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Thinking Out of the Black Box: Accurate Barrier Heights of 1,3-Dipolar Cycloadditions of Ozone with Acetylene and Ethylene

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Accurate barriers for the 1,3-dipolar cycloadditions of ozone with acetylene and ethylene have been determined via the systematic extrapolation of *ab initio* energies within the focal point approach of Allen and co-workers. Electron correlation has been accounted for primarily via coupled cluster theory, including single, double, and triple excitations, as well as a perturbative treatment of connected quadruple excitations [CCSD, CCSD(T), CCSDT, and CCSDT(Q)]. For the concerted [4 + 2] cycloadditions, the final recommended barriers are $\Delta H^{\ddagger}_{(0K)} = 9.4 \pm 0.2$ and 5.3 ± 0.2 kcal mol^{-1} for ozone adding to acetylene and ethylene, respectively. These agree with recent results of Cremer *et al.* and Anglada *et al.*, respectively. The reaction energy for $O_3 + C_2H_2$ exhibits a protracted convergence with respect to inclusion of electron correlation, with the CCSDT/cc-pVDZ and CCSDT(Q)/cc-pVDZ values differing by 2.3 kcal mol^{-1}. Recommended enthalpies of formation (298 K) for cycloadducts 1,2,3-trioxole and 1,2,3-trioxolane are +32.8 and −1.6 kcal mol^{-1}, respectively. Popular composite *ab initio* approaches [CBS-QB3, CBS-APNO, G3, G3B3, G3(MP2)B3, G4, G4(MP3), and G4(MP2)] predict a range of barrier heights for these systems. The CBS-QB3 computed barrier for ozone and acetylene, $\Delta H^{\ddagger}_{(0K)} = 4.4$ kcal mol^{-1}, deviates by 5 kcal mol^{-1} from the focal point value. CBS-QB3 similarly underestimates the barrier for the reaction of ozone and ethylene, yielding a prediction of only 0.7 kcal mol^{-1}. The errors in the CBS-QB3 results are significantly larger than mean errors observed in application to the G2 test set. The problem is traced to the nontransferability of MP2 basis set effects in the case of these reaction barriers. The recently published G4 and G4(MP2) approaches perform substantially better for $O_3 + C_2H_2$, predicting enthalpy barriers of 9.0 and 8.4 kcal mol^{-1}, respectively. For the prediction of these reaction barriers, the additive corrections applied in the majority of the composite approaches considered lead to *worse agreement* with the reference focal point values than would be obtained relying only on single point energies evaluated at the highest level of theory utilized within each composite method.

I. Introduction

The ozonolysis of alkenes and alkynes by the atmospheric component O_3 results in insertion of oxygen into double and triple C−C bonds. Highly useful in synthesis[1] and materials chemistry,[2] ozonolysis generates various oxidation products including ketones, aldehydes, epoxides, peroxides, anhydrides, and polymers depending on alkene or alkyne substitution and reaction conditions.[3−9] Olefin ozonolysis has even been implicated in the pathogenesis of diseases with an inflammatory component, including autoimmunity and atherosclerosis.[10−14] Nearly all proposed mechanisms involve the initial rate-determining 1,3-dipolar cycloadditions of ozone with double or triple bonds to form primary ozonides (Scheme 1).[15] It is perhaps not surprising that the barriers for the parent ozonation reactions ($O_3 + C_2H_2$ or C_2H_4) are problematic to compute accurately given the biradical character of ozone (see later discussion). Nevertheless, the wide range of reported activation barriers from ordinarily reliable theoretical methods is unnerving. Reported values for the concerted cycloaddition barriers range from 5 to 22 kcal mol^{-1} for acetylene[16−19] and 2 to 18 kcal mol^{-1} for ethylene.[20−25]

Composite *ab initio* methods, such as the popular Gaussian-*n* methods (G3, and G4)[26−28] and CBS-Q[29−35] series of model chemistries, have become popular due to their ease of use and typical high-accuracy. Each of these approaches consists of a prescribed set of energy evaluations that are combined, along with small empirical corrections, to yield a final predicted energy. On the basis of results from numerous benchmark studies, these approaches are generally regarded as reliable, "black box" methods. As such, in typical applications little attention is paid to individual contributions to the final energy. However, we have found that among popular composite methods [CBS-QB3, CBS-APNO, G3, B3B3, G3(MP2)B3, G4, G4(MP3), and G4(MP2)] there is significant disagreement for the concerted activation energies for $O_3 + C_2H_4$ and C_2H_2, with predictions spanning 8 kcal mol^{-1} in the latter case. This is in contrast to predicted barriers for 1,3-dipolar cycloadditions of

SCHEME 1

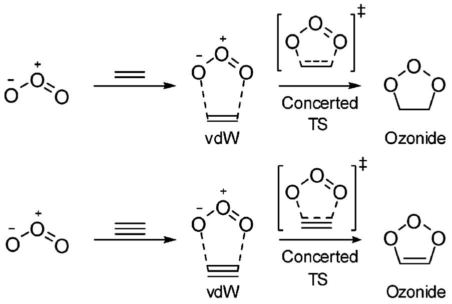

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TABLE 1: Reported Activation Energies and Enthalpies (kcal mol^{-1}) for the 1,3-Dipolar Cycloadditions of Ozone with Ethylene and Acetylene[a]

reference	method	$\Delta E^{\ddagger}$ ($\Delta H^{\ddagger}_{0K}$)
	$O_3 + C_2H_2$	
16, 17	B3LYP/6-311+G(2d,2p)	3.8 (5.2)
16, 17	RCCSD(T)/6-311+G(2d,2p)	9.1 (10.5)
16, 17	RCCSD(T)/Basis set Extrap.//RCCSD(T)/6-311+G(2d,2p)	7.1 (8.5)
19	BHandHLYP/6-311+G(d,p)	6.8 (8.3)
19	(U)BHandHLYP/6-311+G(d,p)	20.3 (22.7)
19	CCSD(T)/6-311+G(2d,p)//BHandHLYP/6-311+G(d,p)	6.7 (8.2)
19	UCCSD(T)/6-311+G(2d,p)//BHandHLYP/6-311+G(d,p)	11.4 (13.8)
this work	**focal point extrapolation**	**7.7 (9.4)**
	$O_3 + C_2H_4$	
20	CCSD(T)/6-311G(2d,2p)//CASSCF/6-31G(d)	2.6 (5.0)
21	QCISD(T)6-311++G(d,p)//MP2/6-311++G(d,p)	1.1 (2.4)
22	BHandHLYP/6-31+G(d)	14.5 (17.6)
22	PMP4/6-311+G(2d,p)//BHandHLYP/6-31+G(d)	4.2 (7.0)
22	RCCSD(T)/6-311+G(2d,p)//BHandHLYP/6-31+G(d)	4.8 (7.6)
22	UCCSD(T)/6-311+G(2d,p)//BHandHLYP/6-31+G(d)	6.1 (8.9)
23	CASPT2(10,9)/cc-pVTZ//CASSCF(10,9)/cc-pVTZ	4.7
24, 25	MP4(SDQ)/6-31G(d,p)	1.9 (3.5)
this work	**focal point extrapolation**	**3.4 (5.3)**

[a] All energies are given relative to separated reactants.

diazonium, nitrilium, and azomethine betaines with ethylene and acetylene, for which these and other popular approaches yield results within 1.5 kcal mol^{-1} of each other and experiment.[36]

