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High Accuracy ab Initio Calculations on Reactions of OH with 1-Alkenes. The Case of Propene

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Abstract: The energetics of terminal, central OH-additions as well as allylic H-abstractions by OH in its reaction with propene was studied as proxies for the 1-alkenes + OH reactions using several single and multireference ab initio techniques with basis set extrapolation where possible. Selection of the localized occupied orbitals forming the active space for multireference methods is discussed. Initial geometries of the reactants, prereaction complex (π-complex), and transition states were determined at the [5,5]-CASPT2/cc-pVTZ level of theory. Frequency analysis was also carried out at this level with the introduction of a scale factor. Analyzing the results, it will be concluded that multireference effects are negligible, and from the various single reference models we will opt for UCCSD(T)/cc-pVTZ for final geometry optimizations and vibrational frequency analysis. These results will be compared with those from approximate models yielding information on the reliability of the latter. Triples contributions are found to be very important, except for the π-complex, which has a UCCSD(T)/CBS relative enthalpy of -10.56 kJ/mol compared to infinitely separated propene + OH. The addition transition states are found to have relative enthalpies of -9.93 kJ/mol for the central and -9.84 kJ/mol for the terminal case. Allylic abstraction mechanisms, although lying significantly higher, still have only slightly positive barriers - a value of 3.21 kJ/mol for the direct and 1.67 kJ/mol for the consecutive case. Conventional transition state theory was used as a rough estimation for determining rate constants and turned out to agree well with experimental data.

1. Introduction

As a result of their importance in a variety of fields, hydrogen transfer reactions are well studied both experimentally and theoretically, making comparisons possible. These reactions are favored model systems for the study of chemical reactivity. In their simplest forms they serve as models for reactive scattering and dynamics[1] or models for heavy + light-heavy atom reaction systems, e.g. symmetric H exchange between halogen atoms and hydrogen halogenids.[2,3]

They have served as useful model systems for testing standard theoretical approaches,[4,5] and many attempts have been made to describe similar systems with simple yet reliable approximations.[6,7]

An important special case of asymmetric H-transfer reactions plays an important role among hydrocarbon oxidation mechanisms. These are important in many areas of science, from understanding and reducing pollutant formation in combustion to describing partial oxidation in fuel cells.[8,9] It is widely accepted that the most common initial reaction of hydrocarbons in the atmosphere[10] and in all hydrocarbon frames[11] is the attack by an OH radical. Since propene can be a prototype of 1-alkenes, it is essential to characterize its

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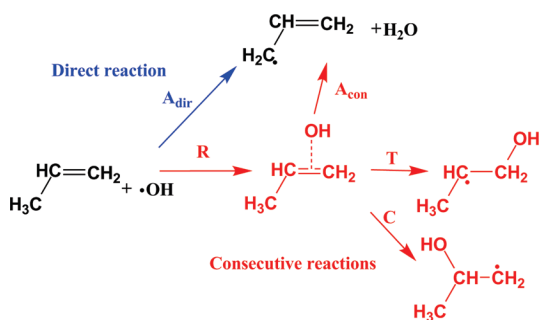
relevant reactions to understand the chemical behavior of 1-alkenes with the OH radical.

It is well-known that OH is able to attack the double bond of alkenes in terminal (**T**) and central (**C**) positions (Scheme 1). These addition reactions take place via a van der Waals complex (vdW-complex), a so-called π-complex (**R**). However, the importance of the hydrogen transfers such as the consecutive (**A**$_{con}$) and direct (**A**$_{dir}$) allylic H-abstractions in the case of alkenes + OH reactions has been recognized only recently.[12]

