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LETTERS

Ring Opening of Dioxiranylmethyl Radical: A Caution on the Use of G2-Type ab Initio MO Methods for Mechanistic Analysis

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This letter reports the apparent failure of a nominally high-accuracy ab initio calculation of a modified G2 type for a reaction that is of considerable importance in hydrocarbon combustion. The failure is traced to the reliance on single-reference methods in the treatment of electron correlation. Its occurrence serves as a general caution about the use of such calculations for mechanistic analysis.

The development of both high-performance hardware and efficient algorithms for ab initio electronic-structure calculations has made the computation of properties with "chemical accuracy"[1] a relatively routine procedure for small molecules. The potential value of these calculations for the study of reaction mechanisms is self-evident, especially when the reactions under study are of such complexity that experimental methods of investigation are unavailable or unreliable. A case in point is the study of combustion mechanisms, where the hundreds or even thousands of elementary steps make experimental elucidation of an overall mechanism extremely challenging.[2] However, the intermediates generated in combustion reactions also provide challenges for computational techniques. There are two principal reasons: (1) the intermediates often have more atoms than can currently be handled by calculations that simultaneously use large basis sets and extensive configuration interaction and (2) most of the intermediates have open-shell electronic structures.[3]

The first of these problems has been addressed by the development of composite methods (notably G1−G3,[4] the various CBS methods,[5] and Martin's infinite basis set extrapolation[6]) that seek to simulate direct high-accuracy calculations with semiempirical additivity schemes, using results from more approximate and computationally tractable procedures. The second problem has been addressed by modification of the composite schemes in an effort to deal with difficulties that can arise from spin contamination in unrestricted wave functions. Notable among these approaches are the G2M[7] and CBS-RAD[8] methods, both of which rely on ROCCSD(T) as the highest level electron-correlation treatment but use unrestricted methods for geometry optimization and vibrational-frequency calculation.

All of these calculations are calibrated against experimental data on stable molecules or on intermediates that sit in relatively deep local potential-energy minima. Transition structures have not been included in the calibration sets for the obvious reason that experimental data are simply unavailable for many such species. However, questions of reaction mechanism inevitably involve the geometries and relative energies of transition structures, and so it has been something of an act of faith to trust that the computational models can give reliable insight into reaction mechanisms. The example described here suggests that such faith may not always be well founded.

The reaction of interest is the formation and subsequent rearrangement of the dioxiranylmethyl radical, **2**, from the vinylperoxy radical, **1**.[9] This sequence is now believed to be the principal route to CHO and CH_2O from reaction of the vinyl radical with O_2.[10] It also serves as a prototype for the ring opening of aromatic radicals by O_2 (Scheme 1).[9a,11] The formation and reactions of the vinylperoxy radical have been subjected to extensive study by Mebel et al., using the G2M(RCC,MP2) method.[10] On the basis of these calculations, the

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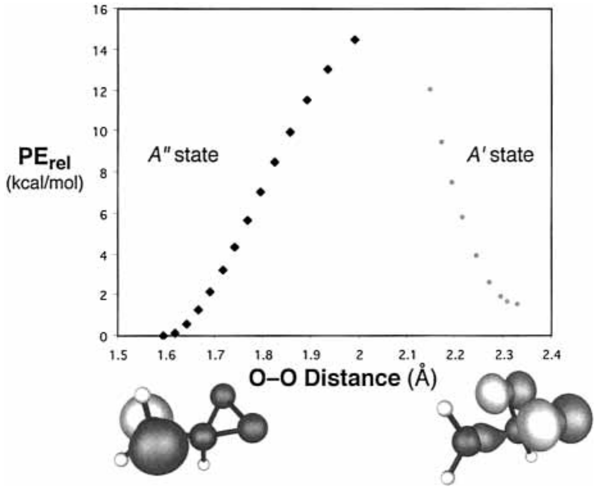
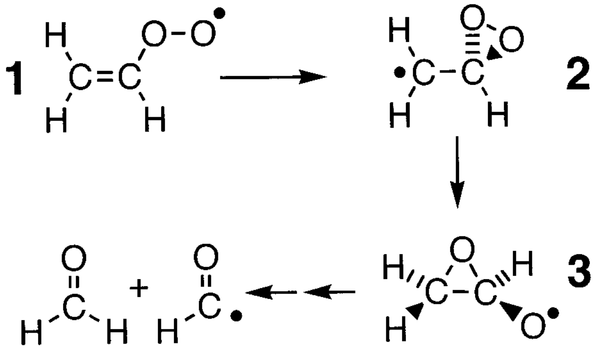


