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The $C_2H_3 + O_2$ Reaction Revisited: Is Multireference Treatment of the Wave Function Really Critical?

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This letter revisits critical intermediates and transition states of the $C_2H_3 + O_2$ reaction. To obtain their accurate relative energies, ab initio calculations are performed using sophisticated single and multireference theoretical methods with various basis sets. The energy difference between two crucial transition states, for ring opening in dioxiranylmethyl radical and its isomerization to C_2H_3OO, is calculated as ~2 kcal/mol both at multireference MRCI and at single-reference CCSD(T) levels extrapolated to the complete basis set limit. The deviation from the earlier G2M(RCC,MP2) value (~7 kcal/mol) is caused by a deficiency of the 6-311+G(3df,2p) basis set as compared to correlation-consistent Dunning's basis sets.

The reaction of vinyl radicals with molecular oxygen is of immense importance in the combustion of hydrocarbon fuels, as it represents a key step in the high-temperature oxidation of C_2H_4 in ethylene and acetylene flames.[1−3] Successive reaction products of vinyl radicals with unsaturated hydrocarbons have been shown to be a potential source of benzene,[4] the initial building block of polyaromatic hydrocarbons (PAH), which are precursors to soot.[5−7] The $C_2H_3 + O_2$ reaction retards soot formation by competing with the reactions of vinyl radicals with unsaturated hydrocarbons. Therefore, to model PAH formation in combustion, it is critical to accurately predict the reaction rate constants and product branching ratios as functions of combustion conditions, i.e., temperature and pressure.

Many product channels of the $C_2H_3 + O_2$ reaction may be energetically accessible, but the most important ones are believed to be the following:[8−14]

$$\begin{aligned} C_2H_3 + O_2 &\rightarrow C_2H_3OO + 46.4\ \text{kcal/mol} \\ &\rightarrow C_2H_3O + O + 9.0\ \text{kcal/mol} \\ &\rightarrow CHO + CH_2O + 87.5\ \text{kcal/mol} \\ &\rightarrow C_2H_2 + HO_2 + 13.4\ \text{kcal/mol} \end{aligned}$$

Recently, Yang et al.[15] carried out a matrix isolation study of this reaction in solid argon and identified among the products the vinylperoxy radical C_2H_3OO, which can undergo visible photon-induced dissociation to the $CH_2OH(CO)$ complex or $CH_2OH + CO$. Our earlier theoretical ab initio/RRKM study of multichannel rate constants and product branching ratios[16] demonstrated that, at atmospheric pressure and at room temperature, the reaction is dominated by the stabilization of vinylperoxy radical C_2H_3OO; in the 500−900 K temperature range, the $CHO + CH_2O$ products become preferable; at $T \geq$ 900 K, $C_2H_3O + O$ are the major products; and at very high temperatures, the channel leading to $C_2H_2 + HO_2$ starts to compete, although its contribution remains relatively minor.

According to the potential energy surface (PES) calculated at the G2M(RCC,MP2) level of theory,[16] the reaction mechanism can be briefly outlined as follows (see Figure 1). The reaction initiates by barrierless addition of O_2 to the radical site of C_2H_3 to produce the vinylperoxy radical. The latter can either lose the terminal oxygen atom to yield the $C_2H_3O + O$ products via TS **23** (and a weak $C_2H_3O{\cdot}O$ complex **24**) or rearrange to the dioxiranylmethyl radical **3** via TS **8**. At the next reaction step, **3** undergoes an O-atom insertion into the C−C bond via TS **9′** (it can be also described as ring opening of dioxiranylmethyl radical) and then, eventually, the $CHO + CH_2O$ products are formed. The O-insertion reaction step is strongly exothermic and its reverse barrier is very high, ~94 kcal/mol,[16] making this step practically irreversible. Thus, if the ring opening via TS **9′** does occur, $CHO + CH_2O$ will be the dominant products. Therefore, branching ratios of the major products, C_2H_3OO, $C_2H_3O + O$, and $CHO + CH_2O$, will be mostly controlled by relative energies and molecular parameters of five stationary points on the PES, intermediates **1** and **3** and transition states **23**, **8**, and **9′**. The total reaction rate constant, the experimental value of which[9,11,12] was quantitatively reproduced by our calculations,[16] is mostly determined by the PES for the entrance step, the addition of O_2 to C_2H_3, and is not very sensitive to the energies of the $C_2H_3O_2$ species mentioned above. However, the product branching ratios are expected to be very sensitive to their thermodynamical parameters.