Although the propene and hydroxyl radical system has been studied previously and reported in several theoretical papers,[13-18] allylic H-abstraction channels were neglected in most cases. Earlier studies[13-16] have focused mostly on the ratio of the terminal and central addition reaction rates. Although Cvetanović reported in his work that 65% of the additions occur at the terminal carbon atom,[19] theoretical calculations at both the MP2/6-31+G(d)[16] and MP4(SDTQ)/6-31G(d,p)//MP2/6-311G(d,p)[13] levels of theory showed that central addition is preferred. However, it is emphasized in both theoretical works that the energy and entropy differences of the terminal and central transition states are quite small.[14] The interest in the kinetic behavior of the 1-alkene + OH system is also shown by papers published very recently[17,18] in this field, in which theoretical calculations offered a mainly kinetic description of the system. These works are mostly based on PMP2/aug-cc-pVQZ//MP2/cc-pVTZ[17] and CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ[18] methods. We have found relevant discrepancy between these latter two potential energy surfaces, although both state that their results are good descriptions of the overall kinetics. These results will be discussed to some extent later on. All this has led us to determine the accurate energetics of transition states corresponding to the energetically favored reaction channels with small difference in their energetics. Based on this set of calculations we are able to provide a highly accurate framework for kinetic modeling as well as a procedure for the logical choice for the active space in such asymmetric species. On the other hand, our aim was also to provide highly reliable results from benchmark ab initio calculations for further tests with density functional methods for larger alkene homologues.

2. Methodology

The relevant structures of the reaction system were determined by geometry optimizations performed at two different levels of theory. Initial optimizations were carried out at the [5,5]-CASPT2/cc-pVTZ level. This method allows for choosing relevant correlation contributions by selecting the proper active space, and, therefore, it reduces computational requirements compared to more accurate models. On these geometries, various single point calculations were then performed to study some factors such as the effect of multireference treatment, spin contamination, basis sets, and triples contributions. Based on these results, the UCCSD(T)/cc-pVTZ level of theory was chosen for the final geometry optimizations. Harmonic vibrational analysis was carried out at both levels ([5,5]-CASPT2 and UCCSD(T)). Results on these geometries will be compared in the following section.

For the [5,5]-CASPT2/cc-pVTZ level of theory, the active space should involve the SOMO in all cases. For **C** and **T** the π bond must be involved, since it participates in the C−O bond formation, and in the remainder of cases, this orbital corresponds to the most mobile electrons out of doubly occupied orbitals (highest orbital energy in RHF reference). For **A**$_{dir}$ and **A**$_{con}$ the breaking C−H bond must also be involved. For consistency, a C−H bond is involved in the active space for all cases. This makes the treatment balanced since the active space contains contributions for all non-hydrogen atoms for all species. Reactants (1-propene and OH) were treated in the supermolecular approach with a 1000 Å separation and share the same active space structure. This results in an active space of 5 electrons placed in 5 orbitals, 2 of which are unoccupied in the Hartree−Fock configuration. The occupied orbitals are chosen by first localizing the initial RHF orbitals, and then after analyzing the basis function contributions, the relevant orbitals may be identified. Similar procedures have been discussed in the literature, addressing the difficulty of choosing a balanced active space resulting in a correct correlation treatment.[5,20] Local orbitals simplify the choice of occupied orbitals; however, the difficulty of choosing the right virtual orbitals still remains. Here only the active occupied orbitals are preselected, and the virtuals are chosen purely on the basis of energetic order from the RHF reference. This procedure seems sufficient, since after the MCSCF optimization the active virtuals are the π^*(C−C) and the σ^*(C−H) antibonding orbitals as desired, see Figure 1. For further details see the following section.