Ozone has a zwitterionic (dipole) all-octet resonance structure and cycloadds at the 1,3 termini with alkenes and alkynes.[37−40] Typically represented by closed-shell zwitterionic structures, natural orbital occupation and generalized valence bond computations estimate diradical character of ozone to be nearly 33%.[41−43] The significant diradical character of 1,3-dipoles lead to a vigorous debate of concerted versus stepwise mechanisms for 1,3-dipolar cycloadditions.[44−46] Early *ab initio* studies by Goddard,[47] Hiberty,[48] Houk,[49] and others[50−53] showed that ozone and its concerted TS have a triplet instability at the RHF and MP2 levels of theory. Unrestricted Hartree−Fock theory predicts a stepwise pathway to be favored over the concerted pathway, whereas second-order unrestricted Møller−Plesset perturbation theory (UMP2) computations favor the concerted cycloaddition, with a barrier around 10 kcal mol^{-1}.[49] van der Waals (vdW) and weak σ-complexes have been postulated to exist, preceding the concerted TS along the reaction coordinate. Gillies, Cremer, and co-workers[18,24] have expended considerable experimental and theoretical effort to identify and characterize these complexes. Most evidence supports a C_s symmetrical vdW complex similar to the concerted TS. After the very exothermic formation of the ozonide cycloadduct, diradical or zwitterionic intermediates are likely involved in the decomposition via Criegee-like mechanisms.[54,55]

After these early *ab initio* studies, more sophisticated DFT and correlated *ab initio* methods have been employed to predict reaction barriers with disturbingly inconsistent results (Table 1).[16−25] For the concerted cycloaddition of ozone with acetylene, Cremer *et al.*[16,17] computed CCSD(T) energies (coupled cluster theory including single and double excitations with a perturbative treatment of triple excitations), evaluated at CCSD(T)/6-311+G(2d,2p) optimized geometries. These energies were then extrapolated to the complete basis set (CBS) limit using the correlation consistent basis sets of Dunning, to give $\Delta H^{\ddagger}_{0K} = 8.5$ kcal mol^{-1}, relative to reactants. At this same level of theory, the vdW complex is stable by 2.7 kcal mol^{-1}. Cremer *et al.*[16,17] found that B3LYP gives a much lower enthalpy barrier of 5.2 kcal mol^{-1}. A stepwise diradical pathway could not be located using complete active space self-consistent field (CASSCF) or restricted open-shell density functional theory approaches. In 2007, Chan *et al.*[19] reported that the spin-restricted BHandHLYP (RBHandHLYP) optimized concerted TS is unstable toward spin symmetry breaking. They found that reoptimization using the spin unrestricted formulism (UBHandHLYP) leads to an asynchronous diradicaloid TS. RBHandHLYP predicts $\Delta H^{\ddagger}_{0K} = 8.3$ kcal mol^{-1} for the concerted TS, and UBHandHLYP gives a barrier of 22.7 kcal mol^{-1}. CCSD(T)/6-311+G(2d,p) energies computed at the concerted BHandHLYP geometries gave $\Delta H^{\ddagger}_{0K} = 8.2$ kcal mol^{-1}. Although Chan *et al.*[19] located stationary points along a stepwise, diradical pathway, they showed that the concerted cycloaddition of ozone and acetylene is favored.

For the concerted cycloaddition of ozone and ethylene, Li *et al.*[21] reported an enthalpy barrier of 2.4 kcal mol^{-1} based on MP2/6-311+G(d,p) geometries and QCISD(T)/6-311++G(d,p) energies. Using CASSCF/6-31G(d) geometries and CCSD(T)/6-311G(2d,2p) energies, Anglada *et al.*[20] reported $\Delta H^{\ddagger}_{0K} = 5.0$ kcal mol^{-1}, relative to reactants. On the basis of CASPT2 energies computed at CASSCF/cc-pVTZ optimized geometries, Ljubic *et al.*[23] reported a $\Delta E^{\ddagger}$ of 4.7 kcal mol^{-1}. Most recently, Chan and Hamilton[22] used BHandHLYP/6-31+G(d) geometries with spin-projected MP4/6-311+G(2d,p) and CCSD(T)/6-311+g(2d,p) energies, giving $\Delta H^{\ddagger}_{0K}$ values of 7.0 and 7.6, respectively. UCCSD(T)/6-311+G(2d,p) energies yielded $\Delta H^{\ddagger}_{0K} = 8.9$ kcal mol^{-1}.

For the practical computational chemist, popular composite approaches (CBS-QB3, G3, etc.) are particularly attractive because they are applicable to systems up to about 15−20 heavy atoms, all packaged in a black box approach and promising thermochemical predictions often accurate to within 1 kcal mol^{-1}.[56,57] Although these composite approaches generally yield consistently accurate thermochemistry, cases arise in which these veteran methods yield exiguous predictions. Through detailed studies of these problematic systems we can further understand the limitations of these methods and suggest pathways to more reliable, widely applicable model chemistries. Accurate barriers and reaction energies for the cycloadditions of ozone with acetylene and ethylene have been determined via systematic extrapolations of *ab initio* energies within the focal point approach of Allen and co-workers.[58−61] Through comparisons with these benchmark values, deficiencies in popular compound and *ab initio* approaches are dissected and discussed.

II. Theoretical Methods

The focal point approach of Allen and co-workers[58−61] was utilized to predict accurate relative energies for the four stationary points along the reaction coordinate (reactants, van der Waals complex, concerted transition state, and cycloadduct) for the cycloadditions of ozone with actetylene and ethylene. Within the focal point approach, one executes dual expansions of the one- and N-particle basis sets, allowing for the systematic approach to the complete basis set Born−Oppenheimer limit. Details of the procedure have been described previously.[58−61] The salient feature of the approach is the explicit examination of the convergence of computed energies with respect to completeness of the one-particle basis set and inclusion of electron correlation. By examining each contribution to the final extrapolated energy, one can quantify remaining errors and tailor the approach as the system of interest requires and computational resources permit. Corrections to the extrapolated valence electronic energies are appended to account for core−electron correlation, non-Born−Oppenheimer effects, zero point vibrational energy, and scalar relativistic effects.

All energies were computed at fixed geometries, optimized using CCSD(T)[62−67] paired with the correlation consistent polarized valence triple-ζ basis set (cc-pVTZ).[68] Within the focal point procedure, valence energies are computed via systematic extrapolations using the aug-cc-pVXZ hierarchy of basis sets.[69] For brevity, these basis sets will be denoted by AVXZ. In this work, Hartree−Fock energies were extrapolated to the CBS limit using an exponential form[70] based on energies computed with the AVXZ (X = T, Q, 5) basis sets, and the correlation energies were extrapolated using[71]