At the G2M(RCC,MP2) level, the barriers for isomerization of the dioxiranylmethyl radical to vinylperoxy and oxiranyloxy radicals occurring at TSs **8** and **9′** were calculated to be 16.9 and 24.0 kcal/mol, respectively,[16] meaning that the dioxiranylmethyl intermediate **3** can more easily rearrange back to **1** than move forward to the $CHO + CH_2O$ products. Later, however, Carpenter[17] argued that wave functions of these critical transition

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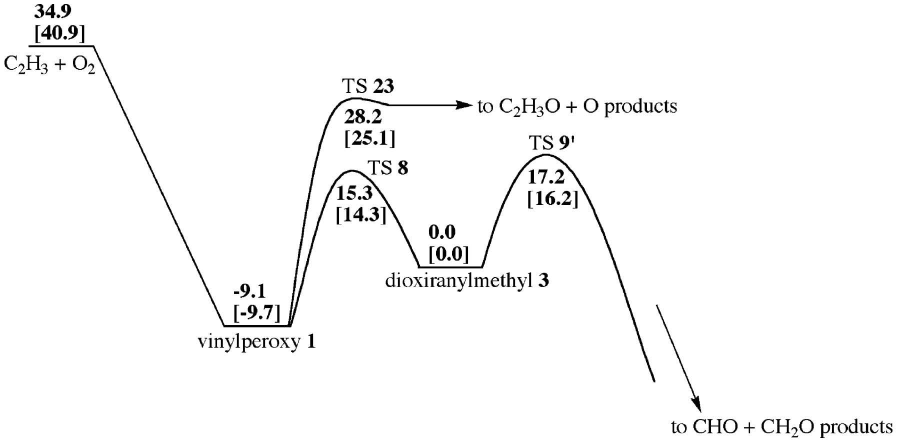


Figure 1. Schematic profile of PES for the $C_2H_3 + O_2$ reaction. The numbers show relative energies (in kcal/mol) estimated at the CCSD(T)/∞ and MRCI+Q/∞ (in brackets) levels of theory.