The multiconfiguration nature of the wave function assures that the wave function is qualitatively correct, the long-range static correlation effects having been considered - avoiding the dissociation related problems of single reference methods. The choice of the CASPT2 method ensures that the most relevant short-range dynamic electron correlation effects important for geometry optimization are also considered. In the optimizations, the active space described above was used in all cases, for consistency, even in the cases, where the C−H bond remains intact. The removal of this orbital and a corresponding virtual one from the active space or the choice of an alternative C−H orbital, however, does not influence the result of the optimization significantly. Neither does the use of a basis set augmented with diffuse functions results in any relevant change. In both the case of the modified active space and the basis set augmentation, the resulting change
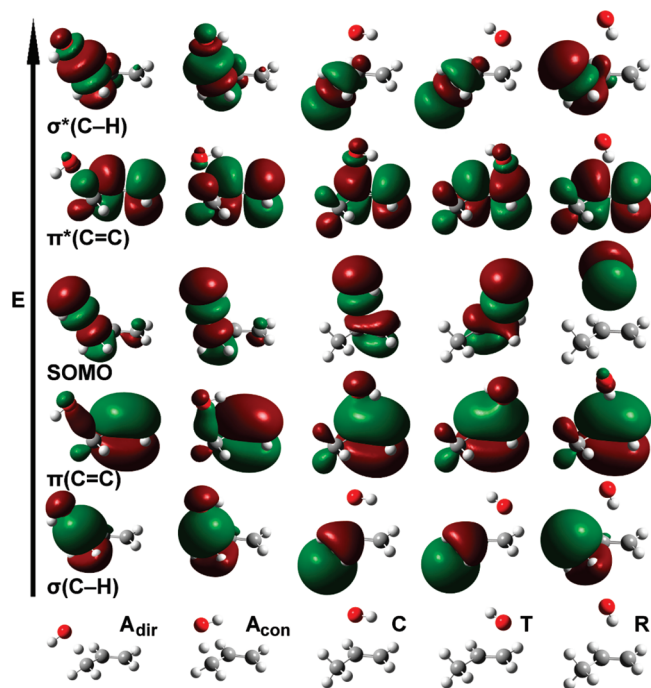
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Figure 1. [5,5]-CASSCF/cc-pVTZ active orbitals for the π-complex (**R**) as well as transition state structures of direct (**A**$_{dir}$) and consecutive (**A**$_{con}$) allylic H-abstraction; terminal (**T**) and central (**C**) OH-addition reaction channels.

is of the order of a few 0.01 Å in bond lengths and a few 0.1 degrees in angles, corresponding to perhaps a few 0.01 kJ/mol in the calculated energies due to reoptimization.

For a further improvement in our results various single point calculations were carried out with different basis sets and high level correlated methods. Various kinds of multi-reference (MR) methods were used, beginning with CASPT2 and CASPT3 perturbative methods. Although in some ways CASPT3 is an improvement over CASPT2, for barrier heights it definitely seems inferior.[21] These methods are cheaper alternatives of the more expensive MRCI method, namely in our calculations the internally contracted MRCI with singles and doubles (ICMRCISD)[22] was used. With the MRCI results, denoted by Q1 and Q2, the Davidson corrected energies for fixed and relaxed references respectively are given in an attempt to make the wave function size consistent by adding approximate quadruple corrections. As observed in the literature,[23] Q2 usually yields poorer agreement with FCI and should be used only in special cases. Following this, iterative size consistency correction methods follow, namely MRACPF and MRAQCC, which are two variants of an approximate MRCC. Both have a tendency to overshoot the correlation energy, the first one more than the latter.[24] For some further details about these methods, see e.g. ref 24.

Various single reference (SR) methods are also presented, the reliability of which depends on whether the wave function is dominated by one configuration during the calculation. To answer this, one can first take the T1 diagnostics (from CCSD calculations) which indicates the significance of higher excitations and therefore the possibility of a need for a multireference treatment.[25] For all transition states, with cc-pVQZ basis, the T1 values are roughly equivalent or less than the critical 0.02 value (and well below for minima). As

will be seen later on, the contribution of connected triple excitations has an important role, and with that included using a perturbative ansatz, a single reference treatment seems sufficient. One can also say based on multiconfiguration calculations that the weight of the ground state configuration is dominating (about 0.97) over all the rest (about 0.02 or less) at all examined geometries, and this dominance shows itself in the occupation numbers as well, those being quite close to the reference state values. This slightly changes with relaxation in MR calculations (see the difference between Q1 and Q2 corrections) and more significantly with the expansion of the active space (the dominance is still conserved although less evident). All this well justifies the use of single reference methods, and a further advantage will be that higher excitations are more feasible to include in the SR case.