Figure 1. CASSCF(23,13)/6-31G(d) relative energies of the *A″* and *A′* states for the dioxiranylmethyl radical. The apparent minimum on the left is a true minimum. The apparent minimum on the right is a transition structure connecting the enantiomers of radical **3**, once the C_s symmetry restriction is lifted. The two orbitals are the singly occupied MOs in the principal configurations of each state.

SCHEME 1: Formation and Rearrangement of the Dioxiranyl-methyl Radical, 2



authors concluded that the rate-determining step in the conversion of vinylperoxy radical, **1**, to CHO + CH$_2$O is the rearrangement of dioxiranylmethyl radical, **2**, to oxiranyloxy radical, **3**. The activation enthalpy at 0 K for the conversion of **2** to **3** was calculated to be 24.0 kcal/mol, which was 7.1 kcal/mol higher than the barrier for ring opening of **2** back to **1**. The transition structure between **2** and **3** was found to be of C_1 symmetry. However, the authors also found a C_s-symmetry transition structure (similar in geometry to **2** but with an O−O distance of 2.38 Å) that was only 4.3 kcal/mol above **2**. IRC analysis showed this to be the transition structure for interconversion of the enantiomers of **3**. One can conclude from these results that the simple re-formation of the O−O bond from this latter transition structure, by contraction of the OCO angle in C_s symmetry, would have to have a barrier in excess of 19.7 kcal/mol. Because the origin of this barrier is not intuitively obvious, the reaction has been reinvestigated with CASSCF methods.[12] The results are reported here.

The changes in CASSCF(23,13)/6-31G(d) energy[13] on stretching the O−O bond in **2** or contracting the O−O distance in the C_s-symmetry transition structure are shown in Figure 1. Apparently the barrier between **2** and the C_s transition structure arises in part because these two species have different symmetries for their electronic ground states. The principal configuration for **2** singly occupies the *A″* orbital shown in Figure 1. For the C_s transition structure, the principal configuration has the singly occupied *A′* MO shown in Figure 1. The *A″* and *A′* potential-energy curves seem destined to cross at an O−O distance of around 2.15 Å, although the CASSCF calculations would not converge in this region, and so, the exact value is not known. It is apparent that this crossing should occur at about 16 kcal/mol above **2**. However, a lower barrier could be expected if the C_s symmetry were relaxed, allowing the erstwhile *A′* and *A″* configurations to mix.

If the only mixing on relaxation to C_1 were between the highest doubly occupied MO of one configuration and the singly occupied MO of the other, the resulting state could still be reasonably well described by a single-determinant wave function. However, closer analysis reveals a much more complex series of crossings. This is illustrated in Figure 2, which correlates the ROHF/6-31G(d) orbitals of dioxiranylmethyl radical and the C_s-symmetry transition structure. Of special note is the dramatic drop in energy of the LUMO of dioxiranylmethyl, the O−O σ^* MO, upon opening the ring. Even in C_s symmetry, this orbital mixes strongly with the other *A″* orbitals. Relaxation to C_1 would permit additional mixing with one of the *A′* orbitals. The resulting wave function might be poorly described by any single-determinant model or even a multideterminant model that used a single reference. These expectations were confirmed by CASPT2(23,15)/cc-pVTZ//CASSCF-(23,15)/cc-pVTZ calculations.[14]