$$E^{\mathrm{corr}} = a + bX^{-3}$$

In the case of the acetylene reactions, the resulting estimate of the complete basis set CCSDT energies[72−75] were further corrected for effects of quadruple excitations by adding the difference between CCSDT(Q)/cc-pVDZ and CCSDT/cc-pVDZ energies. For $O_3 + C_2H_4$, CCSDT(Q) energies could not be evaluated with available computational resources. Instead, corrections for connected quadruple excitations were taken from the $O_3 + C_2H_2$ computations. The final values should provide a reliable estimate of the CBS limit CCSDT(Q) valence energy. The inclusion of effects of quadruple excitations is often vital for high accuracy, particularly for systems exhibiting multireference character.[77−80] The CCSDT(Q) approach relies on a perturbative treatment of connected quadruple excitations, analogous to the popular CCSD(T) method for approximate triple excitations, and has been shown to provide a robust estimate of full CCSDTQ energies.[76] Further corrections to these valence electronic energies were appended to account for smaller effects as follows. Zero point vibrational energy (ZPVE) corrections were computed on the basis of harmonic vibrational frequencies computed at the CCSD(T)/cc-pVTZ level of theory for the reaction of ozone and actylene. In this case, utilization of more economical CCSD(T)/cc-pVDZ harmonic vibrational frequencies results in very minor changes in ZPVEs (less than 0.1 kcal mol^{-1}). Specifically, for the reaction barrier, the difference in CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVDZ ZPVE corrections was only 0.03 kcal mol^{-1}. As such, CCSD(T)/cc-pVDZ frequencies were used for reaction of ozone and ethylene. Core−electron correlation effects were accounted for by taking the difference between all electron CCSD(T)/aug-cc-pCVTZ and frozen core CCSD(T)/aug-cc-pCVTZ energies. Non-Born−Oppenheimer effects were accounted for through the diagonal Born−Oppenheimer correction (DBOC),[81−84] which constitutes the first-order perturbative correction to the Born−Oppenheimer approximation, evaluated at the HF/aug-cc-pVTZ level of theory using ACES II.[85] Special relativity was accounted for by the application of standard perturbation formulas for the mass-velocity and one-electron Darwin scalar relativistic effects,[86−90] evaluated at the all-electron CCSD(T)/aug-cc-pCVTZ level of theory. For the focal point results, Molpro 2006.1 was utilized to compute the MP2, CCSD, and CCSD(T) energies,[91] and the Mainz−Austin−Budapest version of ACES II[85] was used to compute the CCSD(T) optimized geometry and vibrational frequencies as well as the CCSDT energies and relativistic corrections. CCSDT(Q) energies[76] were computed using MRCC[92,93] in conjunction with ACES II.[85]

All structures have been confirmed to be minima or first-order saddle points by harmonic vibrational frequency analysis, with the exception of the C_s-symmetric van der Waals complex of ozone and ethylene. In this case, there is a small C_s-symmetry-breaking imaginary frequency (14i cm^{-1}) at the CCSD(T)/cc-pVDZ level of theory. This imaginary mode corresponds to a twisting of the ozone relative to ethylene. The energy is nearly invariant with respect to this motion, with reoptimization along this symmetry-breaking mode lowering the energy by less than 0.05 kcal mol^{-1} at the CCSD(T)/cc-pVDZ level. The C_s-symmetric structure was utilized in subsequent computations. For the ZPVE corrections and thermochemical analysis, vibrational frequencies from the C_1-symmetric, minimum energy structure were used, optimized at the CCSD(T)/cc-pVDZ level of theory.

Reaction barriers and energies were also computed using popular composite *ab initio* approaches using the Gaussian03 suite of programs.[94] These include G3 theory[95] and the G3B3 and G3(MP2)B3 variants,[96,97] as well as the economical CBS-QB3 and more expensive CBS-APNO approaches.[34,35,57] The recently published G4, G4(MP3), and G4(MP2) approaches were also used.[28,98]

III. Results and Discussion

Popular composite *ab initio* approaches predict notably different energy barriers for the concerted cycloadditions of ozone with acetylene and ethylene. We have examined the sources of these deficiencies through comparison with reliable extrapolated *ab initio* results. As demonstrated previously,[16−18,24] the reaction in both cases proceeds via formation of a C_s-symmetric van der Waals complex, followed by a concerted cycloaddition. Although the enthalpy of the van der Waals complex is 1 kcal mol^{-1} below that of the separated reactants for both ethylene and acetylene, the entropic cost of complexation results in a free energy gain upon complex formation. As such, the precise energy of the van der Waals complex is not of primary interest, and all energies are given relative to separated reactants.

A. Geometric Structures. Key bond lengths and angles for the van der Waals complex, concerted TS, and cycloadduct for the addition of ozone to acetylene and ethylene are given in Figure 1, optimized at the CCSD(T)/cc-pVTZ level of theory. Compared to the optimized structures of the reactants (Figure 2), formation of the van der Waals complex is accompanied by negligible structural perturbations. Similarly, for both reactions only minor distortions (bond changes less than 0.05 Å, ozone angle changes less than 6°) of the reactants occur upon formation of the transition state. The majority of the structural changes occur after crossing the transition state.

B3LYP/6-311G(d,p) optimized parameters are also included for comparison. These B3LYP/6-311G(d,p) geometries are

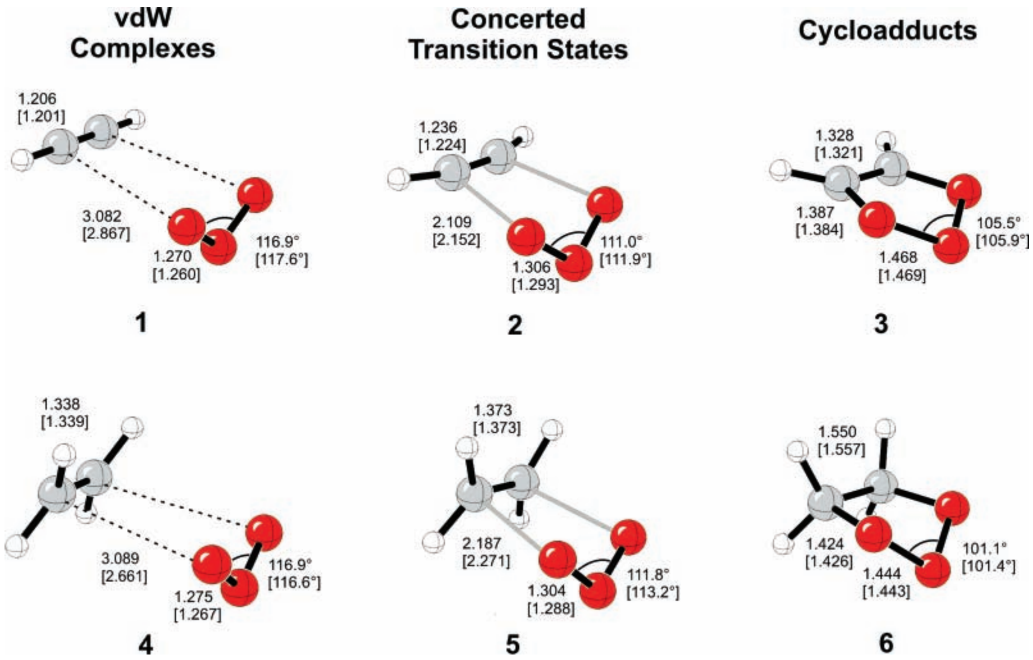

Figure 1. Selected optimized CCSD(T)/cc-pVTZ bond lengths (Å) and angles (degrees) for the van der Waals complexes (**1** and **4**), concerted transition states (**2** and **5**), and cycloadducts (**3** and **6**) for the cycloadditions of ozone with acetylene and ethylene. B3LYP/6-311G(d,p) optimized parameters are in brackets.

