron correlation level (for a given one-electron basis set) is called full configuration interaction (FCI), and the convergence of the one-electron basis set (at any level of electron correlation) is called the complete basis set (CBS) limit. Simultaneous convergence of both correlation level and basis set is called complete configuration interaction (CCI). Wheeler et al.² carried out a focal point analysis for the ozone addition reactions. The CBS limit of CCSD(T) gave barriers (in kcal/mol) of 7.0 for C_2H_2 and 2.8 for C_2H_4 , whereas CCSDT gave 7.9 and 3.6, respectively. Experience, in general, has shown that neither CCSD(T) nor CCSDT is reliable when they disagree,⁴⁴ and experience with ozone itself has shown a significant contribution of quadruple

excitations.⁴⁵ Wheeler et al. added quadruple excitations perturbatively for one of the reactions, yielding a level called CCSDT(Q),⁴⁶ and found a change of only –0.2 kcal/mol with an estimated CCSDT(Q) barrier of 7.7 kcal/mol for C_2H_2 . We will reexamine the effect of quadruples with a larger basis set and also examine the effect of quadruple excitations for C_2H_4 . Among the levels tested will be the CCSDT(2)_Q method, which was found to be the most accurate CC method (of 14 tested) for the highly multireference symmetric dissociation of H_2O and triple-bond dissociation in N_2 .⁴⁷ Note that CCSDT(2)_Q is much more complete than CCSDT(Q) because it contains all of the second-order terms in the quadruple excitation operator T_4 .

(ii) Besides the popular CCSD(T) model, a variety of CR-CC methods have been developed.^{48–58} These methods include a few approaches that, by analogy to CCSD(T), correct the CCSD energy for the effects of the connected triply excited clusters, such as CR-CCSD(T)^{49,50,53,54,57} and CR-CC(2,3),^{55–57} and several approaches that describe the combined effect of the connected triply and quadruply excited clusters, including CCSD(TQ),^{48,51,53,54} CR-CCSD(TQ),^{48,51,53,54} and CR-CC(2,3)+Q.⁵⁷ We will compare the results of CC and CR-CC calculations at various levels.

(iii) Multilevel methods (also called composite methods) have already been mentioned in the context of correlation methods. Another category of multilevel methods is based on scaling.^{59–75} Such methods, especially multicoefficient versions,^{65–75} have a potential advantage over additive methods for multireference systems because they can involve different factors, for example, for scaling double excitations that represent dynamical correlation and for scaling triple excitations that may make a relatively greater contribution in multireference systems.⁶⁵ The multilevel methods considered here represent an attempt to extrapolate to the CCI limit rather than calculating it directly. Therefore, they are affordable for larger systems than those for which either CCI or focal point methods are practical. Cost savings are quantified elsewhere^{70–74} but are typically one to two orders of magnitude. We will therefore explore five multicoefficient correlation methods of the scaling type (MCSAC-CCSD(T)/pTZ,⁶⁷ G3SX(MP3),⁶⁹ MCG3/3,⁷⁰ BMC-CCSD,⁷¹ and MCG3-MPW^{72,73}) and one single-coefficient scaling method (SAC-CCSD(T)/pTZ⁶⁷). For comparison primarily with G3SX(MP3), we will also employ an additive method with the same components that was optimized for the same data (G3X(MP3)⁶⁹). It is also worthwhile to mention another advantage of scaling-type multilevel methods over additive-type ones for dynamics, namely, that they yield continuous potential surfaces with continuous gradients^{65,66} and can readily be used for multilevel geometry optimization of both stable molecules and transition states.⁷⁵

There are many other composite methods in the literature, for example, HEAT⁷⁶ and CEEIS.⁷⁷ We do not compare with these here. One reason for our special interest in methods like MCG3-MPW is their high efficiency, which makes them applicable to larger systems. For example HEAT involves a series of calculations including HF/aug-cc-pCV5Z, CCSD(T)/aug-cc-pVQZ, CCSDT/cc-pVQZ, and CCSDTQ/cc-pVDZ, and CEEIS involves up to octuple excitations in a single-reference or multireference configuration interaction calculation with a large basis set, for example, cc-pVQZ. In contrast, MCG3-MPW involves much smaller basis sets and levels of electron excitation. For example, for systems (like the present ones) with no atom heavier than Ne, MPWX/6-311+G(2df,2p), MP2/6-

311+G(2df,2p), MP4SDQ/6-31G(2df,2p), MP2/6-31+G(d,p), and QCISD(T)/6-31G(d) are involved.

(iv) Density functional theory⁷⁸ (DFT) provides an efficient way to calculate barrier heights for large systems, and several density functionals have been reported to have good accuracy for barrier heights.^{34,79,80} A recent study²² of calculated values for a database, DBH24,³⁴ of 24 representative barrier heights for diverse reactions found an average error of only 1.0 kcal/mol for barriers calculated by the M06-2X^{79,80} density functional with the MG3S basis set. However, M06-2X has 54% Hartree–Fock exchange, and it has been shown that density functionals with a high fraction of Hartree–Fock exchange are often inaccurate for multireference systems.⁸¹ We define the class of local functionals to include those that depend on the local value of quantities such as the spin densities, ρ_α and ρ_β , the spin density gradients, $\nabla\rho_\alpha$ and $\nabla\rho_\beta$, and the spin kinetic energy densities, τ_α and τ_β . It is well known that density functional exchange includes some static correlation⁸² (although in a “haphazard” way⁸³), and it often provides useful results for multireference systems, especially when Hartree–Fock exchange is excluded; that is, when the density functional is local. Recently, we have developed the first local density functional, called M06-L,⁸⁴ that predicts more accurate barrier heights than the popular B3LYP^{85–88} functional (which has 20% Hartree–Fock exchange), and in the present article, we will test this functional, along with B3LYP,^{85–88} M06-2X,⁸¹ and 45 other^{21,72,79–81,84–119} functionals.

(v) Finally, we will consider multireference perturbation theory. Although single-reference methods have been extensively systematized as theoretical model chemistries in both single-level¹²⁰ and multilevel^{1,24–30,59–75,120} form, multireference methods have been harder to define, primarily because of the human judgment required in the selection of configurations to include. Recently, however, we have defined and tested three multireference model chemistries based on different schemes for constructing reference wave functions called nominal correlated participating orbital (*nom*-CPO), moderate CPO (*mod*-CPO), and extended CPO (*ext*-CPO).²² All three model chemistries employ multireference Møller–Plesset second-order perturbation theory^{123,124} (MRMP2) based on a complete active space self-consistent field^{6,7} (CASSCF) zero-order wave function. For barrier heights in DBH24,³⁴ the *nom*-CPO level performed as well as the *mod*-CPO and *ext*-CPO levels with an average error of 1.4 kcal/mol, and it remains affordable for large systems. We will consider MRMP2/*nom*-CPO here.

In this article, the focus is on potential energy differences without zero-point vibrational energy because that provides the purest test of electronic structure theory. As in ref 2, we consider, for each reaction, the energy differences to form the van der Waals complex, the transition state, and the cycloadduct (product).

Section 2 summarizes the details of our calculations, and Section 3 presents the tables of results and discusses them. Section 4 has concluding remarks.

2. Methods

2.1. Basis Sets. We will use abbreviations for the correlation consistent basis sets;¹²⁵ namely, ccXZ denotes cc-pVXZ and accXZ denotes aug-cc-pVXZ, with X = D, T, or Q. Other basis sets employed are in order of increasing size: 6-31G(d),^{121,126,127} 6-31G(2df,p),^{121,126,127} 6-311+G(2df,2p),^{121,128,129} and G3Large.²⁴ For brevity, in the rest of this article, we abbreviate 6-311+G(2df,2p) as MG3S¹³⁰ because these two basis sets are identical for H through Si. The reason for using shorthand names for basis sets is to make the article easier to read.

2.2. Geometries and Zero of Energy. In ref 2, many calculations were carried out at CCSD(T)/ccTZ geometries, which would ordinarily be expected to be reasonably accurate. In the present article, except in one table where explicitly indicated otherwise and except for multilevel calculations from ref 2 that use special choices of geometry defined by the method, we use these same CCSD(T)/ccTZ geometries for consistency. All energies in tables are given in kcal/mol with respect to reactants.