The RMP2 values are gained as intermediate values in the coupled cluster procedure. The MP2 model suffers from some artifacts due to its lack of treating single excitations (for a study with FHF see Fox and Schlegel;[4] the arguments should hold for any H transfer with lone pairs close to the radical center). A variety of CC methods were also used, these are as follows: RHF-RCCSD and RHF-UCCSD models, RHF here referring to the reference orbitals. RCCSD is the partially spin restricted coupled cluster method (spin adapted in linear terms, which results in virtually no spin contamination).[26] Triples are treated in a variety of ways: the standard CCSD(T),[27] the simpler CCSD[T] missing the usually important singles contributions and CCSD-T[28] which considers some higher order perturbation terms compared to CCSD(T).

To approximate the nonrelativistic limit, extrapolations were carried out based with the cc-pVXZ bases[29,30] (X=D,T,Q), where the three point exponential formula of Feller[31] was used for HF and MCSCF results, and the two point X^{-3} function form[32] was used for correlation energies with X=T,Q. This latter choice is usually not too different from X=D,T, the most significant difference being with Davidson corrected energies, which show a slower convergence. In the multiconfiguration calculations the choice of the RHF or MCSCF wave functions as a reference in the Davidson correction does not introduce significant differences - which might be the case if there was a significant amount of dynamic correlation in the active space. In the RHF case, the extrapolation was checked against cc-pV5Z results, and it was found that the difference in predicted RHF barriers is less than 0.01 kJ/mol. The effect of augmented bases were also studied using aug-cc-pVXZ bases[30,33] with X=D,T for correlation energies, and for the references an additional X=Q was calculated.

Finally, some additional calculations were carried out in a less systematic fashion with smaller basis sets due to their computational cost. These include calculations with extended active spaces and some UHF-UCCSD(T) calculations for comparison. The explicitly correlated model UCCSD(T)-F12a[34] with the recommended basis (AVTZ) was calculated on the UCCSD(T) geometries. Similarly, the extrapolated UCCSD(T) energies for these structures were determined. In some cases, restricted active space (RASSCF) calculations,

Table 1. Method Dependence of Relative Standard Enthalpy Values (in kJ/mol) Obtained by Extrapolation of cc-pVXZ Basis Sets for the π-Complex (**R**), Transition States of Direct (**A**$_{dir}$), and Consecutive (**A**$_{con}$) Allylic H-Abstractions As Well As Terminal (**T**) and Central (**C**) OH-Additions

	A$_{dir}$	A$_{con}$	C	T	R
[5,5]-CASPT2	4.62	2.44	−9.00	−7.45	−10.37
[5,5]-CASPT3	22.10	20.63	6.66	7.08	−8.61
[5,5]-MRCI	28.88	28.19	11.70	11.50	−6.26
[5,5]-MRCI+Q1	15.36	13.97	2.39	6.44	−8.95
[5,5]-MRCI+Q2	16.64	15.20	3.60	7.22	−9.28
[5,5]-MRACPF	16.67	15.19	1.50	2.11	−8.78
[5,5]-MRAQCC	18.49	17.13	3.05	3.54	−8.41
RMP2	15.94	13.95	−3.91	−3.69	−10.96
RCCSD	16.60	15.29	−0.28	−0.19	−8.32
RCCSD[T]	5.69	3.91	−9.41	−8.60	−10.08
RCCSD-T	7.21	5.44	−8.12	−7.44	−10.00
RCCSD(T)	7.20	5.44	−8.19	−7.54	−10.03
UCCSD	14.35	13.04	−2.05	−1.84	−8.38
UCCSD[T]	2.89	1.15	−11.54	−10.60	−10.26
UCCSD-T	4.60	2.87	−10.16	−9.33	−9.96
UCCSD(T)	4.79	3.06	−10.02	−9.24	−10.01

and the corresponding correlated methods[35] prefixed with RAS were used. This means that we only allow certain excitations in certain regions of the active space. Here in the case of an extended [9,9] active space only double excitations are allowed from the lower two occupied and to the upper two unoccupied orbitals, which reduces computational cost (singles are eliminated due to numerical reasons rather than due to their quantity).