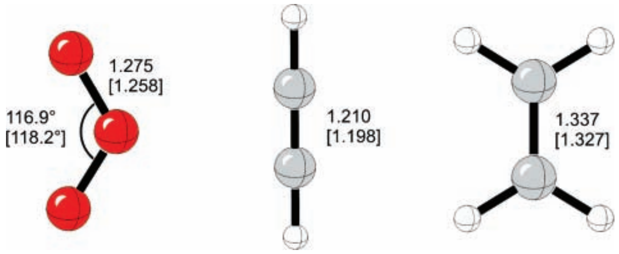

Figure 2. Optimized CCSD(T)/cc-pVTZ bond lengths (Å) and angles (degrees) for ozone, acetylene, and ethylene. B3LYP/6-311G(d,p) optimized parameters are in brackets.

utilized in the CBS-QB3 approach. Similar B3LYP/6-31G(d) structures are used in the G3B3 and G3(MP2)B3 approaches, whereas the G4, G4(MP3), and G4(MP2) methods rely on B3LYP/6-31G(2df,p) optimized structures. The overall agreement between the B3LYP and CCSD(T) geometries is modest, with notable differences in key bond lengths and angles. The intermolecular distance in the weakly bound van der Waals complexes differ substantially. However, given the expected flatness of the potential energy surface along the interfragment coordinate, even major deviations will have modest effects on computed energies. In both transition states, B3LYP/6-311G(d,p) overestimates the forming C−O bond length by 0.05 Å. We will see below, however, that these differences in structures between CCSD(T)/cc-pVTZ and B3LYP/6-311G(d,p) have negligible effects on final computed barriers. A more complete comparison of CCSD(T)/cc-pVTZ optimized structures with previously reported structures is provided in the Supporting Information.

B. Reference Focal Point Energies. Valence focal point tables for the stationary points along the reaction pathway for the concerted cycloaddition of ozone and acetylene are given in Table 2. The energy of the van der Waals complex relative to reactants converges rapidly with respect to inclusion of electron correlation. The contribution of triple excitations [the sum of the CCSD(T) and CCSDT columns] amounts to less than 0.1 kcal mol^{-1} at the CBS limit, to yield an estimated CBS limit CCSDT energy of −1.83 kcal mol^{-1}. Similarly, the computed energies are well-converged with respect to the one-particle basis set, with the difference between the largest explicitly computed energy and the extrapolated results not exceeding 0.03 kcal mol^{-1}. Upon further corrections for higher-order excitations, core−electron correlation effects, ZPVE, DBOC, and scalar relativistic effects (see Table 3), the final predicted energy of the van der Waals complex is −1.07 kcal mol^{-1}. The contribution from connected quadruple excitations [computed here at the CCSDT(Q)/cc-pVDZ level of theory] is a mere 0.05 kcal mol^{-1}, indicating that the present results are well converged toward the full configuration interaction limit. This is despite significant diradical character in both ozone and the vdW complex.

For the reaction barrier the convergence with respect to basis set is similarly rapid. The energy of the transition state relative to the reactants converges much more slowly with respect to electron correlation; the contribution from triple excitations amounts to −2.1 kcal mol^{-1} to yield a final CBS limit CCSDT barrier of 7.89 kcal mol^{-1}. Upon the inclusion of further corrections, the final predicted barrier height is 9.37 kcal mol^{-1}, including a correction of −0.20 kcal mol^{-1} for the effects of connected quadruple excitations. The small size of the CCSDT(Q) correction suggests that this computed barrier is well converged and should be accurate to ± 0.2 kcal mol^{-1}. This final recommended barrier height is slightly larger than the results of Cremer *et al.* (8.5 kcal mol^{-1}) or Chan and co-workers (8.2 kcal mol^{-1}). This difference is largely due to complete treatment of triple excitations included in the present work, which increase the barrier by 0.88 kcal mol^{-1} compared to the extrapolated CCSD(T) value of 7.01 kcal mol^{-1}. These theoretical predictions are also in accord with available experimental activation energies.[4,5]

The convergence of the overall reaction energy mirrors the computed barrier height. The energy of the products converges rapidly with respect to basis set, yet the correlation energy exhibits a protracted, oscillatory convergence. The contribution of triple excitations is 7.7 kcal mol^{-1}, yielding a final CBS limit CCSDT value of −65.20. Despite the slow convergence of the

TABLE 2: Incremental Valence Focal Point Extrapolation for the Relative Energies of the Stationary Points on the Ozone + Acetylene Reaction Surface[a]

basis set	ΔE_e[HF]	+δ[MP2]	+δ[CCSD]	+δ[CCSD(T)]	+δ[CCSDT]	=ΔE(CCSDT)
			$O_3 + C_2H_2 \rightarrow$ vdW Complex (**1**)			
AVDZ	−0.824	−2.001	+1.074	−0.071	+0.119	−1.703
AVTZ	−0.888	−2.241	+1.107	−0.037	[+0.119]	[−1.941]
AVQZ	−0.845	−2.267	+1.126	−0.039	[+0.119]	[−1.905]
AV5Z	−0.797	−2.263	[+1.120]	[−0.040]	[+0.119]	[−1.859]
AV6Z	[−0.776]	[−2.261]	[+1.117]	[−0.040]	[+0.119]	[−1.840]
CBS limit	[−0.767]	[−2.258]	[+1.114]	[−0.040]	[+0.119]	[**−1.832**]
			$O_3 + C_2H_2 \rightarrow$ Concerted TS (**2**)			
AVDZ	18.379	−16.868	+6.389	−2.429	+0.884	6.356
AVTZ	20.435	−18.524	+7.429	−2.731	[+0.884]	[7.493]
AVQZ	20.810	−18.648	+7.614	−2.841	[+0.884]	[7.820]
AV5Z	20.895	−18.648	[+7.636]	[−2.880]	[+0.884]	[7.886]
AV6Z	[20.913]	[−18.648]	[+7.645]	[−2.898]	[+0.884]	[7.897]
CBS limit	[20.919]	[−18.648]	[+7.659]	[−2.921]	[+0.884]	[**7.892**]
			$O_3 + C_2H_2 \rightarrow$ Cycloadduct (**3**)			
AVDZ	−91.998	+39.964	−18.657	+6.948	−0.112	−63.855
AVTZ	−91.177	+38.253	−19.116	+7.708	[−0.112]	[−64.443]
AVQZ	−90.577	+37.687	−19.366	+7.753	[−0.112]	[−64.614]
AV5Z	−90.556	+37.545	[−19.513]	[+7.769]	[−0.112]	[−64.868]
AV6Z	[−90.580]	[+37.481]	[−19.579]	[+7.776]	[−0.112]	[−65.013]
CBS limit	[−90.600]	[+37.395]	[−19.668]	[+7.785]	[−0.112]	[**−65.200**]
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points (X=)	3,4,5	4,5	3,4	3,4		

[a] All energies evaluated at CCSD(T)/cc-pVTZ optimized geometries. The symbol δ denotes the *increment* in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), and unbracketed numbers were explicitly computed. [b] δ[CCSDT(Q)/cc-pVDZ] = E[CCSDT(Q)/cc-pVDZ] − E(CCSDT/cc-pVDZ).