2.3. Coupled Cluster Theory. A key issue that we address first is the effect of quadruple excitations on the ethylene reaction. We note that previous work^{44,131–136} has shown that CCSDT is often less accurate than CCSD(T), and the full inclusion of triple excitations only increases reliability when one also includes the effect of quadruple excitations. This results in part because the CCSD(T) \rightarrow CCSDT and CCSDT \rightarrow CCSDTQ contributions are often individually much larger than their sum.¹³⁷ Therefore, it is important to have results for both reactions that include the effect of quadruple excitations. The two highest levels presented in ref 2 for all six species were CCSD(T)/accQZ and CCSDT/accDZ, and a quadruples level was presented² only for the C₂H₂ reactions. We will present new calculations to reexamine the convergence, especially with respect to including connected quadruple excitations. The connected quadruple excitations were included in the present CC calculations by two methods. First is a perturbative approach based on the similarity-transformed Hamiltonian, that is, by the CCSDT(2)_Q method,⁴⁷ which is a method whose cost scales (for a given composition and a given basis set for each atomic number) as N^9 , where N is the number of atoms. The second method corresponds to adding the (Q) corrections to the CCSD(T) energies. The (Q) corrections used in the resulting CCSD(TQ) method are very similar to the factorized quadruples CCSD(TQ)_f approach of ref 138. To be more precise, they correspond to variant ‘b’ of CCSD(TQ) described in detail in refs 48, 51, 53, and 54. The only difference between the CCSD(TQ) approach used here and the CCSD(TQ)_f method of ref 138 is in the treatment of the doubly excited clusters that enter the definition of the (Q) correction, which in the former case are taken from the converged CCSD calculations and in the latter case are partially approximated by their first-order perturbation theory estimates. (We refer the reader to refs 48, 51, 53, and 54 for further details). As in the case of CCSD(TQ)_f, the advantage of the CCSD(TQ) approach is the relatively low cost of the determination of the (Q) correction, which scales as $n_o^2 n_u^5$, as opposed to the $n_o^4 n_u^6$ (where n_o is the number of occupied orbitals and n_u is the number of unoccupied orbitals) steps that characterize CCSDTQ.¹³⁸

The cost of determining the quadruples corrections of CCSD(TQ) was too large to allow us to perform calculations for the accTZ basis set. Therefore, we consider a mixed approach in which we define the CCSD(T)+Q(DZ) energy as the sum of the CCSD(T)/accTZ energy and the difference of the CCSD(TQ) and CCSD(T) energies with the accDZ basis. The “+Q(DZ)” notation is further explained in Section 2.4.

To put the coupled-cluster results in context, we will also present a few comparisons to lower-level theories, namely, Møller–Plesset¹²² perturbation theory (MP2,¹³⁹ MP3,¹⁴⁰ MP4,¹⁴¹), quadratic configuration interaction with single and double excitations (QCISD¹³⁹), and QCISD with a quasiperturbative treatment of connected triple excitations (QCISD(T)¹³⁹).

2.4. Completely Renormalized Coupled Cluster Theory. There are several CR-CC methods, and they are discussed elsewhere,^{48–58} so we provide here only a brief summary,

primarily to make it clear what was done and how these methods compare with conventional coupled-cluster calculations. In analogy to the popular CCSD(T) approach, in the CR-CCSD(T) and CR-CC(2,3) calculations, we add a correction due to the connected triply excited clusters to the CCSD energy. The difference between the CCSD(T) approach and these CR approaches is the definition of the connected triples correction, which in the CR-CCSD(T) and CR-CC(2,3) cases uses the complete form of the triply excited moments of the CCSD equations (projections of the CCSD equations on triply excited determinants) rather than the leading contributions to these moments used in CCSD(T).^{49,50,53–58} Moreover, in the CR-CCSD(T) and CR-CC(2,3) approaches, one renormalizes the connected triples correction so that one can avoid the well-known failures of CCSD(T) in certain multireference situations, such as bond breaking and biradicals.^{49,50,53,54} Because the multireference character of ozone is primarily of the biradical type, it is very interesting to compare CR calculations with conventional CC calculations for the reactions under consideration here. In the CR-CCSD(T) approach, the renormalization is accomplished by dividing the connected triples correction by the overlap of the suitably designed trial wave function that enters the energy expressions defining the method of moments of CC equations,^{49,50,53,54} on which all CR-CC approaches are based, and the CCSD wave function. In the CR-CC(2,3) approach, the renormalization of the connected triples correction is accomplished through the use of the left eigenstate of the similarity transformed Hamiltonian of CC theory, as required by the biorthogonal formulation of the method of moments of CC equations.^{55–58} The CPU times of the most expensive noniterative steps of CR-CCSD(T) and CR-CC(2,3) scale as $n_o^3 n_u^4$, as compared with $n_o^3 n_u^4$ for CCSD(T), where n_o and n_u represent, respectively, the number of occupied and unoccupied orbitals used in the post-RHF calculations. Unlike CCSD(T) and CR-CC(2,3), the CR-CCSD(T) approach is not strictly size extensive (the extensivity errors of CR-CCSD(T) calculations amount to about 0.5 to 1% of the correlation energy^{52,54}), so the CR-CCSD(T) energies of the stationary points along the reaction pathways are calculated relative to the CR-CCSD(T) energy of the noninteracting complex formed by the reactants separated by a large distance (we used 500 Å), as is usually done in multireference configuration interaction calculations, rather than the sum of CR-CCSD(T) energies of individual reactant molecules. This reduces the small extensivity errors in the CR-CCSD(T) calculations to about 0.5 to 1% of the changes in the correlation energy along a given reaction pathway.

The CCSD(T), CR-CCSD(T), and CR-CC(2,3) methods are also augmented by the (Q) corrections to take account of the connected quadruply excited clusters using a method called CR-CCSD(TQ),^{48,51,53,54} in which the CR-CCSD(T) energy is corrected for the effect of the connected quadruply excited clusters through the completely renormalized form of the (Q) correction resulting from the method of moments of CC equations.^{49,50,53,54} To be consistent with the CCSD(TQ) results, we use variant 'b' of CR-CCSD(TQ), as described in detail in refs 48, 51, 53, and 54. As in the case of triples corrections, the difference between the CCSD(TQ) and CR-CCSD(TQ) approaches lies in the definition of the energy correction to CCSD, which in the CR-CCSD(TQ) case uses the complete form of the triply and quadruply excited moments of the CCSD equations (projections of the CCSD equations on triply and quadruply excited determinants) rather than the leading contributions to these moments used in CCSD(TQ).^{48–51,53,54} We also renormalize the correction due to triples and quadruples in the

CR-CCSD(TQ) scheme, so that one can avoid the potential failures of CCSD(T) and CCSD(TQ) in multireference situations.^{49,50,53,54} By analogy to CR-CCSD(T), in the CR-CCSD(TQ) approach, this is done by dividing the correction due to connected triples and quadruples by the overlap of the appropriate trial wave function that enters the energy expressions defining the method of moments of CC equations^{49,50,53,54} and the CCSD wave function. The cost of the most expensive steps of CR-CCSD(TQ) scale as $n_o^2 n_u^5$ as compared with $n_o^2 n_u^5$ for CCSD(TQ). As with CR-CCSD(T), the CR-CCSD(TQ) approach is not strictly size extensive, so the CR-CCSD(TQ) energies of the stationary points along the reaction pathways are calculated relative to the energy of the subsystems separated by a large distance. The CR-CC(2,3) approach has a natural extension to connected quadruples through the CR-CC(2,4) corrections to the CCSD energy,^{55–57} which enables one to describe the coupling of the connected triple and quadruple excitations via the off-diagonal matrix elements of the CC similarity-transformed Hamiltonian,⁵⁷ but we do not have a computationally efficient implementation of the CR-CC(2,4) approach that could be used in this work, so we correct the CR-CC(2,3) results for the dominant quadruples effects by forming the difference of the CR-CCSD(TQ) and CR-CCSD(T) energies. The resulting CR-CC(2,3)+Q energies are calculated as CR-CC(2,3) + [CR-CCSD(TQ) – CR-CCSD(T)]. (See ref 57.)

The CR-CCSD(T)/accTZ+Q(DZ) energy is defined as a sum of the CR-CCSD(T)/accTZ energy and the difference of the CR-CCSD(TQ) and CR-CCSD(T) energies with the accDZ basis. Finally, we define the CR-CC(2,3)/accTZ+Q(DZ) energy as a sum of the CR-CC(2,3)/accTZ energy and the same difference.

2.5. Multilevel Methods and Density Functional Theory. We examine the MCG3-MPW,⁷³ BMC-CCSD,⁷¹ MCG3/3,⁷⁰ SAC-CCSD(T)/pTZ,⁶⁷ and MCSAC-CCSD(T)/pTZ⁶⁷ methods from our own group as well as methods from Petersson, Pople, Curtiss, and Raghavachari and their coworkers. We also consider Kohn-Sham (KS) calculations with 48 density functionals, both local and hybrid.

2.6. Multireference Theory. The multireference calculations are carried out using the correlated participating orbitals (CPO) scheme, which is based on two principles: (i) to correlate the orbitals in the active space properly, there is one correlating orbital for every doubly occupied orbital in the active space, and (ii) only the orbitals that participate most strongly in bond breaking and bond forming are included in the active space. In the *nom*-CPO scheme, which is used in the present article, the participating orbitals are those that describe bonds that break or form during the reaction; the *nom*-CPO active space for the two reactions considered here consists of four electrons in four orbitals (denoted (4/4)). In the product regions of the potential energy surfaces, these orbitals correspond to the bonding and antibonding orbitals (σ , σ^*) of the two C–O bonds, whereas in the reactant regions of the potential energy surfaces, they correspond to the π and π^* orbitals describing the CC bonds of the ethyne and ethene molecules and to the HOMO and LUMO of ozone.