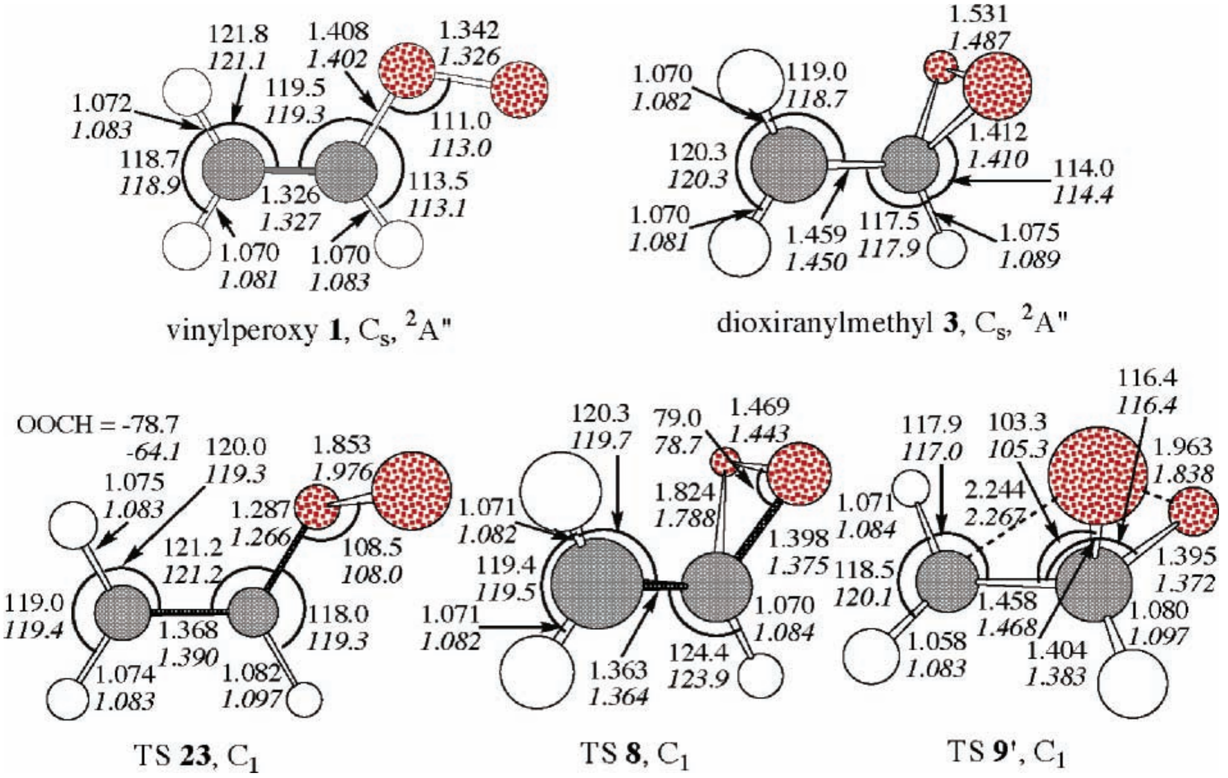
states have a multireference character and their energies cannot be accurately described by the single-reference CCSD(T) method, which is in the core of G2M schemes.[18] Using a CASPT2//CASSCF approach, Carpenter obtained the barrier heights (with respect to intermediate **3**) of 11.9 and 12.5 kcal/mol at TSs **8** and **9′**, respectively.[17] The deviations from our earlier results are rather significant, 11.5 kcal/mol for TS **9′**; moreover, the energy difference between the two transition states decreases from ∼7 kcal/mol at G2M(RCC,MP2) to only 0.6 kcal/mol at CASPT2, which may have a significant effect on the product branching ratios. On this basis, Carpenter questioned the applicability and reliability of single-reference computational models to bond-breaking events in general and concluded that "the assumption that composite ab initio methods of the G2 type can be applied reliably to transition structures merits closer examination".[17]

Indeed, the differences between the G2M(RCC,MP2) and CASPT2 results are much larger than the normally expected error bars for Gaussian 2-type model chemistries,[19] and they certainly deserve to be examined closely. Usually, the CCSD(T) method performs quite well for systems with moderate multireference wave functions[20] as compared to MRCI or CASPT2 and has the advantage that all regions of the PES can be treated uniformly and the results do not depend on the active space choice, which could be biased at times. Multireference CASPT2 or MRCI methods with large and flexible basis sets, which take into account both nondynamical and dynamical contributions into electron correlation,[20] are in principle more robust than CCSD(T), but only if all valence electrons and valence orbitals are included in the calculations as part of the active space or at least through single and double excitations at the post-CASSCF stage. Otherwise, these methods may suffer from the subjectivity in the active space choice, and the results could be active-space-dependent. Also, the CASPT2 and MRCI energies may be of a rather poor quality if single and double excitations are not included from all valence electrons (beyond the active space), because a large portion of dynamical electron correlation then remains unaccounted for. Ideally, the proper active space for the $C_2H_3O_2$ species should include 23 valence electrons distributed over 19 orbitals. This large active space can be reduced to a more reasonable size if one includes only those orbitals that are involved in particular bond cleavage/bond formation processes and are important for description of nondynamical electron correlation; they are usually characterized by the orbital occupation numbers in the CASSCF wave function ranging from 1.98 to 0.02.[20] In his CASPT2//CASSCF calculations, Carpenter used a (23, 15) active space.[17] Although seemingly large, this active space may not be flexible enough, as it includes only 3 unoccupied orbitals and the number of configuration state functions (CSF) is rather moderate, 305 760. Another concern is that, while the CASPT2 method is in general reliable, it is still a perturbation theory method, inferior with respect to the more expensive MRCI approach.[20,21]