TABLE 3: Determination of Relative Energies for the 1,3-Dipolar Cycloaddition of Ozone with Acetylene and Ethylene, in kcal mol^{-1}[a]

reaction	ΔE(CCSDT)	Δ(Q)	Δ(core)	ΔDBOC	ΔRel	ΔE(final)	ΔZPVE	$\Delta H_{(0K)}$
$O_3 + C_2H_2 \rightarrow$ vdW complex	−1.83	0.05	−0.07	0.00	0.00	−1.85	0.79	**−1.07**
$O_3 + C_2H_2 \rightarrow$ concerted TS	7.89	−0.20	0.04	0.00	0.01	7.74	1.62	**9.37**
$O_3 + C_2H_2 \rightarrow$ cycloadduct	−65.20	2.29	−0.26	−0.04	0.17	−63.04	5.18	**−57.86**
$O_3 + C_2H_4 \rightarrow$ vdW complex	−1.86	0.05[b]	−0.03	0.00	0.00	−1.84	0.64	**−1.20**
$O_3 + C_2H_4 \rightarrow$ concerted TS	3.61	−0.20[b]	0.03	−0.01	0.00	3.43	1.91	**5.34**
$O_3 + C_2H_4 \rightarrow$ cycloadduct	−58.60	2.29[b]	−0.22	−0.06	0.15	−56.43	5.50	**−50.93**

[a] ΔE(CCSDT) = valence focal point energy difference from Tables 2 and S1; Δ(Q) = CCSDT(Q)/cc-pVDZ − CCSDT/cc-pVDZ; Δ(core) = CCSD(T)(full)/aug-cc-pCVTZ − CCSD(T)(fc)/aug-cc-pCVTZ; ΔDBOC = diagonal Born−Oppenheimer correction (HF/aug-cc-pVDZ); ΔRel = scalar relativistic corrections [CCSD(T)/cc-pCVDZ]; ΔE(final) = sum of previous five columns; ΔZPVE = harmonic zero-point vibrational energy correction [CCSD(T)/cc-pVTZ for acetylene reactions, CCSD(T)/cc-pVDZ for ethylene]; $\Delta H_{(0K)}$ = sum of ΔE(final) and ΔZPVE. All energies computed at CCSD(T)/cc-pVTZ optimized geometries. [b] Δ(Q) corrections for $O_3 + C_2H_4$ taken from the corresponding $O_3 + C_2H_2$ computations.

coupled cluster series in this case, the venerable CCSD(T) approach yields energies only about 0.1 kcal mol^{-1} from the full CCSDT results, with the aug-cc-pVDZ basis set. Correction for smaller effects yields a final predicted reaction energy of −57.86 kcal mol^{-1}. The CCSDT(Q) correction is large (2.29 kcal mol^{-1}), indicative of the difficulty with which even robust coupled cluster methods describe ozone. The cycloadduct exhibits significantly less diradical character than ozone, with the largest T2 amplitude of 0.06. This can be compared to ozone, the van der Waals complex, and the transition state, for which the largest T2 amplitudes are 0.18, 0.18, and 0.15, in order. Thus, it appears that the slow convergence of the coupled cluster series for the reaction energy is due to an *imbalance* of multireference effects in the product and reactants. Given the magnitude of the CCSDT(Q)-derived quadruples correction, the uncertainty in the final recommended reaction energy is at least 2 kcal mol^{-1}.

The convergence of energies for the addition of ozone and ethylene is strikingly similar to that observed for acetylene; convergence is rapid with respect to basis set incompleteness, and the convergence of the coupled cluster series is painfully slow, oscillating about the full configuration interaction limit. Valence focal point tables are given in Table 4. The contributions to the final relative energies at each level of theory are very similar between the ethylene and acetylene reactions. Notably, the size of the CCSDT contribution is essentially identical for van der Waals complex, transition state, and product for the two reactions. As such, higher-order corrections are expected to be similar. Because CCSDT(Q) energies could not be computed for the reaction of ozone with ethylene, corrections for connected quadruple excitations were taken from those computed for the corresponding $O_3 + C_2H_2$ stationary points. The final predicted energies (Table 3) of the van der Waals complex, concerted TS, and cycloadduct are −1.20, +5.34, and −50.93 kcal mol^{-1} relative to separated reactants.

Despite the large uncertainty in the reaction energy for the cycloadditions of ozone with acetylene and ethylene, the presently recommended values should be significantly more reliable than any previous computational results (see Table 1). This is due to the full inclusion of triple excitations and consideration of connected quadruples, in addition to corrections for core−electron correlation and non-Born−Oppenheimer and scalar relativistic effects in the present work. More importantly, the final recommended reaction barriers are well converged with respect to inclusion of electron correlation, and should be accurate to well within 0.2 kcal mol^{-1}. The final $\Delta H_{(0K)}$ values

TABLE 4: Incremental Valence Focal Point Extrapolation for the Relative Energies (kcal mol^{-1}) of the Stationary Points on the Ozone + Ethylene Reaction Surface[a]

basis set	ΔE_e[HF]	+δ[MP2]	+δ[CCSD]	+δ[CCSD(T)]	+δ[CCSDT]	=ΔE(CCSDT)
			$O_3 + C_2H_4 \rightarrow$ vdW Complex (**4**)			
AVDZ	0.698	−4.661	+1.757	−0.532	+0.154	−2.584
AVTZ	0.919	−4.664	+1.837	−0.520	[+0.154]	[−2.273]
AVQZ	1.042	−4.603	+1.887	−0.522	[+0.154]	[−2.041]
AV5Z	1.109	−4.559	[+1.883]	[−0.523]	[+0.154]	[−1.936]
AV6Z	[1.134]	[−4.539]	[+1.881]	[−0.524]	[+0.154]	[−1.894]
CBS limit	[1.145]	[−4.513]	[+1.878]	[−0.524]	[+0.154]	[**−1.859**]
			$O_3 + C_2H_4 \rightarrow$ Concerted TS (**5**)			
AVDZ	13.381	−18.964	+8.863	−2.499	+0.810	1.592
AVTZ	15.442	−20.69	+9.825	−2.727	[+0.810]	[2.660]
AVQZ	15.967	−20.679	+10.050	−2.800	[+0.810]	[3.347]
AV5Z	16.081	−20.671	[+10.125]	[−2.826]	[+0.810]	[3.519]
AV6Z	[16.106]	[−20.667]	[+10.158]	[−2.838]	[+0.810]	[3.569]
CBS limit	[16.113]	[−20.662]	[+10.204]	[−2.853]	[+0.810]	[**3.611**]
			$O_3 + C_2H_4 \rightarrow$ Cycloadduct (**6**)			
AVDZ	−88.090	+40.476	−17.289	+8.037	−0.125	−56.990
AVTZ	−86.952	+37.626	−17.837	+8.875	[−0.125]	[−58.413]
AVQZ	−86.079	+37.118	−18.027	+8.948	[−0.125]	[−58.166]
AV5Z	−86.015	+36.958	[−18.116]	[+8.974]	[−0.125]	[−58.324]
AV6Z	[−86.035]	[+36.887]	[−18.155]	[+8.985]	[−0.125]	[−58.443]
CBS limit	[−86.057]	[+36.789]	[−18.208]	[+9.001]	[−0.125]	[**−58.600**]
fit	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	
points (X=)	3,4,5	4,5	3,4	3,4		

[a] All energies evaluated at CCSD(T)/cc-pVTZ optimized geometries. The symbol δ denotes the *increment* in the energy difference (ΔE) with respect to the previous level of theory. Bracketed numbers are the result of basis set extrapolations (using the fits denoted in the table), and unbracketed numbers were explicitly computed.

in Table 3 are taken as reference values for comparisons with popular composite *ab initio* results below.