2.7. Software. DFT calculations were performed with a locally modified *Gaussian03* program.^{143,144} Multilevel calculations were performed with the MLGAUSS program.¹⁴⁵ MRMP2 calculations were performed using the GAMESS package.^{146,147} All of the CR-CC calculations were performed with the computer codes described in refs 48, 51, 52, 55, and 56 that form part of the GAMESS package.^{146,147} Conventional CC

TABLE 1: Convergence of Single-Reference Methods

method	O ₃ + C ₂ H ₂			O ₃ + C ₂ H ₄		
	vdW	TS	adduct	vdW	TS	adduct
CCSDT/ccDZ ^a	-1.56	9.34	-61.19	-2.15	5.13	-52.96
CCSDT(2) _Q /ccDZ ^a	-1.54	9.30	-59.77	-2.20	5.00	-51.38
CCSDT(Q)/ccDZ ^b	-1.51	9.14	-58.90	n.a. ^c	n.a. ^c	n.a. ^c
QCISD(T)/ccTZ ^a	-1.95	8.27	-63.50	-2.30	3.88	-56.80
CCSD(T)/ccTZ ^a	-1.99	8.03	-64.06	-2.30	3.62	-57.33
CCSD/accDZ ^a	-1.75	7.90	-70.69	-2.21	3.28	-64.90
CCSD(T)/accDZ ^a	-1.82	5.47	-63.74	-2.74	0.78	-56.86
CCSDT/accDZ ^b	-1.70	6.36	-63.86	-2.58	1.59	-56.99
CCSD(TQ)/accDZ ^b	-1.78	5.99	-62.98	-2.72	1.14	-56.12
CCSD/accTZ ^d	-2.02	9.34	-72.04	-1.91	4.58	-67.16
CCSD(T)/accTZ ^d	-2.06	6.61	-64.33	-2.43	1.85	-58.29
CCSD(T)/accTZ+Q(DZ) ^a	-2.02	7.12	-63.57	-2.41	2.21	-57.54
CCSD(T)/accQZ ^b	-1.98	6.94	-64.50	-2.20	2.39	-58.04
CCSDT/CBS ^e	-1.83	7.89	-65.20	-1.86	3.61	-58.60
CCSDT/CBS+CAR ^e	-1.90	7.94	-65.33	-1.89	3.63	-58.73
best estimate ^f	-1.90	7.74	-63.80	-1.94	3.37	-57.15
ε ₁ ^g	0.10	0.28	1.09	0.04	0.24	1.16
ε ₂ ^g	0.06	0.44	0.06	0.08	0.41	0.06
ε ₃ ^g	0.08	0.33	0.17	0.23	0.54	0.25
ε ^g	0.14	0.62	1.10	0.25	0.72	1.19

^a Present; see text. ^b Ref 2. ^c Not available. ^d Ref 2 and repeated in the present work as a check. ^e CBS limit of CCSDT estimated by focal point analysis in ref 2 plus corrections for core correlation (C), adiabatic Born–Oppenheimer terms (A), and relativistic effects (R). ^f Table 2. ^g See Section 3.1.

TABLE 2: Benchmark Results

method	O ₃ + C ₂ H ₂			O ₃ + C ₂ H ₄		
	vdW	TS	adduct	vdW	TS	adduct
Wheeler et al. ^a	-1.85	7.74	-63.04	-1.84	3.43	-56.43
CBS CCSDT+(2) _Q ^b	-1.88	7.90	-63.91	-1.94	3.50	-57.15
CBS CCSD(T)+Q ^c	-1.98	7.58	-64.46	-2.03	3.18	-57.86
average = best estimate	-1.90	7.74	-63.80	-1.94	3.37	-57.15
standard deviation σ	0.07	0.16	0.72	0.09	0.17	0.71
2σ	0.14	0.33	1.43	0.19	0.34	1.42

^a From ref 2, calculated as CCSDT/CBS+CAR plus a correction for quadruple excitations estimated at the ccDZ basis for C₂H₂ and assumed to be the same as C₂H₄. ^b CBS CCSDT/CBS+CAR from ref 2 plus the quadruple excitation contributions calculated in the present work at the CCSDT(2)_Q/ccDZ level for both C₂H₂ and C₂H₄. ^c CBS CCSD(T)/CBS+CAR from ref 2 plus the quadruple excitation contributions calculated in the present work at the CCSD(TQ)/accDZ level for both C₂H₂ and C₂H₄.

calculations have been carried out with the *MOLPRO* program.¹⁴⁸ CCSDT(2)_Q calculations were carried out with NWChem.¹⁴⁹

3. Results

All energetic quantities in tables are in kcal/mol.

3.1. Completely Renormalized Methods. When the CR-CC methods differ significantly from conventional CC methods, it usually signals a breakdown of the conventional ones. Therefore, in addition to providing a method for improving conventional CC in some cases where it breaks down, CR-CC also serves as a diagnostic in that it gives us more confidence in conventional CC when CR-CC does not differ significantly. In the present case, anticipating results that are discussed in more detail below, we found that CR-CC does not differ significantly from conventional CC; therefore, we will not disqualify conventional CC from consideration in making best estimates. More detailed consideration of the CR-CC and conventional CC results will be delayed until after these best estimates are presented.

3.2. Best Estimates. Table 1 shows the three highest single-level calculations of ref 2, namely, CCSD(T)/accQZ, CCSDT/accDZ, and (available only for the C₂H₂ reaction) CCSDT(Q)/ccDZ. Table 1 also shows several other single-level calculations that are useful for estimating convergence trends and for

obtaining a better estimate of the CCI limit. The top row of Table 2 shows the best estimate of Wheeler et al.,² and the next two rows of Table 2 show two estimates of the CCI limit based on the present calculations. The estimates in the first two rows start with the CCSDT/CBS + CAR result (Table 1) of Wheeler et al., but then they estimate the effect of quadruple excitations differently. Wheeler et al. estimated the quadruples correction as CCSDT(Q) – CCSDT with the ccDZ basis for C₂H₂ with the correction assumed to be the same for C₂H₄. Rows 2 and 3 are each based on separate calculations for C₂H₂ and C₂H₄ rather than assuming that the corrections for C₂H₄ are the same as those for C₂H₂. Row 2 estimates the quadruples correlation as CCSDT(2)_Q – CCSDT with the ccDZ basis set, and row 3 estimates it as CCSD(TQ) – CCSD(T) with the accDZ basis. Therefore, in addition to having an independent estimate for C₂H₄, row 2 treats quadruples at a higher level, and row 3 estimates the triples correction with a more complete basis. Table 2 shows that the three estimations are similar for the van der Waals association and the barrier height, but the new estimates lead to very significant differences for the adduct. We will take the average of rows 1–3 to be the best estimates for the rest of this article, and will take 2σ to be our first estimate of the uncertainty in the best estimate where σ is the standard deviation of the three rows. Note that the errors are not random,

and the three calculations are not a statistical sample. The standard deviation of the three rows should not be misinterpreted as a statistically meaningful quantity; it is just a straightforward way to summarize the differences between the three best estimates. It is a rough lower bound on the uncertainty due to incomplete convergence of the correlation treatment. The average of the six 2σ values is $\langle 2\sigma \rangle = 0.64$ kcal/mol. Because this is not a reliable error estimate, the next paragraph considers an alternative way to estimate uncertainty. The method in the next paragraph is subjective and based on experience, but, in the absence of a converged result, that is probably the best way to estimate the uncertainty.

Another way to estimate the uncertainty in the best estimate is

$$\varepsilon = \sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2} \quad (1)$$

where ε_1 is the average of the magnitude of the difference between CCSDT(2)_Q and CCSDT with the ccDZ basis and the magnitude of the difference between CCSD(TQ) and CCSD(T) with accDZ basis, ε_2 is half of the magnitude of the difference between CCSDT and CCSD(T) with the accDZ basis set, and ε_3 is the magnitude of the difference between using the accQZ and accTZ basis sets at the CCSD(T) level. These estimated uncertainties are given in the last four rows of Table 1. It turns out that they are dominated by the basis set for the vdW complex and the barrier and by the quadruple excitation effect for the reaction energy. The average of the six uncertainties is $\langle \varepsilon \rangle = 0.67$ kcal/mol. Because $\langle \varepsilon \rangle$ is larger than $\langle 2\sigma \rangle$, we will use $\langle \varepsilon \rangle$ as a rough estimate of the reliability of the best estimates.

Because the three calculations used to estimate uncertainties are quite similar, the actual error could be larger than these estimates.

3.3. Single-Reference Single-Level Wave Function Theory.

On the basis of the best estimates in Table 2, we calculated the mean unsigned error, MUE (also called mean absolute deviation), for several single-level single-reference wave function methods, and these mean errors are given in Table 3. All of the errors in Tables 3–13 of this article are averages over six values, namely, the mean unsigned deviations from the best estimates for vdW, TS, and product for C₂H₂ and C₂H₄. In all tables containing errors, the errors are in the last column, and the methods are listed in order of increasing error. In this article, on the basis of the error analysis of the previous sections, any method with an MUE of 0.7 kcal/mol or less will be assumed to agree with the best estimates within their reliability.

Table 3 shows six methods for which the MUE is 0.7 kcal/mol or less. In light of the inadequacy of unaugmented basis sets (Table 1) and the importance of quadruple excitations, the exceptionally good results for the first three entries in Table 3 must arise from a fortuitous cancellation of errors. A popular state-of-the-art calculation would be CCSD(T)/accTZ, with an MUE of 0.8 kcal/mol, which is only slightly larger than the value, 0.64 kcal/mol, of the MUE for this method on DBH24, a diverse barrier height database for reactions with small-to-moderate multireference character. It is interesting that all twelve calculations that include, in any way, connected triple excitations (or higher) have an MUE in the range of 0.2 to 2.4 kcal/mol, whereas calculations limited to connected double excitations have MUEs of 2.6–6.0 kcal/mol, and Hartree–Fock theory without correlation corrections has an error of 13.9 to 14.1 kcal/mol.