Because of this and also with the goal to determine relative energies for the most important intermediates and transition states on the $C_2H_3O_2$ PES as accurately as possible using up-to-date computational methods and hardware, we carried out multireference internally contracted MRCI and CASPT2 calculations for these species.[22] In addition, to understand the basis set influence on the results, we performed CCSD(T) calculations with various basis sets. We also tested the performance of other variants of model chemistries including G2M(RCC),[18] G3(CC), G3(CC,MP2), G3, and G3(MP2).[23] Using all the aforementioned methods, we ran single-point energy calculations at the geometries optimized by the CASSCF(23, 15) method with Dunning's correlation-consistent cc-pVTZ basis set[24] and utilizing zero-point energy (ZPE) corrections obtained at the same CASSCF level and scaled by 0.92 similar to Carpenter's report.[17]

The optimized geometries for **1**, **3**, **8**, and **9′** are available from Carpenter's work,[17] so only the structure of TS **23** was reoptimized at this level. Geometric parameters obtained at the CASSCF(23,15)/cc-pVTZ and B3LYP/6-311G(d,p) levels are illustrated in Figure 2. The differences in geometries obtained at the two levels of theory in general are minor, within 0.01−0.02 Å for bond lengths and 1−2° for bond angles. The exceptions are O−O distances in **3** (the difference is 0.044 Å) and in TSs **23** and **9′** (0.122 and 0.125 Å, respectively). However, these parameters are nonrigid, and their change causes only insignificant alterations of relative energies. For instance, as seen in Table 1, the relative energies of **1**, **23**, **8**, and **9′** with respect to the dioxiranylmethyl radical **3** are calculated as −10.7, 21.4, 16.9, and 19.6 kcal/mol at the CCSD(T)/6-311G(d,p) level with the CASSCF(23,15)/cc-pVTZ optimized geometries and ZPE corrections obtained at CASSCF(23,15)/cc-pVTZ and scaled by 0.92. These values are close to the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p)+ZPE[B3LYP/6-311G(d,p)] values reported in our earlier work, −11.1, 21.0, 15.4, and 19.6 kcal/mol for **1**, **23**, **8**, and **9′**, respectively.[16] Therefore, the change of the theoretical method for geometry optimization and ZPE from B3LYP to CASSCF does not greatly affect the higher-level single-point relative energies.

We turn now to the results of multireference MRCI and CASPT2 calculations, which were carried out with the cc-pVTZ basis set. We have chosen a larger active space, which included



vinylperoxy **1**, C_s, $^2A''$

dioxiranylmethyl **3**, C_s, $^2A''$

TS **23**, C_1

TS **8**, C_1

TS **9′**, C_1

Figure 2. Geometries of critical intermediates and transition states in the $C_2H_3 + O_2$ reaction optimized at the CASSCF(23,15)/cc-pVTZ (plain numbers) and B3LYP/6-311G(d,p) (in italic) levels of theory. Bond lengths are given in Å and bond angles in degrees.