Most of the calculations were carried out with the MOLPRO program package of Werner and Knowles.[36] For the CCSDT and UHF-UCCSD(T) calculations, the MRCC package of Kállay[37] was used. Vibrational frequencies were calculated on the optimized geometries at the [5,5]-CASPT2/cc-pVTZ and UCCSD(T)/cc-pVTZ levels. To ensure a better agreement with experiment, the scale factor 0.958 ± 0.004 was determined for [5,5]-CASPT2 by fitting the calculated frequencies against the experimental values for propene[38] and OH.[39] For the UCCSD(T) frequencies the scale factor used is 0.975 ± 0.0021.[40] For comparative purposes, a variation of G3MP2B3 procedure[41] was also carried out where the B3LYP/6-31G(d) geometry optimization and normal node analysis were replaced by the BH&HLYP/6-31G(d) level of theory due to the fact that the B3LYP functional is not able to characterize the transition state for the consecutive allylic H-abstraction.[12] The BH&HLYP harmonic frequencies were scaled by 0.935.[12] In analogy to G3MP2B3, we term this method G3MP2BH&H, and refer to its earlier use in our publications.[42] All the DFT results were obtained using the Gaussian program package.[43] All enthalpy values are relative to that of the level of propene and OH.

3. Results and Discussion

First, let us discuss the single point results at the [5,5]-CASPT2 geometries. In Table 1 relative enthalpy results extrapolated from the cc-pVXZ basis sets are shown. The first obvious observation is that there is a significant difference between the multireference and the single refer-

ence results, especially when comparing the size consistency corrected MR and the triple corrected CC results, the ones that can be considered as the most reliable from the corresponding sets; this difference is approximately 10 kJ/mol.

Let us first analyze the SR results. The RMP2 result agrees with the CCSD results best, which is not surprising. The CCSD models show a considerable difference between results with and without triples corrections in both the restricted and unrestricted cases. Since the triples are important (see Table 1), the most reliable result must be among the corrected results. The CCSD[T] model as described above does not account for some important contributions and is therefore inferior to the others, while the other two methods agree very well, again in accordance with general experience. Therefore the choice of the standard CCSD(T) model is justified. One can still observe some difference between RHF-RCCSD and RHF-UCCSD results. We will return to this later; here we only say that in accordance with previous recommendations,[44,45] we choose the RHF-UCCSD results as the most reliable single reference ones and will use this for comparison.

The MR results appear somewhat divergent. The CASPT2 results agree well with the UCCSD(T) single point ones within $1-2$ kJ/mol, which supports the choice of the inexpensive CASPT2 method for geometry optimization. The CASPT3 results seem to overestimate the barrier heights, and so does MRCI because of the size consistency error. It should be noted that in the supermolecular approach size consistency is already approximately dealt with, but the inclusion of higher excitations may still be important. For this reason, the theoretically most reliable results here are the ones with some kind of a correction for the latter error. These (MRCI+Q1, MRCI+Q2, MRACPF, and MRAQCC) give results within a broad 3 kJ/mol range. In all cases the difference between these is significantly smaller compared to that with the MRCI results, indicating the importance of higher excitations, and also the fact that the active space may be too small to involve all significant higher excitations. Indeed, if one compares these with the CCSD results (that is without triples correction), one finds a good agreement, showing that the MR calculations with the present active space is comparable with considering only SD excitations. We will come back to this later.