In reporting the CR-CC(2,3) results and their augmented CR-CC(2,3)+Q counterparts, we distinguish between variants A–D

TABLE 3: Mean Unsigned Errors (kcal/mol) for Single-Level Single-Reference Wave Function Methods

method	MUE
QCISD(T)/6-31G(d) ^a	0.2
CCSD(T)/ccTZ ^b	0.2
QCISD(T)/ccTZ ^a	0.4
CCSD(T)/accTZ+Q(DZ) ^a	0.5
CCSD(T)/accQZ ^b	0.6
CCSDT/accDZ ^b	0.7
CCSD(T)/accTZ ^{a,b}	0.8
CCSD(T)/accDZ ^a	1.0
CCSD(TQ)/accDZ ^a	1.1
CCSDT/ccDZ ^a	1.8
CCSDT(2) _Q /ccDZ ^a	2.3
MP4/6-31G(d) ^a	2.4
CCSD/accDZ ^a	2.6
QCISD/ccTZ ^a	3.1
CCSD/accTZ ^a	3.5
CCSD/ccTZ ^a	3.7
MP2/6-31G(d) ^a	4.9
MP3/ccTZ ^a	5.1
MP2/ccTZ ^a	5.5
MP3/6-31G(d) ^a	5.6
MP2/6-31G(2df,p) ^a	5.9
MP2(full)/G3Large ^a	5.9
MP2/MG3S ^a	6.0
MP3/6-31G(2df,p) ^a	6.2
HF/MG3S ^a	13.9
HF/G3Large ^a	13.9
HF/6-31G(d) ^a	14.0
HF/ccTZ ^a	14.1

^a Present results. ^b Ref 2, calculated.

of CR-CC(2,3), which we designate as CR-CC(2,3),A–D. This is associated with the fact that the CR-CC(2,3) triples correction is defined, in particular, through the diagonal matrix elements $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$, which enter the relevant perturbative energy denominator. Here $\bar{H}^{\text{CCSD}} = e^{-T_1-T_2} \text{He}^{T_1+T_2}$ is the similarity-transformed Hamiltonian of CCSD, with T_1 and T_2 representing the CCSD singly and doubly excited cluster operators, and $|\Phi_{ijk}^{abc}\rangle$ represents the triply excited determinants. The CR-CC(2,3) method in which no terms in $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$ are neglected is referred to as CR-CC(2,3),D. By retaining only one- and two-body contributions to $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$, we obtain the CR-CC(2,3),C approach. By retaining only the one-body contributions to $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$, we obtain CR-CC(2,3),B, and by replacing the one-body terms in $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$ by the usual orbital energy differences for triples, that is, $(\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k)$, while neglecting other many-body terms in $\langle \Phi_{ijk}^{abc} | \bar{H}^{\text{CCSD}} | \Phi_{ijk}^{abc} \rangle$, we obtain the CR-CC(2,3),A method. As explained in ref 58, variants A and B of the CR-CC(2,3) approach are closely related to the triples parts of the CCSD(2) corrections developed by Hirata et al.^{47,140} (variant A) and Head-Gordon et al.^{141–144} (variant B). In particular, the CR-CC(2,3),A method is equivalent to the CCSD(2)_T approach of refs 47 and 150 when the canonical Hartree–Fock orbitals are employed. The CR-CC(2,3),B approach is equivalent, up to small details, to the triples correction of the CCSD(2) method of refs 151–154. Table 4 presents the CR-CC results for the accDZ basis set. With this double- ζ basis set, CR-CC(2,3),C and CR-CC(2,3),D have smaller errors than the CCSD(T)/accDZ error of 1.0 kcal/mol in Table 3. Furthermore, CR-CC(2,3),C+Q and CR-CC(2,3),D+Q outperform CCSD(TQ). Table 5 shows CR-CC calculations with the larger accTZ basis set. The smallest error is now 0.9 kcal/mol, which indicates that the values smaller

TABLE 4: Energetics (kcal/mol) by CR-CC Methods with the accDZ Basis Set

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ cycloadduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ cycloadduct	MUE
CR-CC(2,3),D	-0.72	7.11	-63.12	-1.56	2.79	-56.54	0.7
CR-CC(2,3),C	-0.68	7.30	-62.83	-1.52	2.98	-56.26	0.7
CR-CC(2,3),D+Q	-0.72	7.14	-62.20	-1.60	2.78	-55.59	1.0
CR-CC(2,3),C+Q	-0.67	7.34	-61.92	-1.55	2.97	-55.31	1.0
CR-CC(2,3),A+Q	-1.83	5.87	-64.69	-2.68	1.15	-58.08	1.1
CR-CC(2,3),B+Q	-1.85	5.98	-65.64	-2.68	1.26	-59.12	1.4
CR-CC(2,3),A	-1.83	5.84	-65.60	-2.64	1.16	-59.04	1.4
CR-CCSD(TQ)	-1.86	6.53	-66.27	-2.59	1.71	-59.82	1.5
CR-CC(2,3),B	-1.86	5.94	-66.56	-2.64	1.27	-60.07	1.7
CR-CCSD(T)	-1.87	6.49	-67.19	-2.56	1.72	-60.77	1.8

TABLE 5: Energetics (kcal/mol) by CR-CC Methods with the accTZ Basis Set

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ cycloadduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ cycloadduct	MUE
CR-CC(2,3),D	-0.52	8.78	-63.78	-0.51	4.36	-57.86	0.9
CR-CC(2,3),A+Q(DZ)	-2.06	7.20	-65.26	-2.36	2.38	-59.51	1.0
CR-CC(2,3),C	-0.48	8.95	-63.54	-0.46	4.53	-57.62	1.0
CR-CC(2,3),D+Q(DZ)	-0.51	8.81	-62.87	-0.55	4.36	-56.90	1.0
CR-CC(2,3),C+Q(DZ)	-0.47	8.98	-62.63	-0.50	4.52	-56.66	1.2
CR-CC(2,3),A	-2.06	7.17	-66.18	-2.32	2.39	-60.46	1.3
CR-CC(2,3),B+Q(DZ)	-2.10	7.32	-66.25	-2.40	2.51	-60.60	1.3
CR-CCSD(T)+Q(DZ)	-2.13	7.85	-67.36	-2.30	2.90	-61.79	1.6
CR-CC(2,3),B	-2.11	7.29	-67.16	-2.37	2.52	-61.55	1.6
CR-CCSD(T)	-2.14	7.81	-68.28	-2.26	2.91	-62.75	1.9

TABLE 6: Energetics (kcal/mol) by Multilevel Methods

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ adduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ adduct	MUE
MCG3-MPW	-1.81	7.28	-64.72	-1.97	3.54	-57.53	0.3
G3X(MP3)	-1.90	8.47	-61.80	-2.19	4.11	-55.05	1.0
G3SX(MP3)	-2.03	7.73	-61.10	-2.39	3.27	-54.26	1.0
BMC-CCSD	-2.16	6.53	-61.44	-2.50	1.44	-56.29	1.2
MCG3/3	-1.85	7.39	-60.36	-2.26	3.18	-53.21	1.4
SAC-CCSD(T)/ccTZ	-2.06	6.55	-60.68	-2.63	2.22	-53.61	1.6
MCSAC-CCSD(T)/ccTZ	-2.13	5.55	-57.36	-2.84	0.97	-50.13	3.2

TABLE 7: Mean Unsigned Errors (kcal/mol) for Multilevel Methods^a

method	MUE
MCG3-MPW	0.3
G4 ^b	0.9
G3X(MP3)	1.0
G3SX(MP3)	1.0
G4(MP2) ^b	1.2
BMC-CCSD	1.2
G3//B3LYP ^b	1.3
G4(MP3) ^b	1.4
MCG3/3	1.4
G3(MP2)//B3LYP ^b	1.5
CBS-APNO ^b	1.4
SAC-CCSD(T)/ccTZ	1.6
CBS-QB3 ^b	2.1
G3 ^b	2.6
MCSAC-CCSD(T)/ccTZ	3.2

^a Present calculations except where otherwise indicated. ^b Ref 2.

than this in Table 4 arise by cancellation of errors. Furthermore, the CR methods no longer outperform their quasiperturbative analogs.

3.4. Multilevel Methods. Table 6 shows our calculations for seven multilevel methods calculated here, and Table 7 shows MUEs for these methods and compares them with the MUEs for the eight multilevel methods calculated in ref 2. Table 7 shows that only one of the multilevel methods agrees with the best estimates to better than 0.7 kcal/mol, and six agree within

1.2 kcal/mol. Of these, BMC-CCSD and G3SX(MP3), which have similar costs and are less expensive than most of the methods in Table 7, were singled out as being particularly cost efficient in a recently published review⁷⁴ that considered mainly single-reference test data (that is, test data corresponding to systems with small-to-moderate multireference character). As far as the issues mentioned in the introduction are concerned, Table 7 shows no tendency for scaling methods to outperform additive ones, and MCSAC is surprisingly much less accurate than SAC. The poor performance of MCSAC is consistent with our experience^{64,67,70} that a multilevel method provides the most significant benefits when it includes two or more basis sets. (MCSAC methods involve only one basis set.)