TABLE 1: Relative Energies (kcal/mol) of Various Species in the $C_2H_3 + O_2$ Reaction Calculated at Different Theoretical Levels[a]

	$C_2H_3 + O_2$	$C_2H_3O_2$ **1**	$C_2H_3O_2$ **3**	TS **23**	TS **8**	TS **9′**
CCSD(T)/6-311G(d,p)	27.51	−10.73	0.00	21.38	16.90	19.63
CCSD(T)/6-311+G(3df,2p)	34.32	−8.69	0.00	27.12	16.51	21.65
G2M(RCC,MP2)	38.30	−8.10	0.00	30.50	16.90	24.00
G2M(RCC)	38.68	−8.36	0.00	26.72	18.02	22.55
G3(CC,MP2)	34.17	−9.76	0.00	26.60	16.27	23.33
G3(CC)	33.88	−10.65	0.00	26.59	16.20	23.28
G3(MP2)	33.96	−10.84	0.00	26.63	17.03	23.45
G3	34.21	−9.95	0.00	26.62	17.10	23.50
CCSD(T)/cc-pVDZ	26.50	−11.08	0.00	19.49	14.63	16.04
CCSD(T)/cc-pVTZ	32.96	−9.51	0.00	26.76	15.52	17.91
CCSD(T)/cc-pVQZ	34.11	−9.28	0.00	27.63	15.40	17.49
CCSD(T)/aug-cc-pVTZ	34.45	−8.88	0.00	26.59	14.84	16.55
CASSCF(13,11)/cc-pVTZ	75.50	−1.67	0.00	8.02	23.10	4.74
CASPT2(9,9)/cc-pVTZ	22.34	−11.90	0.00	20.14	10.62	10.46
MRCI(9,9)/cc-pVTZ	47.89	−6.45	0.00	22.34	16.35	23.47
MRCI+Q(9,9)/cc-pVTZ	38.99	−10.13	0.00	23.64	14.50	16.89
CCSD(T)/∞	34.90	−9.12	0.00	28.23	15.32	17.21
MRCI+Q/∞	40.92	−9.74	0.00	25.11	14.29	16.18

[a] All single-point energy calculations were carried out at CASSCF(23,15)/cc-pVTZ optimized geometries, and ZPE corrections were obtained at the same CASSCF level and scaled by 0.92.

11 electrons distributed at 13 orbitals at the CASSCF stage. This means that 7 unoccupied orbitals were involved in the active space and the number of CSFs was 981 552, larger than that for the (23, 15) active space by more than a factor of 3. CASPT2 and MRCI calculations with the (11, 13) active space were not feasible, and they were carried out with a smaller (9, 9) active space; however, all occupied valence orbitals (23 electrons) were subject to single and double excitations at the post-CASSCF stage. It should be noted that even the (9, 9) active space safely includes all molecular orbitals (MOs) with occupation numbers between 1.98 and 0.02 and is still larger than the (23, 15) active space in terms of the number of CSFs (474 516 vs 305 760). The dynamical correlation effects for the 14 remaining valence electrons, which are not in the active space, were included through single and double excitations from the corresponding occupied MOs at the MRCI or CASPT2 stage. The MRCI(9,9)-CASSCF(11,13) calculations are extremely demanding computationally; a single-point run for a nonsymmetric structure takes about 29 days on a 64-bit Itanium 2 1.5-GHz processor with 4 GB RAM (this time decreased by a factor of 2.1 when 8 GB RAM was used; actually, about 14 GB RAM is required for the most efficient performance). CASPT2 calculations with the same active space are faster approximately by a factor of 10.9.