The active space in the CASSCF calculations consisted of all of the valence bonding orbitals plus the singly occupied MO[13] and three antibonding MOs. For dioxiranylmethyl radical, **2**, and the two transition structures flanking it, the antibonding orbitals were the O−O σ^* and the two C−O σ^* MOs. For the vinylperoxy radical, **1**, the antibonding orbitals were the π^*, C−O σ^*, and O−O σ^* MOs. All valence electrons were treated as active. The calculation generated 305 760 configuration state functions with the correct spin; these served as the reference configurations for the single-point CASPT2 calculations.

The calculations were applied to radicals **1**−**3** and to the transition structures connecting them. The barrier (activation enthalpy at 0 K) to ring closure of **1** was found to be 23.9 kcal/mol, in quite good accord with the value of 25.0 kcal/mol found by the G2M(RCC,MP2) method.[10] However, the barrier to rearrangement of **2** was found to be 12.5 kcal/mol − only slightly more than half of the value from the G2M(RCC,MP2) calculations.

In the absence of experimental data on this reaction, one has to recognize that there is no objective way to prove that the CASPT2 results are more reliable than the G2M(RCC,MP2) values. However, circumstantial evidence can be used to suggest that this is the case. In Table 1, the CASPT2//CASSCF geometries and relative energies for the four stationary points are compared with the G2M(RCC,MP2) values. One sees that there is an apparent correlation of the discrepancy between the two methods with θ_{pop}, the angle between the vector of CASSCF natural orbital populations and the population vector for a single ROHF configuration. The population vectors respectively have elements ρ_i^{CASSCF}, the population of CASSCF natural orbital *i*, and ρ_i^{ROHF}, the population (2, 1, or 0) of orbital *i* in a ROHF wave function. The angle between the vectors is calculated as shown in eq 1:

$$\theta_{\mathrm{pop}} = \cos^{-1}\left(\frac{1}{45}\sum_{i=5}^{19}\rho_i^{\mathrm{CASSCF}}\,\rho_i^{\mathrm{ROHF}}\right) \qquad (1)$$

The larger the deviation from the ideal single-configuration population the less reliable single-reference models such as G2M(RCC,MP2) are expected to be and the greater the disagreement found between the two methods.