3.5. Density Functional Theory. Table 8 gives results for 48 density functionals^{21,72,79–81,84–119} plus Hartree–Fock¹²¹ (HF) and Møller–Plesset second-order perturbation theory¹²² (MP2). The *X* column gives the percentage of Hartree–Fock exchange, and the “ref” column gives the reference or references for the density functional. The most obvious general trend in the table is that methods with high *X* perform poorly for these multireference reactions. For example, 11 of the 13 worst performing density functionals have *X* ≥ 42, whereas the 34 best performing density functionals have *X* ≤ 31. This is not unexpected on the basis of previous²¹ work, which indicates that low-*X* functionals are more robust for systems with multireference character.

None of the density functionals meet the criterion of MUE ≤ 0.7 kcal/mol that distinguished the best performing wave

TABLE 8: Energetics (kcal/mol) by DFT^a

	X	ref	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ cycloadduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ cycloadduct	MUE
best estimate			-1.90	7.74	-63.80	-1.94	3.37	-57.15	
M05	28	89	-2.98	5.82	-62.69	-2.79	0.73	-57.71	1.4
B3LYP	20	85–88	-1.30	3.14	-66.15	-1.40	-0.73	-56.85	2.1
B97-2	21	90	-1.22	4.51	-67.75	-1.08	0.84	-58.62	2.1
B97-3	26.93	91	-1.42	5.69	-69.15	-1.22	1.86	-60.27	2.2
B1LYP	25	85, 86, 92	-1.27	4.08	-67.49	-1.22	0.08	-58.59	2.2
B3LYP*	15	85, 86, 93	-1.45	1.77	-65.08	-1.72	-1.94	-55.41	2.5
TPSS1KCIS	13	72, 94, 95	-1.53	1.53	-67.02	-1.71	-2.15	-57.41	2.6
X3LYP	21.8	86, 96	-1.80	2.41	-68.06	-1.86	-1.47	-58.94	2.7
O3LYP	11.61	97, 98	0.11	7.78	-59.44	0.06	4.35	-49.40	2.9
MPW3LYP	20	86, 99, 100	-2.17	1.76	-67.70	-2.29	-2.12	-58.48	2.9
τ-HCTHh	15	101	-1.78	0.41	-68.37	-2.00	-3.08	-58.87	3.4
B98	21.98	102	-1.93	2.24	-70.20	-1.98	-1.40	-61.10	3.4
TPSSh	10	103	-1.43	0.20	-68.33	-1.71	-3.40	-58.65	3.5
B97-1	21	104	-2.21	1.86	-69.79	-2.32	-1.78	-60.63	3.5
TPSS	0	95	-1.30	-0.81	-63.63	-1.94	-4.30	-53.19	3.5
M06-L	0	84	-3.17	0.88	-61.89	-3.54	-4.07	-53.87	3.7
B1B95	28	85, 105	-1.51	3.35	-71.97	-1.19	-0.16	-63.35	3.9
TPSSKCIS	0	94, 95	-1.36	0.22	-60.91	-2.02	-3.32	-50.31	4.1
τ-HCTH	0	98	-1.37	1.81	-59.33	-1.82	-1.50	-48.71	4.1
PBE	0	106	-1.98	-1.32	-61.99	-2.71	-4.40	-51.18	4.2
mPWPW91 ^b	0	99, 107	-1.24	-0.27	-60.88	-1.94	-3.39	-50.01	4.2
PW6B95	28	108	-2.63	2.23	-72.32	-2.36	-1.49	-63.80	4.4
BP86	0	85, 109	-0.69	-0.35	-60.49	-1.45	-3.43	-49.66	4.6
MPWLYP1M	5	81, 86, 99	-1.80	0.94	-58.66	-2.50	-2.78	-48.33	4.6
M06	27	79, 80	-3.18	1.82	-69.56	-3.19	-3.31	-64.68	4.7
HCTH	0	104	-1.54	6.96	-52.33	-1.88	3.36	-41.46	4.7
MPWB95	0	92, 105	-1.86	-0.48	-59.16	-2.53	-3.61	-48.44	4.9
mPW1PW91 ^c	25	99	-1.68	1.88	-73.77	-1.49	-1.60	-64.85	4.9
BB95	0	85, 105	-0.65	1.43	-57.00	-1.29	-1.67	-46.15	5.2
MPW1B95	31	99, 100, 105	-2.45	2.22	-75.12	-2.06	-1.34	-66.79	5.3
PBEh ^d	25	110, 111	-2.23	1.06	-74.66	-2.07	-2.36	-65.77	5.4
MPWLYP	0	86, 99	-1.74	0.51	-56.12	-2.64	-3.14	-45.41	5.7
BLYP	0	85, 86	-0.55	2.40	-53.97	-1.41	-1.23	-43.15	5.9
OLYP	0	97	0.79	8.48	-51.88	0.38	5.26	-40.90	6.0
MP2 ^e	100	122	-3.11	3.16	-51.68	-3.66	-3.85	-47.93	6.0
BMK	42	112	-1.75	3.71	-78.12	-1.43	-0.20	-70.82	6.0
G96LYP	0	86, 113	1.55	4.63	-53.24	0.81	1.22	-42.21	6.2
BB1K	42	85, 105, 114	-2.03	4.30	-79.71	-1.30	0.62	-72.16	6.3
BHandHLYP	50	85, 86, 115	-2.21	5.76	-81.50	-1.39	1.47	-74.43	6.6
VSXC ^f	0	116	-7.42	-0.09	-56.70	-7.89	-4.71	-47.42	7.4
MPWB1K	44	99, 100, 105	-2.79	3.35	-82.04	-2.01	-0.35	-74.69	7.5
M06-2X	54	79, 80	-3.68	2.70	-79.65	-3.23	-0.90	-74.62	7.6
MPW1K	42.8	117	-2.13	3.39	-83.26	-1.39	-0.29	-75.69	7.8
PWB6K	46	108	-3.36	3.32	-82.79	-2.55	-0.55	-75.61	8.0
M05-2X	56	21	-3.35	1.57	-81.07	-2.88	-1.94	-75.13	8.2
M06-HF	100	118	-3.88	0.66	-95.89	-2.96	-1.30	-91.93	13.6
HF ^e	100	121	-1.23	20.22	-90.40	0.56	15.07	-86.45	13.9
BHandH	50	85, 115	-5.30	-4.83	-98.03	-4.48	-8.25	-91.07	16.4
HFLYP	100	86, 119	-4.31	9.58	-110.15	-2.22	4.90	-106.30	16.9
MOHLYP	0	81	4.56	21.82	-29.91	3.99	17.88	-18.86	18.9

^a 6-311+G(2df,2p) basis set was employed with the CCSD(T)/cc-pVTZ geometries taken from Wheeler et al. ^b Originally called mPWPW. ^c Originally called mPW1PW and mPW0. Also called MPW25. ^d Originally called PBE0. Also called PBE1PBE. ^e Not density functional theory, but included for perspective. ^f Also called VS98.

function methods, but one functional, M05, has distinctly better performance than any other and has MUE = 1.4 kcal/mol. Somewhat surprisingly, the “old” but extremely popular B3LYP functional has the second best performance with MUE = 2.1 kcal/mol. The best local functionals are TPSS and M06-L, which have MUEs of 3.5 and 3.7 kcal/mol. Three functionals (BHandHLYP, HFLYP, and MOHLYP) have worse performance than the Hartree–Fock method. The hope that the static correlation inherent in density functional exchange would make DFT a preferred one for multireference systems is not borne out in the present case, except perhaps for M05.

The success of M05 is not particularly surprising because when it was first announced, it was noted⁸⁹ that it had a uniquely

broad ability to predict reasonably accurate barrier heights while remaining valid for transition-metal systems, which are notoriously multireference in their character. However, the poor performance of the next-generation M06 is disappointing.

3.6. Effect of Geometries. To test the usefulness of the M05 and B3LYP functionals further, Table 9 gives results with other basis sets and geometries. In fact, two of the three variations considered for M05 lower the MUE below 1.0 kcal/mol, whereas B3LYP does not improve below 1.9 kcal/mol.