The results are summarized in Table 1. First, one can clearly see that the MRCI relative energies (with Davidson's corrections for quadruple excitations, MRCI + Q) closely agree with the CCSD(T) values calculated with the same cc-pVTZ basis set and with scaled CASSCF(23,15)/cc-pVTZ ZPE corrections. The differences are ~1 kcal/mol or less for **1** and TSs **8** and **9′** and 3.1 kcal/mol for TS **23**. The T1 diagnostic values[20] in CCSD(T)/cc-pVTZ calculations are 0.017, 0.032, 0.036, 0.056, and 0.023 for **3**, **1**, **8**, **9′**, and **23**, respectively. Although these values are close to or exceed 0.02, the single-reference CCSD(T) method is able to describe the energies of these structures properly, in good agreement with the most sophisticated multireference approach, MRCI. On the other hand, the CASPT2 results significantly disagree with the MRCI + Q values; the barriers at TSs **8** and **9′** are underestimated by 4.9 and 6.4 kcal/mol, respectively. Interestingly, the present CASPT2(9,9)-CASSCF(11,13) relative energies of **8** and **9′**, 10.6 and 10.5 kcal/mol, are close to the values obtained by Carpenter at CASPT2(23,15)-CASSCF(23,15), 11.9 and 12.5 kcal/mol, respectively.[17] This indicates that the results are not so sensitive to the active space choice, as long as it includes MOs most significant for the description of nondynamical correlation and all valence electrons are accounted for in calculations of dynamical correlation. The deviations of the CASPT2 values from presumably most accurate MRCI ones in this case may be caused by deficiencies of CASPT2 as a perturbation theory method. As the CCSD(T) energies are reasonably close to the MRCI results, the multireference treatment of the wave function does not appear to be critical for this particular species; at least, CCSD(T) performs more accurately than CASPT2.

Nevertheless, there are still significant deviations of the G2M(RCC,MP2) energies from the present MRCI/cc-pVTZ values, up to 7 kcal/mol for TSs **23** and **9′**. To understand the origin of this difference, we performed CCSD(T) calculations with a variety of basis sets and also using different G2- and G3-type composite schemes. The G2M family of methods targets the approximation of CCSD(T)/6-311+G(3df,2p) energies with a "higher-level correction" (HLC) depending on the number of electron pairs and unpaired electrons.[18] As we count relative energies with respect to **3**, HLC cancels out for all species but $C_2H_3 + O_2$ and does not affect the barrier heights. Hence, let us first compare the CCSD(T) results with the 6-311+G(3df,2p) and cc-pVTZ basis sets. They are close to each other, within 1 kcal/mol, for all species except TS **9′** for the ring opening of the dioxiranylmethyl radical, for which the CCSD(T)/6-311+G(3df,2p) value, 21.6 kcal/mol, overestimates the CCSD(T)/cc-pVTZ result by 3.7 kcal/mol. The rest of the difference between the G2M(RCC,MP2) and MRCI/cc-pVTZ relative energies of **9′**, totally 7.1 kcal/mol, accumulates from the error in the basis set correction from 6-311G(d,p) to 6-311+G(3df,2p), which is 3.0 kcal/mol at the CCSD(T) level vs 5.4 kcal/mol at the UMP2 level within the G2M(RCC,MP2) scheme, and from the difference in the CCSD(T)/cc-pVTZ and MRCI/cc-pVTZ values, 1.0 kcal/mol. The basis set correction error is much smaller in the G2M(RCC) scheme; the difference between the CCSD(T)/6-311+G(3df,2p) and G2M(RCC) relative energies of TS **9′** is only 0.9 kcal/mol. For TS **23**, the deviation between the G2M(RCC,MP2) and MRCI/cc-pVTZ energies is 6.9 kcal/mol, and it is due to the difference between the CCSD(T)/cc-pVTZ and MRCI/cc-pVTZ energies, 3.2 kcal/mol, and the error in the basis set correction, 3.8 kcal/mol. When G2M(RCC) is used, the basis set correction error decreases to 0.6 kcal/mol, and all values obtained by various G3 schemes are also close to those obtained by CCSD(T)/6-311+G(3df,2p) and G2M(RCC). Finally, for $C_2H_3 + O_2$, the CCSD(T)/6-311+G(3df,2p), CCSD(T)/cc-pVQZ, and various G3 energies are close to 34 kcal/mol, while the G2M(RCC) and G2M(RCC,MP2) values exceed 38 kcal/mol. In this case, the deviation is due to a large HLC, ~3.5 kcal/mol, employed in the G2M schemes.[18]