In Table 2, we present some results coming from extrapolation using augmented basis sets for selected methods. In general, there is a good agreement between the two extrapolations, they mostly differ for **A**$_{dir}$ and **A**$_{con}$ in MR calculations and for **R** in general. **R** being a weakly bound π-complex, longer range interactions are usually more important, which the augmented basis sets handle better (diffuse functions). The augmented basis sets also show a faster convergence. For all these reasons we will prefer results with augmented bases in the followings and refer to the extrapolations from these as the complete basis set (CBS) limit (see Table 3).

Table 3 begins with the [9,9]-RAS-MRCI+Q1 results. This [9,9] active space is the [5,5] extended with the two C−C bonds and two unoccupied orbitals (and with excita-

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Table 2. Method Dependence of Relative Standard Enthalpy Values (in kJ/mol) Obtained by Extrapolation of aug-cc-pVXZ Basis Sets for the π-Complex (**R**), Transition States of Direct (**A$_{dir}$**), and Consecutive (**A$_{con}$**) Allylic H-Abstractions As Well As Terminal (**T**) and Central (**C**) OH-Additions

	A$_{dir}$	A$_{con}$	C	T	R
[5,5]-CASPT2	4.66	2.55	−9.01	−7.58	−10.93
[5,5]-MRCI	28.73	28.07	11.45	11.19	−6.85
[5,5]-MRCI+Q1	16.93	15.59	2.17	11.19	−9.06
[5,5]-MRCI+Q2	18.33	17.01	3.33	4.62	−9.03
UCCSD	14.38	13.16	−2.21	5.56	−9.16
UCCSD[T]	3.05	1.43	−11.51	−10.66	−10.96
UCCSD-T	4.70	3.08	−10.18	−9.43	−10.64
UCCSD(T)	4.90	3.28	−10.02	−9.34	−10.68

tions restricted from/to these extensions). This extension of the active space improves the agreement with single reference methods on the same double-ζ basis, except for **R**. In the next step, we improve the basis set by augmentation and the active space by removing the restriction of double excitations. The resulting [9,9]-MRCI+Q1 values are now even comparable with the extrapolated UCCSD(T) results, but in the case of **R** there is no improvement. If we now take the [5,5]-MRCI+Q1 results (Table 2), it is obvious that the major differences between SR and MR methods are in the case of the transition states, in the case of **R** there is actually a rather good agreement (differing by 1 kJ/mol only). Furthermore, for **R**, the triples contribution yields a contribution of 1 kJ/mol only in CCSD indicating that a consistent treatment of the triples does not change the result significantly. This would explain why [5,5]-MRCI+Q1, which was described above to have an overall SD quality agrees well with UCCSD(T) for the π-complex. In case of the transition state structures, the extension of the active space brings the desired improvement, indicating that the chosen active space gives a consistent treatment of important higher order excitations. With **R** this does not seem to be the case, that is some important higher order contributions are included, whereas others are left out in the extended active space, which causes an unbalanced, inconsistent treatment. To recover consistency, one should change the active space. However, as it was described earlier, this is not an easy task,[5] which seems only necessary for **R**.

How to control which orbitals go into the active space? We have control over the occupied orbitals, but the virtual ones are harder to choose. First, there is no symmetry condition which could help. One could perhaps see that orbitals with large contributions from the transferring H are involved, but, even so, care should be taken to choose such that are only related to the transfer directly and not to other interactions. This is a hard task in the case of a π-complex, where there are several competing noncovalent interactions. If we decide on not manipulating the virtual orbitals, one could try to change the occupied orbitals and hope that the MCSCF optimization will result in the desired virtuals. There are many possibilities to do this, here we only note that a [9,9] active space where the two C−C bonds and the C−H bond is replaced with the O−H bond and the two lone pairs of the oxygen yields no better results (−22.77 kJ/mol for **R**). Since the [9,9] results did not bring improvement, one