Table 10 shows the effect of repeating some of the WFT results at M05/MG3S geometries. There is no systematic effect of changing the geometry; the MUE sometimes increases and sometimes decreases. Usually, the effect of geometry on the

TABLE 9: Comparison of B3LYP Results to M05 Results for Different Basis Sets and Geometries^{a,b}

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ adduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ adduct	MUE
M05/accTZ//CC	-2.35	7.29	-62.47	-2.10	2.23	-57.26	0.6
M05/accTZ//M05/MG3S	-1.58	7.78	-61.05	-1.55	2.74	-55.66	0.9
M05/MG3S//opt	-2.23	6.86	-61.70	-2.49	1.85	-56.56	1.0
M05/MG3S//CC	-2.98	5.82	-62.69	-2.79	0.73	-57.71	1.4
B3LYP/accTZ//B3LYP/MG3S	-0.72	4.11	-65.96	-1.14	0.25	-56.51	1.9
B3LYP/MG3S//opt	-1.60	3.26	-66.13	-2.08	-0.66	-56.87	1.9
B3LYP/MG3S//CC	-1.30	3.14	-66.15	-1.40	-0.73	-56.85	2.1
B3LYP/accTZ//CC	-1.04	3.31	-66.57	-1.11	-0.49	-57.08	2.1

^a Energies are in kcal/mol. MG3S denotes the 6-311+G(2df,2p) basis set, and CC denotes CCSD(T)/ccTZ geometries. ^b //opt denotes a consistently optimized geometry. This is usually denoted by the absence of //, but it is explicitly indicated in this article because the convention in this article is //CC except where otherwise indicated. (The only calculations that are not //CC are those indicated otherwise in this table and in the next table.)

TABLE 10: Energetics (kcal/mol) for Single-Reference, Single-Level WFT at the M05/MG3S Geometries

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ cycloadduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ cycloadduct	MUE
CR-CC(2,3),D/accTZ+Q(DZ)	-0.62	8.02	-63.29	-0.74	3.46	-57.52	0.6
CR-CC(2,3),C/accTZ+Q(DZ)	-0.59	8.14	-63.11	-0.70	3.58	-57.34	0.7
CR-CC(2,3),C/accTZ	-0.56	8.21	-63.88	-0.64	3.68	-58.13	0.8
CR-CC(2,3),D/accTZ	-0.58	8.08	-64.06	-0.68	3.55	-58.31	0.8
CR-CC(2,3),D/accDZ	-1.11	6.09	-63.46	-1.87	1.44	-57.10	0.8
CR-CC(2,3),C/accDZ	-1.08	6.24	-63.25	-1.84	1.58	-56.90	0.8
CCSD(T)/accTZ + Q(DZ)	-2.24	6.27	-64.19	-2.68	1.23	-58.28	1.0
CR-CC(2,3),D+Q/accDZ	-1.15	6.03	-62.69	-1.93	1.34	-56.31	1.1
CR-CC(2,3),C+Q/accDZ	-1.12	6.17	-62.48	-1.90	1.48	-56.11	1.1
CCSD(T)/accTZ	-2.26	5.82	-64.90	-2.69	0.90	-58.97	1.4
CR-CC(2,3),A/accTZ+Q(DZ)	-2.18	6.53	-65.58	-2.57	1.54	-59.91	1.4
CCSD(TQ)/accDZ	-2.48	4.73	-63.50	-3.17	-0.21	-56.89	1.5
CR-CC(2,3),A/accTZ	-2.14	6.60	-66.35	-2.51	1.64	-60.70	1.6
CR-CC(2,3),B/accTZ+Q(DZ)	-2.18	6.72	-66.39	-2.58	1.73	-60.79	1.6
CCSD(T)/accDZ	-2.50	4.29	-64.21	-3.18	-0.54	-57.58	1.7
CR-CCSD(T)/accTZ+Q(DZ)	-2.10	7.31	-67.30	-2.44	2.24	-61.78	1.7
CR-CC(2,3),A+Q/accDZ	-2.43	4.82	-64.91	-3.07	-0.06	-58.52	1.8
CR-CC(2,3),B/accTZ	-2.14	6.79	-67.16	-2.52	1.82	-61.58	1.9
CR-CCSD(TQ)/accDZ	-2.34	5.58	-66.17	-2.93	0.65	-59.91	1.9
CR-CCSD(T)/accTZ	-2.07	7.37	-68.07	-2.38	2.34	-62.57	2.0
CR-CC(2,3),B+Q/accDZ	-2.42	4.98	-65.67	-3.04	0.11	-59.35	2.0
CR-CC(2,3),A/accDZ	-2.39	4.88	-65.68	-3.01	0.04	-59.32	2.0
CR-CCSD(T)/accDZ	-2.31	5.64	-66.94	-2.87	0.75	-60.70	2.1
CR-CC(2,3),B/accDZ	-2.39	5.04	-66.44	-2.98	0.21	-60.14	2.2
CCSD/accDZ	-2.00	7.47	-69.90	-2.38	2.69	-64.22	2.4
CCSD/accTZ	-1.76	9.34	-71.27	-1.89	4.41	-66.36	3.3

TABLE 11: Multireference Diagnostics

process or system ^a	O ₃ + C ₂ H ₂				O ₃ + C ₂ H ₄			
	GB1 ^b	ROD ^c	%TAE[(T)] ^c	M ^b	GB1 ^b	ROD ^c	%TAE[(T)] ^c	M ^b
ozone	^d	^d	18.4	0.43 ^e	^d	^d	18.4	0.43 ^e
C ₂ H ₄ ^f	^d	^d	2.0	0.06 ^g	^d	^d	1.2	0.09 ^g
vdW	0.7	0.0	6.1	0.41	0.2	0.1	4.6	0.42
TS	1.7	0.1	6.7	0.32	1.3	0.1	4.9	0.35
adduct	13.5	0.3	4.2	0.02	15.4	0.4	3.0	0.02

^a Process for GB1 and ROD; system for M and %TAE[(T)]. ^b Computed with the MG3S basis set. ^c Computed with the cc-pVTZ basis set. ^d Not a process. ^e From HOMO and LUMO of reactants separated by 50 Å. ^f *n* = 2 or 4. ^g From HOMO-1 and LUMO+1 of reactants separated by 50 Å.

MUE is ≤ 0.5 kcal/mol, but in a few cases, it is slightly larger. Because our estimated mean uncertainty in the best estimates is 0.7 kcal/mol, the results in Table 10 confirm that our general conclusions are not affected by the choice of geometry, as long as we do not interpret the results more finely than 0.7 kcal/mol.

3.7. Multireference Diagnostics. Next, we attempt to assess the multireference character of the various stationary points more quantitatively. In three recent studies, we proposed multireference diagnostics, which we call the B1 diagnostic,²¹ the ROD

diagnostic,¹⁸ and the M diagnostic.²² We will take these to be a starting point for the present analysis and also consider the %TAE[T] diagnostic of Karton et al.¹³⁷

The B1 diagnostic was originally²¹ only defined for bond energies. Therefore, we introduce here a generalization called the generalized B1 (GB1) diagnostic. The GB1 diagnostic, for any quantity with units of energy, is simply the absolute value of the difference between the quantity calculated with the BLYP density functional and the same quantity calculated with the B1LYP density functional. We apply this to the six single-point

TABLE 12: Energetics (kcal/mol) for CCSD(T)(KS)^a

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ cycloadduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ cycloadduct	MUE
CCSD(T)(KS)/accDZ//CCSD(T)/ccTZ	−1.83	5.57	−63.46	−2.83	0.87	−56.45	1.1
CCSD(T)(KS)/accDZ//M05/MG3S	−2.51	4.30	−64.08	−3.26	−0.51	−57.32	1.6

^a CCSD(T) calculations with BLYP geometries.**TABLE 13: Energetics (kcal/mol) by MRMP2/*nom*-CPO^a**

method	O ₃ + C ₂ H ₂ vdW	O ₃ + C ₂ H ₂ TS	O ₃ + C ₂ H ₂ cycloadduct	O ₃ + C ₂ H ₄ vdW	O ₃ + C ₂ H ₄ TS	O ₃ + C ₂ H ₄ cycloadduct	MUE
MRMP2/ <i>nom</i> -CPO/accTZ	−2.16	8.77	−48.19	−2.09	3.43	−43.32	5.2
MRMP2/ <i>nom</i> -CPO/MG3S	−2.21	9.91	−46.79	−2.07	4.66	−41.75	6.1

^a All calculations at CCSD(T)/ccTZ geometries.

relative energies we have been discussing, where “single-point energy” is the usual language for “fixed-geometry electronic energy (including nuclear repulsion)” or “clamped-nuclei Born–Oppenheimer energy.” As a rough guide to multireference character, we previously²¹ established a guideline that 10 kcal/mol is the boundary of severe multireference character.

The reference-orbital diagnostic (ROD)¹⁸ is defined as the absolute value of the difference between the quantity calculated with CCSD(T) with the BLYP density functional orbitals and the same quantity calculated with CCSD(T) with the Hartree–Fock orbitals. We used CCSD(T)/ccTZ geometries for ROD. In the rest of this article, CCSD(T) calculations with KS orbitals are denoted CCSD(T) (KS). Furthermore, the density functional used to generate KS orbitals is always BLYP in this article.

The %TAE[(T)] diagnostic was proposed by Karton et al.¹³⁷ it is defined as the percentage of the CCSD(T) total atomization energy (AE) that comes from the (T) correction, that is

$$\%TAE[(T)] = \frac{|AE[CCSD(T)] - AE[CCSD]|}{AE[CCSD(T)]} \quad (2)$$

Karton et al.¹³³ suggest the following interpretation of %TAE[(T)]: <2%: system dominated by dynamical correlation; 2–10%: mild-to-moderate nondynamical correlation; >10%: severe, nondynamical correlation. We used the cc-pVTZ basis set for the %TAE[(T)] diagnostic.