TABLE 2: RMS Deviations of G2M and G3 Relative Energies from the CCSD(T)/∞ Best Estimates

level of theory	RMS, kcal/mol
CCSD(T)/6-311+G(3df,2p)	2.14
G2M(RCC,MP2)	3.64
G2M(RCC)	3.26
G3(CC,MP2)	2.90
G3(CC)	2.96
G3(MP2)	3.11
G3	3.05

To generate best estimates for relative energies of all species considered here, we extrapolated our best CCSD(T) and MRCI + Q results to the infinite basis set limit. For CCSD(T), we used the following expression to make such extrapolation[25]

$$E[\mathrm{CCSD(T)}/\infty] \approx E[\mathrm{CCSD(T)/cc\text{-}pVQZ}] + \{E[\mathrm{CCSD(T)/cc\text{-}pVQZ}] - E[\mathrm{CCSD(T)/cc\text{-}pVTZ}]\} \times 0.6938$$

For MRCI + Q, we were able to carry out calculations only with the cc-pVTZ basis, so we used the basis set correction from cc-pVTZ to cc-pVQZ and the extrapolation from CCSD(T)

$$E[\mathrm{MRCI{+}Q}/\infty] \approx E[\mathrm{MRCI{+}Q/cc\text{-}pVTZ}] + \{E[\mathrm{CCSD(T)/cc\text{-}pVQZ}] - E[\mathrm{CCSD(T)/cc\text{-}pVTZ}]\} + \{E[\mathrm{CCSD(T)/cc\text{-}pVQZ}] - E[\mathrm{CCSD(T)/cc\text{-}pVTZ}]\} \times 0.6938$$

As seen from the results in Table 1, the barriers at TSs **9′**, 16−17 kcal/mol, and **8**, 14−15 kcal/mol, differ by about 2 kcal/mol, less than the 7 kcal/mol predicted by G2M(RCC,MP2)[16] but more than the 0.6 kcal/mol obtained by Carpenter at the CASPT2 level.[17] The difference is caused mostly by a deficiency of the 6-311+G(3df,2p) basis set for **9′**, but not by a failure of CCSD(T) to reproduce a multireference character of wave functions for these species. Significant differences between the CCSD(T) and MRCI + Q results are found for $C_2H_3 + O_2$ (~6 kcal/mol) and TS **23** (~3 kcal/mol), but we believe CCSD(T) to be more reliable for these cases because of size-consistency problems with the MRCI method.[20] Although the MRCI calculations were performed for a supermolecule, i.e., two fragments separated by 100 Å, the active space used was still far from complete, which may bias the energy of $C_2H_3 + O_2$ relative to the compact $C_2H_3O_2$ species. The same could be the case for TS **23**, which is constructed from the C_2H_3O and O fragments separated by a relatively large distance.

Let us finally compare the performance of various composite G2M and G3 methods vs the best CCSD(T)/∞ estimates. As seen in Table 2, the smallest root-mean-square (RMS) deviation, 2.14 kcal/mol, is found for CCSD(T)/6-311+G(3df,2p), which can be considered as "full G2M" without HLC. The largest RMS deviation, 3.64 kcal/mol, is computed for G2M(RCC,MP2), and the values for G2M(RCC) and various G3 schemes are close to 3 kcal/mol. The RMS deviations for this system are somewhat larger than what is typically expected from G2M and G3 methods (1−2 kcal/mol)[19,23] and are apparently caused by the deficiency of Pople's type basis sets as compared to correlation-consistent Dunning's basis sets.

In summary, the single-reference CCSD(T) method is shown to closely reproduce most accurately the MRCI results for the $C_2H_3O_2$ system if calculations are performed with the same basis set. Both B3LYP and CASSCF give similar optimized geometries and ZPEs, so that the choice of the geometry optimization method between the two does not practically affect the higher-level single-point relative energies. The present study reconfirms the value of the CCSD(T) method as an efficient, generally reliable, and uniform alternative to multireference calculations, applicable to chemical processes (including bond-breaking events), which involve single-reference and moderately multireference wave functions, especially where MRCI calculations with appropriate active spaces are not feasible or too costly.

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