C. Performance of Composite *ab Initio* Methods. CBS-QB3, CBS-APNO, G3, G3B3, and G3(MP2)B3 predicted reaction barriers for the cycloaddition of ozone and acetylene are provided in Table 5. Also included are results from the recently described G4 theory and the lower-scaling G4(MP3) and G4(MP2) variants.[28,98] Even among these ordinarily reliable methods, predicted enthalpy barriers span 8 kcal mol^{-1}. Compared to the focal point value of 9.4 kcal mol^{-1}, the CBS-QB3 prediction (4.4 kcal mol^{-1}) is too low by 5 kcal mol^{-1}. This is in contrast to previous work, in which it was shown that CBS-QB3 reliably reproduces experimental activation energies for a range of cycloadditions.[36] The recently described G4 approaches perform noticeably better than older composite *ab initio* approaches, with G4, G4(MP3), and G4(MP2) all predicting barrier heights within 1 kcal mol^{-1} of the focal point value. The span of predicted enthalpy barriers for $O_3 + C_2H_4$ (Table 6) is similar though not as pronounced, ranging from 0.5 kcal mol^{-1} (G3) to 5.9 kcal mol^{-1} [G4(MP3)], compared to the focal point value of 5.5 kcal mol^{-1}. Notably, the G3 and CBS-QB3 methods predict the electronic energy of the $O_3 + C_2H_4$ transition state to lie *below* that of the separated reactants. Only after the inclusions of ZPVE effects do these approaches predict a positive reaction barrier.

Examining predicted electronic energy barriers for these two reactions reveals a more troubling trend: in a majority of cases, the energy predicted by the highest level correlation method within each composite approach [CCSD(T/)6-31+G† for CBS-QB3; QCISD(T)/6-311++G(2df,p) for CBS-APNO; QCISD(T)/6-31G(d) for G3, G3B3, and G3(MP2)B3; and CCSD(T)/6-31G(d) for G4, G4(MP3), and G4(MP2)] is *more accurate* than the final composite electronic energy. In other words, in most cases the additive "corrections" utilized in these methods shift the predicted barriers in the wrong direction! This is perhaps most pronounced for the CBS-APNO predicted barrier for $O_3 + C_2H_2$, for which the underlying QCISD(T)/6-311+G(2df,p) electronic energy barrier (7.8 kcal mol^{-1}) is in excellent agreement with the focal point result (7.7 kcal mol^{-1}), yet the final CBS-APNO prediction is too small by almost 3 kcal mol^{-1}.

TABLE 5: Predicted Energies, Enthalpies, and Free Energies for the van Der Waals Complex Concerted TS, and Cycloadduct for the Cycloaddition of Ozone with Acetylene

method	ΔE(highest)[a]	ΔE	$\Delta H_{(0K)}$	$\Delta H_{(298K)}$	$\Delta G_{(298K)}$
		$O_3 + C_2H_2 \rightarrow$ vdW Complex (**1**)			
CBS-QB3	−2.1	−2.0	−1.2	−1.0	5.6
CBS-APNO	−2.1	−2.0	−1.6	−1.1	3.1
G3	−0.2	−0.1	0.3	0.8	4.8
G3B3	−1.7	−1.6	−0.8	−0.7	6.1
G3(MP2)B3	−1.7	−1.5	−0.7	−0.6	6.2
G4	−1.9	−1.6	−0.8	−0.7	5.9
G4(MP3)	−1.9	−1.2	−0.4	−0.3	6.3
G4(MP2)	−1.9	−1.5	−0.7	−0.6	6.0
focal point		**−1.9**	**−1.1**	**−1.2**	**4.4**
		$O_3 + C_2H_2 \rightarrow$ Concerted TS (**2**)			
CBS-QB3	7.3	3.0	4.4	3.3	13.5
CBS-APNO	7.8	4.9	6.6	5.3	15.7
G3	4.3	11.1	12.7	11.5	21.8
G3B3	6.2	6.4	7.8	6.8	16.8
G3(MP2)B3	6.2	5.9	7.3	6.2	16.3
G4	6.3	7.5	9.0	7.9	18.0
G4(MP3)	6.3	8.6	10.0	8.9	19.1
G4(MP2)	6.3	6.9	8.4	7.3	17.4
focal point		**7.7**	**9.4**	**8.6**	**18.8**
		$O_3 + C_2H_2 \rightarrow$ Cycloadduct (**3**)			
CBS-QB3	−59.8	−65.0	−60.8	−62.3	−51.3
CBS-APNO	−62.4	−64.7	−59.9	−61.5	−50.3
G3	−63.6	−62.4	−57.7	−59.3	−48.2
G3B3	−64.6	−61.8	−57.3	−58.9	−47.8
G3(MP2)B3	−64.6	−61.8	−57.3	−58.8	−47.8
G4	−65.5	−61.8	−57.4	−58.9	−47.9
G4(MP3)	−65.5	−61.4	−57.1	−58.6	−47.6
G4(MP2)	−65.5	−61.7	−57.3	−58.8	−47.8
focal point		**−63.0**	**−57.9**	**−55.5**	**−44.4**

[a] Explicitly computed electronic energy barrier at the highest level of correlation considered in the composite methods: CCSD(T/)6-31+G† for CBS-QB3; QCISD(T)/6-311++G(2df,p) for CBS-APNO; QCISD(T)/6-31G(d) for G3, G3B3, and G3(MP2)B3; and CCSD(T)/6-31G(d) for G4, G4(MP3), and G4(MP2).

TABLE 6: Predicted Energies, Enthalpies, and Free Energies for the van Der Waals Complex, Concerted TS, and Cycloadduct for the Cycloaddition of Ozone with Ethylene.

method	ΔE(highest)[a]	ΔE	$\Delta H_{(0K)}$	$\Delta H_{(298K)}$	$\Delta G_{(298K)}$
		$O_3 + C_2H_4 \rightarrow$ vdW Complex (**4**)			
CBS-QB3	−1.4	−1.9	−0.6	−0.6	7.5
CBS-APNO	−2.4	−2.2	−1.8	−1.0	2.0
G3	1.4	1.1	1.6	2.3	5.9
G3B3	−1.3	−1.3	0.0	0.0	8.2
G3(MP2)B3	−1.3	−1.1	0.2	0.2	8.4
G4	−2.0	−1.5	−0.3	−0.3	7.5
G4(MP3)	−2.0	−0.9	0.3	0.4	8.2
G4(MP2)	−2.0	−1.3	−0.1	−0.1	7.7
focal point		**−1.8**	**−1.2**	**−1.3**	**4.5**
		$O_3 + C_2H_4 \rightarrow$ Concerted TS (**5**)			
CBS−QB3	2.7	−1.1	0.7	−0.3	10.5
CBS-APNO	3.2	0.3	2.6	1.3	12.5
G3	0.5	−1.6	0.5	−0.6	10.4
G3B3	1.7	1.3	3.0	2.1	12.6
G3(MP2)B3	1.7	1.3	3.0	2.1	12.6
G4	2.2	2.8	4.6	3.6	14.4
G4(MP3)	2.2	4.1	5.9	4.9	15.7
G4(MP2)	2.2	2.6	4.4	3.4	14.2
focal point		**3.4**	**5.3**	**4.0**	**13.7**
		$O_3 + C_2H_4 \rightarrow$ Cycloadduct (**6**)			
CBS-QB3	−53.6	−59.2	−54.2	−55.8	−43.9
CBS−APNO	−56.2	−58.3	−52.5	−54.1	−42.1
G3	−56.6	−56.1	−50.6	−52.2	−40.4
G3B3	−57.6	−55.7	−50.8	−52.3	−40.5
G3(MP2)B3	−57.6	−55.2	−50.3	−51.9	−40.0
G4	−58.4	−55.2	−50.4	−51.9	−40.0
G4(MP3)	−58.4	−54.4	−49.6	−51.1	−39.2
G4(MP2)	−58.4	−54.8	−49.9	−51.5	−39.6
focal point		**−56.4**	**−50.9**	**−48.3**	**−36.0**

[a] Explicitly computed electronic energy barrier at the highest level of correlation considered in the composite methods: CCSD(T/)6-31+G† for CBS-QB3; QCISD(T)/6-311++G(2df,p) for CBS-APNO; QCISD(T)/6-31G(d) for G3, G3B3, and G3(MP2)B3; and CCSD(T)/6-31G(d) for G4, G4(MP3), and G4(MP2).