The *M* diagnostic is computed from a multiconfiguration wave function;²² here we use the *nom*-CPO CASSCF wave function. For a system with an even number of electrons, the *M* diagnostic is

$$M = \left[1 - \frac{n(\text{MCDONO})}{2} \right] + \frac{n(\text{MCUNO})}{2} \quad (3)$$

where *n*(MCDONO) is the natural orbital occupancy of the most correlated doubly occupied natural orbital (i.e., the one whose occupation number differs most from 2), whereas *n*(MCUNO) is the largest natural orbital occupancy of an unoccupied natural orbital. We found that transition states with *M* > 0.04 show large multireference effects.²²

Table 11 shows the computed diagnostics. Consider first the *M* diagnostic. The *M* values for all species except the product show that they have large multireference character. The %TAE[(T)] diagnostics also show that the cycloadduct has less multireference character than the van der Waals complex or transition state. Interestingly, the GB1 diagnostics show that the errors due to multireference effects largely seem to cancel in producing the van der Waals complex or transition state but

not in the energy of reaction, and the ROD diagnostic gives the same trend as GB1. This analysis seems to explain why the energies of reaction are so difficult to compute for these two reactions.

Other diagnostics of multireference character have also been proposed, and of these, the *T*₁ diagnostic¹⁵⁵ is the most popular. However, we and others^{137,156} have found that it is not completely reliable.

3.8. CCSD(T) (KS) Energetics. We report the energetics for two sets of CCSD(T) (KS) calculations in Table 12. Comparing the results in Table 12 to those in Tables 1 and 10, we found that CCSD(T)(KS) gives similar results to the standard CCSD(T) theory.

3.9. Multireference Energy Calculations. Table 13 gives the results of the multireference energy calculations. Comparison with Table 2 shows that the MRMP2/*nom*-CPO/accTZ//CCSD(T)/ccTZ values for the forward barrier heights deviate from the best estimates by 0.8 kcal/mol on the average. However, the reverse barrier heights and, consequently, the reaction energies have significant errors. Further test calculations (not in the tables) indicate that using larger active spaces obtained by successive inclusion of the orbital pairs to the (4/4) active space up to the *mod*-CPO (14/14) active space does not necessarily improve the overall energetics.

3.10. Comprehensive Error Analysis. So far, we have averaged the errors over the three energy differences (vdW, TS, and adduct) from reactants (R). A more balanced treatment can be based on recognizing that with four stationary energies (R, vdW, TS, and adduct) there are six energy differences; therefore, one can compute the MUE over all six relative energies for each reaction. We do this for both reactions and average over all 12 unsigned errors; we call this the comprehensive mean unsigned error (CMUE), and it is shown in Table 14 for 162 different model chemistries. Table 14 includes, for completeness, four methods (PBEKICIS, mPWKICIS, mPWB95, and mPWB98) that are not included in earlier tables; these methods involve local density functionals created by combining PBE or mPW exchange functionals with KCIS, B95, or B98 correlation functionals. Because the errors in Table 14 are averaged over 12 values rather than 6, they are less likely to benefit from fortuitous cancellation of errors. Also shown in Table 14 are the comprehensive mean unsigned errors averaged over 6 energy differences that represent the subset of the 12 energy differences that do not contain the energies of the adducts. These errors are denoted CMUE(6), and they provide a test of how well the various methods describe the kinetically important entrance channels of the two reactions considered in this article. A separate consideration of CMUE and CMUE(6) will prove to be useful in analyzing the origins of the errors because the

TABLE 14: Comprehensive Mean Unsigned Errors (kcal/mol)^{a,b,c}

method	α	CMUE	CMUE(6)	method	α	CMUE	CMUE(6)
CCSD/accDZ	6	3.73	0.14	B97-3/MG3S	4	2.71	1.59
G3SX(MP3)	7	1.55	0.19	CR-CCSD(TQ)/accDZ//DFT	7	1.57	1.63
MCG3/3	7	2.04	0.24	CCSD(T)/accDZ	7	1.38	1.65
MCG3/3-MPW	7	0.43	0.25	MC-QCISD-MPW	6	3.44	1.67
CR-CCSD(T)/accTZ	7	2.57	0.26	OLYP/MG3S	3	7.24	1.67
CR-CCSD(TQ)/accTZ	7	2.11	0.27	G3(MP2)/B3LYP	7	2.07	1.72
QCISD(T)/6-31G(d)	7	0.29	0.31	MP3/6-31G(d)	6	7.44	1.73
CCSD/accDZ//DFT	6	3.32	0.32	CCSD/ccVTZ	6	5.59	1.82
CCSD(T)/ccTZ	7	0.31	0.33	CR-CC(2,3),B/accDZ//DFT	7	1.81	1.95
M05/accQZ//opt	4	1.34	0.37	CBS-APNO	7	1.62	1.97
HCTH/MG3S	3	7.02	0.40	CR-CC(2,3),B+Q/accDZ//DFT	7	1.71	2.00
CR-CC(2,3),B+Q/accTZ	7	1.53	0.42	HFLYP/MG3S	4	24.94	2.02
CR-CC(2,3),B/accTZ	7	2.00	0.43	CR-CC(2,3),A/accDZ//DFT	7	1.76	2.06
M05/accQZ	4	1.06	0.44	CR-CC(2,3),A+Q/accDZ//DFT	7	1.66	2.12
M05/accTZ//opt	4	1.27	0.45	CCSD(TQ)/accDZ//DFT	7	1.94	2.20
CR-CCSD(T)/accDZ//DFT	7	2.49	0.46	MP3/6-31G(2df,p)	6	7.43	2.24
QCISD(T)/ccTZ	7	0.42	0.48	BB1K/MG3S	4	8.39	2.28
MRMP2/nom-CPO/accTZ	5	7.55	0.50	CCSD(T)(KS)/accDZ//M05/MG3S	7	1.95	2.44
G4	7	1.25	0.52	B97-2/MG3S	4	2.40	2.44
CR-CC(2,3),A/accTZ	7	1.50	0.52	CCSD(T)/accDZ//DFT	7	1.92	2.45
CR-CCSD(TQ)/accDZ//DFT	7	2.10	0.52	MPWB1K/MG3S	4	9.54	2.70
M05/accTZ	4	0.77	0.53	BMK/MG3S	4	7.80	2.75
CCSD(T)/accQZ	7	0.52	0.54	B1LYP/MG3S	4	2.50	2.76
G3X(MP3)	7	1.21	0.57	B3LYP/AVaccQZ//opt	4	2.37	2.76
CR-CC(2,3),A+Q/accTZ	7	1.03	0.57	PWB6K/MG3S	4	9.89	2.78
CCSD(TQ)/accTZ	7	0.52	0.59	MPW1K/MG3S	4	10.29	2.85
G4(MP3)	7	1.32	0.63	B3LYP/accTZ//opt	4	2.42	2.91
MP3/ccTZ	6	7.04	0.74	B3LYP/MG3S//opt	4	2.48	2.94
SAC-CCSD(T)/ccTZ	7	2.32	0.78	B1B95/MG3S	4	4.54	3.02
M05/accTZ//M05/MG3S	4	1.34	0.80	CBS-QB3	7	2.57	3.08
CR-CC(2,3),C+Q/accDZ	7	1.27	0.80	M06-2X/MG3S	4	8.85	3.10
CR-CC(2,3),C/accDZ	7	0.85	0.82	B3LYP/accQZ	4	2.62	3.16
CR-CC(2,3),D/accTZ+Q(DZ)//DFT	7	0.74	0.83	MP2/6-31G(d)	5	6.97	3.22
CR-CC(2,3),D/accTZ+Q(DZ)	7	1.05	0.83	B3LYP/MG3S	4	2.68	3.28
CR-CC(2,3),B/accDZ//DFT	7	2.09	0.83	B3LYP/accTZ	4	2.73	3.32
CR-CC(2,3),D+Q/accDZ//DFT	7	0.74	0.83	MPW1B95/MG3S	4	6.04	3.41
CR-CC(2,3),C/accTZ+Q(DZ)//DFT	7	0.72	0.85	B98/MG3S	4	3.57	3.42
CR-CC(2,3),C+Q/accDZ//DFT	7	0.73	0.85	X3LYP/MG3S	4	3.09	3.45
CR-CC(2,3),D/accDZ//DFT	7	1.04	0.86	PW6B95/MG3S	4	4.56	3.46
G4(MP2)	7	1.60	0.88	MP2/ccVTZ	5	7.75	3.65
CCSD(T)/accTZ	7	0.75	0.88	B97-1/MG3S	4	3.51	3.67
CCSD/accDZ//DFT	6	4.85	0.88	G3	7	2.96	3.79
CR-CC(2,3),C/accDZ//DFT	7	0.99	0.88	MPW3LYP/MG3S	4	3.25	3.82
CR-CC(2,3),B+Q/accDZ//DFT	7	1.70	0.89	G96LYP/MG3S	3	8.20	3.82
CR-CC(2,3),D+Q/accDZ	7	1.21	0.90	τ -HCTH/MG3S	3	5.98	3.82
CR-CC(2,3),D/accDZ	7	0.84	0.92	MPW1PW91/MG3S	4	5.49	3.83
CR-CC(2,3),D+Q/accTZ	7	0.77	0.93	M05-2X/MG3S	4	9.57	3.83
CR-CC(2,3),D/accTZ	7	1.05	0.94	M06-HF/MG3S	4	17.45	3.92
CR-CC(2,3),C+Q/accTZ	7	0.78	0.96	MP2/MG3S	5	8.53	3.93
CR-CC(2,3),A/accDZ//DFT	7	1.70	0.96	BLYP/MG3S	3	8.60	3.94
CR-CCSD(TQ)/accDZ	7	1.48	0.97	B3LYP*/MG3S	4	3.49	3.98
CR-CC(2,3),C/accTZ	7	1.02	0.97	MP2(full)/G3Large	5	8.33	4.00
CR-CCSD(T)/accDZ	7	1.95	0.98	mPWKCIS/MG3S	3	7.39	4.07
CCSD/accTZ	6	5.28	0.98	TPSS1KCIS/MG3S	4	3.37	4.11
CR-CC(2,3),A+Q/accDZ//DFT	7	1.31	1.01	PBE1PBE/MG3S	4	5.87	4.13
BMC-CCSD	6	1.66	1.04	M06/MG3S	4	4.19	4.20
CCSDT/accDZ	8	0.94	1.12	MPWLYP1M/MG3S	4	6.78	4.35
CCSDT(2) _c /ccDZ	9	2.75	1.15	BB95/MG3S	3	7.45	4.41
CCSDT/ccDZ	8	2.00	1.19	PBEKCIS/MG3S	3	7.52	4.44
CCSD(TQ)/accDZ//DFT	7	0.94	1.21	τ -HCTH/MG3S	4	3.99	4.63
MRMP2/nom-CPO/MG3S	5	8.50	1.30	mPWLYP/MG3S	3	8.36	4.63
CR-CC(2,3),B+Q/accDZ	7	1.25	1.31	M06-L/MG3S	3	5.11	4.77
CR-CC(2,3),B/accDZ	7	1.70	1.32	MP2/6-31G(2df,p)	5	8.13	4.85
O3LYP/MG3S	4	3.28	1.34	TPSSKCIS/MG3S	3	6.04	4.92
CR-CC(2,3),A/accTZ	7	1.03	1.35	TPSSH/MG3S	4	4.25	5.00
CCSD(TQ)/accDZ	7	1.53	1.37	mPWB95/MG3S	3	7.19	5.08
CR-CC(2,3),A/accDZ	7	1.29	1.39	mPWPW91/MG3S	3	6.26	5.14
CR-CC(2,3),A+Q/accDZ	7	1.13	1.39	V5XC/MG3S	3	9.14	5.30
CR-CC(2,3),C/accDZ//DFT	7	1.15	1.41	HF/6-31G(d)	4	20.73	5.40
CR-CC(2,3),C+Q/accDZ//DFT	7	1.52	1.43	BP86/MG3S	3	6.56	5.53
MP4/6-31G(d)	7	3.41	1.45	TPSS/MG3S	3	5.21	5.61
G3B3	7	1.79	1.45	PBE/MG3S	3	6.22	5.61
CCSD(T)/accDZ//DFT	7	1.25	1.46	RHF/accDZ	4	20.26	6.88
BHandHLYP/MG3S	4	9.18	1.47	mPWB98/MG3S	3	7.57	7.41
CR-CC(2,3),D/accDZ//DFT	7	1.14	1.48	HF/ccVTZ	4	20.73	7.97
QCISD/ccTZ	6	4.70	1.50	HF/G3Large	4	20.35	8.06
CR-CC(2,3),D+Q/accDZ//DFT	7	1.49	1.50	BHandH/MG3S	4	18.56	8.06
M05/MG3S	4	1.52	1.53	RHF/accTZ	4	20.81	8.26
MCSAC-CCSD(T)/ccTZ	7	4.60	1.53	RHF/accDZ//DFT	4	19.45	8.40
CR-CCSD(T)/accDZ//DFT	7	1.95	1.57	MOHLYP/MG3S	3	19.40	9.53
CCSD(T)(KS)/accDZ	7	1.51	1.58	RHF/accDZ//DFT	4	20.19	9.96