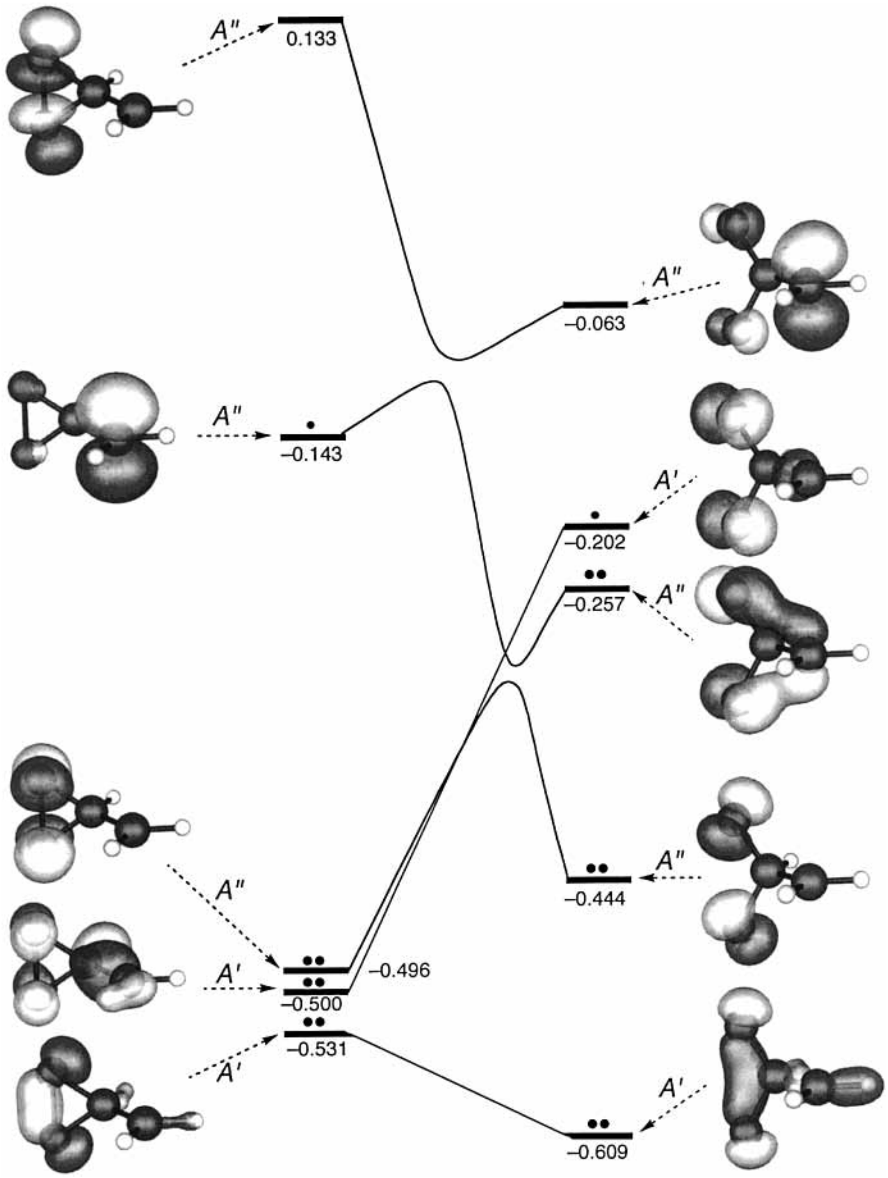


Figure 2. Correlation of ROHF/6-31G(d) orbitals for dioxiranylmethyl radical (left) and the C_s transition structure for degenerate rearrangement of the oxiranyloxy radical (right). The numbers are the orbital energies in hartree.

TABLE 1: Comparison of CASPT2//CASSCF and G2M(RCC,MP2) Results for Four Stationary Points in the Rearrangement of Radical 1 to Radical 3

structure	θ_{pop}[a]	Δr (Å)[b]	E_{rel} (kcal/mol)[c]	ΔE_{rel} (kcal/mol)[d]
1	7.26°	0.0166	−12.0	−3.9
TS **1** → **2**	8.22°	0.0214	11.9	−5.0
2	7.15°	0.0154	[0]	[0]
TS **2** → **3**	12.04°	0.0403	12.5	−11.5

[a] Deviation of CASSCF natural-orbital populations from a single-configuration ROHF ideal; see text for definition. [b] Structural comparison: RMS difference between one triangle of each of the distance matrixes. [c] CASPT2 relative energies including CASSCF ZPE corrections weighted by 0.92. [d] Difference between CASPT2 and G2M-(RCC,MP2) relative energies.

If the CASPT2 results are taken as the more reliable for the reaction described here, the consequences for combustion mechanisms are fairly significant. First, the CHO + CH_2O channel for the oxidation of the vinyl radical should become more important in kinetic models of combustion, as a result of the 7.6 kcal/mol reduction in the barrier to rearrangement of the vinylperoxy radical. Second, the related mechanisms that substituted vinyl radicals and aromatic radicals are believed to follow are presumably going to be similarly affected.[11]

More generally, one can question whether the application of single-reference computational models to bond-breaking events is justifiable even for reactions of closed-shell molecules, because such processes frequently involve transition structures with potential biradical character. At the very least, it would appear that the assumption that composite ab initio methods of the G2 type can be applied reliably to transition structures merits closer examination.

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Supporting Information Available: Cartesian coordinates, energies, and principal configurations of the four stationary points. This information is available free of charge via the Internet at http://pubs.acs.org.

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