To surmise the cause of these underestimations, the CBS-QB3 predicted barrier for the addition of ozone to acetylene are examined in detail. To asses the errors caused by the use of B3LYP geometries, CBS-Q energies were computed following the same prescription as the standard CBS-QB3 procedure but utilizing the more reliable CCSD(T)/cc-pVTZ optimized geometries. The resulting non-ZPVE corrected barrier height (3.1 kcal mol^{-1}) is only 0.1 kcal mol^{-1} higher than that computed using the standard CBS-QB3 approach. Despite differences between the B3LYP and CCSD(T) optimized structures (Figure 1), the B3LYP geometries are clearly not the source of the errors in the CBS-QB3 predicted reaction barrier. Similarly, the scaled B3LYP ZPVE correction of 1.3 kcal mol^{-1} used in CBS-QB3 is in reasonable agreement with the CCSD(T)/cc-pVTZ value of 1.6 kcal mol^{-1}, supporting the use of ZPVE corrections derived from B3LYP harmonic vibrational frequencies in CBS-QB3, G3B3, G3(MP2)B3, and the G4 methods.

The CBS-QB3 energy (without ZPVE correction) is normally written as

$$\begin{aligned} E^{\text{CBS-QB3}} &= E(\text{MP2/CBSB3}) + \\ &E(\text{MP2 CBS extrapolation}) + E(\text{int}) \\ &+ E(\text{MP4/CBSB4}) - E(\text{MP2/CBSB4}) \\ &+ E[\text{CCSD(T)/6-31+G}^{\dagger}] - E(\text{MP4/6-31+G}^{\dagger}) \\ &+ E(\text{empirical}) \end{aligned}$$

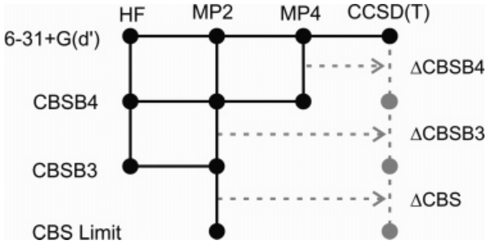

Figure 3. Pictorial representation of basis set corrections in CBS-QB3. The black circles and lines represent explicitly computed energies, and energy differences, respectively. The gray circles depict energies estimated by transferring (depicted by arrows) basis set corrections derived from lower level calculations. The CBS-QB3 energy, before empirical corrections, is an estimate of the CBS limit CCSD(T) energy (lower right).

where the basis set designations CBSB3 and CBSB4 indicate the 6-311++G(2df,2p) and 6-31+G(d,p) basis sets (for elements H through Si), respectively. The E(MP2 CBS Extrapolation) term corrects the MP2/CBSB3 energy for basis set incompleteness, and E(int) approximately accounts for the difference in basis set effects between MP2 and full configuration interaction (FCI). The CBS-QB3 energy expression can be rearranged as follows:

$$\begin{aligned} E^{\text{CBS-QB3}} &= E[\text{CCSD(T)/6-31+G}^{\dagger}] \\ &+ E(\text{MP4/CBSB4}) - E[\text{MP4/6-31+G}^{\dagger}] && (\Delta\text{CBSB4}) \\ &+ E(\text{MP2/CBSB3}) - E(\text{MP2/CBSB4}) && (\Delta\text{CBSB3}) \\ &+ E(\text{MP2 CBS extrapolation}) + E(\text{int}) && (\Delta\text{CBS}) \\ &+ E(\text{empirical}) \end{aligned}$$

Written this way, the CBS-QB3 energy, before small empirical corrections, can be viewed as a CCSD(T)/6-31+G† energy augmented by basis set corrections (ΔCBSB3, ΔCBSB3, and ΔCBS above) derived from MP2 and MP4 computations. This is represented pictorially in Figure 3. Although E(int) is designed to account for differences in basis set incompleteness effects between MP2 and FCI, this correction should be similar to the difference between the basis set effects in MP2 and CCSD(T). The assumption underlying CBS-QB3 and most other composite approaches is that effects of basis set incompleteness can be recovered at the MP2 and MP4 level and added to the CCSD(T) energy. The validity of these corrections, and the underlying assumptions, can be examined by comparing explicitly computed CCSD(T) barriers with the estimates utilized in CBS-QB3, provided in Table 7. The ΔCBSB4 correction [*i.e.*, the difference between CCSD(T)/6-31+G† and CCSD(T)/CBSB4] is recovered accurately at the MP4 level: the estimated ΔCBSB4 correction (+0.14 kcal mol^{-1}) is close to the explicitly computed energy difference of +0.01 kcal mol^{-1}. However, the ΔCBSB3 correction is not accurately estimated from MP2 energies, with the ΔCBSB4 correction of −2.47 kcal mol^{-1} substantially larger than the explicitly computed basis set difference of −0.05 kcal mol^{-1}.

The error resulting from the CBS basis set extrapolation is of a similar magnitude. The CBS-QB3 estimate of ΔCBS for the reaction barrier is 2.1 kcal mol^{-1} more negative than that obtained by explicitly extrapolating CCSD(T) energies computed at the same B3LYP geometries. The uncertainty in this extrapolated CCSD(T) barrier is less than 0.2 kcal mol^{-1}. Additional errors arise in CBS-QB3 due to the neglect of basis set effects in the HF energies beyond the CBSB3 basis set. Again, from the extrapolated HF barrier evaluated at B3LYP/6-311G(d,p) geometries (24.2 kcal mol^{-1}), we see that the HF/

TABLE 7: Components of CBS-QB3 Computed Reaction Barrier (kcal mol^{-1}) for Ozone + C_2H_2 and the Basis Set Corrections Depicted in Figure 3[a]

	HF	MP2	MP4	CCSD(T)
6-31+G(d′)	**20.08**	**2.98**	**10.54**	**7.32**
CBSB4	**20.00**	**3.04**	**10.67**	7.33
CBSB3	**23.40**	**0.57**	11.89	7.28
CBS limit[b]	24.16 ± 0.02			6.80 ± 0.20

	estimated[c]	computed[d]
ΔCBSB4	+0.14	+0.01
ΔCBSB3	−2.47	−0.05
ΔCBS	−2.53	−0.48
Δ (empirical)	+0.54	

[a] Bold values are utilized to determine the CBS-QB3 energy, and nonbold values are provided for diagnostic purposes. All energies evaluated at the standard B3LYP/6-311G(d,p) optimized geometries. [b] Extrapolated HF and CCSD(T) energy barriers evaluated at B3LYP/6-311G(d,p) optimized geometries. The extrapolations were carried out as described in the Theoretical Methods for the focal point approach. Uncertainties in the extrapolated barriers come from the difference between the value computed with the largest basis set [aug-cc-pV5Z for HF, aug-cc-pVQZ for CCSD(T)] and the extrapolated value. [c] Estimated basis set corrections calculated as in CBS-QB3: ΔCBSB4 = E(MP4/CBSB4) − E[MP4/6-31+G†]; ΔCBSB3 = E(MP2/CBSB3) − E(MP2/CBSB4); ΔCBS = CBS extrapolation of MP2 pair correlation energies. [d] Computed basis set corrections from differences in CCSD(T) energies: ΔCBSB4 = E[CCSD(T)/CBSB4] − E[CCSD(T)/6-31+G†]; ΔCBSB3 = E[CCSD(T)/CBSB3] − E[CCSD(T)/CBSB4]; ΔCBS = E[CCSD(T)/CBS limit] − E[CCSD(T)/CBSB3], where E[CCSD(T)/CBS limit] was obtained by extrapolating CCSD(T)/aug-cc-pVXZ (X = T, Q) energies as done in the focal point approach.