^a CMUE is the mean unsigned error over all 12 energy differences between structures (six for ozone plus ethyne and six for ozone plus ethene). CMUE(6) is the mean unsigned error over the six energy differences (three for ozone plus ethyne and three for ozone plus ethene) that do not include the adduct. ^b MG3S denotes the 6-311+G(2df,2p) basis set for the systems in this article. ^c All calculations are at the CCSD(T)/ccTZ geometries except where postscripted with //opt to indicate consistently optimized or with //DFT to indicate optimized with M05/MG3S and except for G3-, G4-, and CBS-type methods, which are each defined to use their own prescribed geometry.

reactants, van der Waals complex, and transition state are similar both geometrically and in terms of dominant configuration state functions, whereas the product cycloadduct is quite different. Table 14 also gives, for each of the 162 methods, in addition to CMUE and CMUE(6), the scaling exponent α , where the computational effort for each method scales in the large- N limit as N^α , with N being the number of atoms.

Table 14 leads to some interesting observations. First, we see that most of the WFT-based methods, especially those that do not include the effect of triple excitations, suffer from a highly unbalanced description of the entrance channel and the products, which leads to CMUE being much larger than CMUE(6). It is encouraging that six methods shown in Table 14 agree on average with the best estimates within their estimated average reliability of 0.67 kcal/mol, and fourteen methods agree with the best estimates for the entrance channel within their estimated average reliability of 0.43 kcal/mol. The ten best performing methods (based on the CMUE) have $\alpha = 7$, and the best performing method with $\alpha = 4$ is M05/accTZ with CMUE = 0.77 kcal/mol; the best with $\alpha < 4$ is M06-L/MG3S with CMUE = 5.11 kcal/mol. If we insist on WFT (as opposed to DFT) and only consider the entrance channels, then we find that the best results for $\alpha < 7$ are those obtained with the MRMP2/accTZ multireference method with CMUE(6) = 0.50 kcal/mol. Again restricting attention to methods with $\alpha < 7$, the best performing WFT-based method based on description of both reactants and the products is the BMC-CCSD multilevel method with CMUE = 1.66 kcal/mol and CMUE(6) = 1.04 kcal/mol. Some further conclusions that one may draw from Table 14 are summarized in the next section.

4. Concluding Remarks

We have examined several issues related to the prediction of accurate reaction energies and transition-state energies for 1,3-dipolar cycloaddition reactions of ozone with ethyne and ethene. These are difficult reactions because of the very high multireference character of ozone and the transition states (as opposed to the reaction products), yet they provide well-controlled test cases for WFT and DFT because, unlike many open-shell multireference systems, the reactants, van der Waals complexes, transition states, and products are all closed shell singlets, and single-configuration reference states do not suffer from spin contamination. Our main conclusions may be summarized as follows (the errors mentioned in the following are comprehensive mean unsigned errors (CMUE and CMUE (6) values, as defined in Section 3.10)). (1) On the basis of CCSDT(2)_Q, CCSD(T_Q), and CR-CC(2,3)+ Q calculations, we provide a thorough examination of the effect of quadruple excitations for both C₂H₂ (previously examined by Wheeler et al.²) and C₂H₄ (not previously studied), and we made new best estimates of the stationary point energetics with an estimated uncertainty of about 0.7 kcal/mol. (2) Calculations explicitly including connected quadruple excitations are not systematically more accurate than those neglecting them. (See Tables 3–5, 10, 13, and 14.) (3) For the reactions studied here, CR-CC(2,3) and CCSDT do not indicate a breakdown of conventional CC, nor do they systematically improve on CCSD(T). (4) WFT calculations including connected triple excitations have CMUEs of 0.3–3.4 kcal/mol, whereas the most accurate MP2 and MP3 calculations, which are limited to double excitations, have CMUEs of 7.0 kcal/mol, and the most accurate CCSD and QCISD calculations, which include single and double excitations and disconnected higher excitations, have mean errors of 3.7 to 5.6 kcal/mol. (5) CCSD(T)(KS) calculations have mean errors

that differ from standard CCSD(T) by only about 0.1 kcal/mol. (6) One of the multilevel methods is quite accurate. In particular, MCG3-MPW has a CMUE of only 0.4 kcal/mol and a CMUE(6) of only 0.25 kcal/mol. The others all have CMUEs of at least of 1.2 kcal/mol. (7) The M05 density functional has a CMUE of only 0.77 kcal/mol with the accTZ basis set, but the other density functionals have CMUEs of at least 2.40 kcal/mol. (8) Multireference perturbation theory based on the *nom*-CPO CASSCF reference wave function in conjunction with the accTZ basis set has large CMUE of 7.55 kcal/mol because of the unbalanced description of the reaction entrance channel versus the cycloadduct. However, CMUE(6), which is averaged over the six energy differences that exclude the cycloadducts, is only 0.50 kcal/mol.

The relative success of M05 and MRMP2 (the latter for the noncovalent well depths and the forward barrier heights but not the overall energy of reaction) is encouraging because these methods scale as N^4 and N^5 , respectively. The HCTH density functional also does well for CMUE (6).

The development of reliable methods for multireference reactions remains one of the outstanding unsolved problems in modern quantum chemistry.

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Supporting Information Available: Energy differences of single-level WFT methods and coordinates of geometries optimized by M06/MG3S. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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