CBSB3 barrier of 23.4 kcal mol^{-1} is 0.8 kcal mol^{-1} from the CBS limit. Thus, the major contributors to the CBS-QB3 error of −4.7 kcal mol^{-1} are as follows:

−2.4 kcal mol^{-1} due to ΔCBSB3;

−2.1 kcal mol^{-1} due to ΔCBS;

−0.8 kcal mol^{-1} due to basis set incompleteness in the HF/CBSB3 barrier.

The empirical correction, E(emp) = +0.5 kcal mol^{-1} does little to compensate for these errors. The largest errors arise from the nontransferability of MP2 basis set effects to CCSD(T) barriers.

For the energy of the van der Waals complex of ozone and acetylene the composite methods tested perform remarkably well. Apart from G3 theory, the predicted enthalpies of the van der Waals complex are within 1 kcal mol^{-1} of the focal point result of −1.1 kcal mol^{-1} relative to separated reactants. G3 theory fails to predict a stabilized complex, yielding an enthalpy (0 K) of +0.3 kcal mol^{-1}. G3 theory fortuitously fares much better for the reaction enthalpy, with the predicted value of −57.7 kcal mol^{-1} in excellent agreement with the focal point value. The G3B3, G3(MP2)B3, G4, G4(MP3), and G4(MP2) approaches also perform superbly, whereas the CBS-QB3 and CBS-APNO slightly overestimate the exothermicity of these reactions. Apart from CBS-QB3, all of these predictions are within the 2 kcal mol^{-1} uncertainty associated with the focal point reaction energy. The performance of these approaches relative to the focal point value is remarkable, given the demonstrated slow convergence of this reaction energy with respect to inclusion of electron correlation and the inclusion of a 2.3 kcal mol^{-1} correction for quadruple excitations in the focal point results. That these composite methods perform significantly better for the more computationally demanding reaction energy than for the reaction barrier suggests the fortuitous cancellation of sizable errors.

For the ozone−ethylene vdW complex the performance of the black box approaches is less satisfactory. Although the focal point extrapolations predict $\Delta H_{(0K)} = -1.2$ kcal mol^{-1}, few of the composite approaches considered predicts an enthalpically bound complex. CBS-QB3 and CBS-APNO predict complexation enthalpies within 1 kcal mol^{-1} of the focal point result. The G*n* methods perform quite well for reaction energy of ozone and ethylene, as was seen for $O_3 + C_2H_2$. The CBS-QB3 approach overestimates the exothermicity by just over 3 kcal mol^{-1}.

IV. Enthalpies of Formation of Primary Ozonides

The computed reaction enthalpies for the 1,3-dipolar cycloadditions of ozone with acetylene and ethylene (Table 3) provide a means of evaluating enthalpies of formation of the primary ozonide cycloadducts (1,2,3-trioxole and 1,2,3-trioxolane). Relative to reference enthalpies of formation for ozone, ethylene, and acetylene,[99,100] the recommended $\Delta_f H^{\circ}_{298}$ values for 1,2,3-trioxole (**3**) and 1,2,3-trioxolane (**6**) are +32.8 and −1.6 kcal mol^{-1}, respectively. The value for 1,2,3-trioxole (**3**) is in reasonable agreement with the value of 30.5 kcal mol^{-1} reported by Cremer *et al.*[16] The recommended enthalpy of formation for the cycloadduct ozone + ethylene; however, is 10 kcal mol^{-1} higher than the value computed by Olzmann et al. (−12.2 kcal mol^{-1}).[25] This large difference is a result of the overestimation of the exothermicity of the reaction of ozone with ethylene in that work.

V. Conclusions

Accurate barriers for the concerted cycloaddition of ozone with acetylene and ethylene have been determined through the systematic extrapolation of *ab initio* energies within the focal point approach of Allen and co-workers. Results from a number of popular composite *ab initio* approaches were also examined, yielding an unsatisfactorily inconsistent set of predicted reaction barriers. Traditionally reliable composite approaches (CBS-QB3 and G3B3) predict barriers that are significantly smaller than reference focal point values. In the case of the CBS-QB3 predicted energy barrier for ozone and acetylene, this underestimation was shown to be due to large basis set effects in MP2 energies not mirrored in CCSD(T) energies. In most cases, the corrections utilized in these black box approaches actually degrade the predictions of these barrier heights. The result is that the predictions from these composite approaches are worse than the computed barrier using the underlying small basis set CCSD(T) or QCISD(T) single points. Interestingly, it was inaccurate thermochemistry for atmospheric reactions involving ozone that spurred the development of the CBS-4 and eventually CBS-Q approaches.[57] That the CBS-QB3 method seems to fail for barriers of 1,3-dipolar cycloadditions involving ozone is a testament to the treacherous electronic structure of this molecule.

The “black box” nature of CBS-QB3 and other popular composite *ab initio* model chemistries is particularly attractive. However, though having an automated, fixed procedure allows for the widespread use of these methods, particularly among nonexperts, some systems are simply not treated properly using such rigidly defined methods. Because these model chemistries are generally designed to yield results within some chosen error threshold with minimum computational expense (and therefore maximal applicability), the general design philosophy is to seek the *minimum* levels of theory required to yield satisfactory theoretical results across a given test set. The result for CBS-QB3 was that large deviations from expected statistical behavior was observed and documented in early applications, with multiple systems exhibiting errors five standard deviations from the mean errors observed for the G2/97 test set.[57] This fact seems to be underappreciated, with results from these black box methods assumed to be of "benchmark quality" and applied with impunity.

Despite going to great lengths to compute converged energies for these prototypical reactions, the final predicted values (−57.9 and −50.9 kcal mol^{-1} for ozone with acetylene and ethylene, respectively) carry uncertainties of at least 2 kcal mol^{-1}. This is due to the painfully slow convergence of the coupled cluster series for these systems. This is in contrast to the final recommended barriers (9.4 ± 0.2 and 5.3 ± 0.2 kcal mol^{-1} for acetylene and ethylene, in order), which are converged with respect to one- and *N*-particle basis set completeness, and represent the most reliable computed barriers available for these systems.

Composite *ab initio* approaches are of great utility in day-to-day applications. Among these, the CBS-QB3 approach has proved invaluable in computing accurate reaction thermochemistry for a wide array of pericyclic reactions.[101] However, results from these approaches must be carefully scrutinized to ensure that the predictions are reliable. Examining the underlying energies for unexpected basis set effects and validating the assumptions upon which these composite approaches rely can identify some problem cases. In those cases more robust computational methods should be applied.

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Supporting Information Available: Comparisons of selected bond lengths and angles between previous work and the present work; Cartesian coordinates for all structures, optimized at the CCSD(T)/cc-pVTZ, B3LYP/6-311G(d,p), QCISD/6-311G(d,p), MP2(full)/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-31G(d,p) levels of theory. This material is available free of charge via the Internet at http://pub.acs.org.

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