could try to increase or decrease the active space of **R**. Increasing the active space further is not feasible, neither is a larger basis set. A decrease would take us back to the already discussed [5,5] space, which indeed seems an improvement in consistency, which due to the less emphasized importance of triples contributions with **R** shows itself as a good agreement with UCCSD(T). Since **R** is a minimum structure, it is less likely to have a multiconfigurational nature, so the UCCSD(T) result can be taken as the final word. This seems to be also the case with the transition states, since the above-mentioned not too high T1 value seems to be taken care of by the triples correction and also because the [9,9]-MRCI+Q1 results seem to converge there anyway (if we could allow the use of larger bases). From all this, our conclusion is that consistent MRCI+Q1 values with large enough active space and UCCSD(T) results agree well, and the latter should be chosen for computational and methodological ease.

The remainder of the first section of Table 3 addresses some spin related issues. Besides the RHF based treatments, here some UHF-UCCSD(T) results are also included. As pointed out earlier, there appears to be a roughly 2 kJ/mol difference between restricted and unrestricted CC results based on an RHF reference.[44,45] A somewhat smaller difference (a few tenths of kJ/mols) is observed between methods based on UHF and RHF orbitals.[44,45] It is difficult to reach firm conclusions on the nature of the spin contamination effects arising from the UHF or the UCCSD(T) procedures from these data. Here, the UCCSD(T) model will be chosen[44,45] with RHF reference[46] as a preferred method for the final geometry optimizations and vibrational frequency calculations. Although the energetic difference between the RCCSD(T) and UCCSD(T) single points remains an open question, the issue may be addressed from a geometrical point of view. As discussed below, **T** (and also **C**) seems to be the most sensitive to correlation methods used for optimization. If one takes this species and optimizes the structure with RCCSD(T) and UCCSD(T) with the 6-31G(d) basis, one gets quite similar geometries: the most sensitive parameter, the C···O distance is 2.13 Å with the unrestricted, and 2.09 Å with the restricted method. If we now perform a UCCSD(T) single point calculation on the RCCSD(T) geometry (or vice versa) and compare it with the UCCSD(T) optimized value, there is only a slight 0.24 kJ/mol difference. On the other hand, the difference between the optimized energies is 2.55 kJ/mol, which corresponds to the above 2 kJ/mol gap between RCCSD(T) and UCCSD(T). This suggests that the choice of restricted or unrestricted CCSD(T) models has only a negligable effect on geometry optimizations in these cases, despite the energetic difference between the two. This is assumed to hold for all species and bases discussed here.

Having chosen the UCCSD(T) method, geometry optimizations and vibrational frequency analysis were performed with the cc-pVTZ basis. It is interesting to compare the [5,5]-CASPT2 and UCCSD(T) geometries to emphasize the good performance of the much cheaper CASPT2 method. In Figure 2, UCCSD(T) results are indicated first, and then in brackets the CASPT2 ones follow. The most significant difference is

Table 3. Method Dependence of Relative Standard Enthalpy Values (in kJ/mol) Obtained at Several Levels of Theory for the π-Complex (**R**), Transition States of Direct (**A**$_{dir}$), and Consecutive (**A**$_{con}$) Allylic H-Abstractions As Well As Terminal (**T**) and Central (**C**) OH-Additions[a]

	A$_{dir}$	A$_{con}$	C	T	R
		[5,5]-CASPT2 geoms&freqs			
[9,9]-RAS-MRCI+Q1/cc-pVDZ	12.30	10.81	−1.64	−1.54	−16.84
[9,9]-MRCI+Q1/aug-cc-pVDZ	5.36	4.33	−10.15	−8.80	−18.22
RCCSD(T)/aug-cc-pVDZ	5.92	4.74	−11.65	−9.99	−12.97
UCCSD(T)/aug-cc-pVDZ	3.96	2.83	−13.13	−11.39	−12.82
UHF-UCCSD(T)/aug-cc-pVDZ	4.36	3.17	−12.59	−10.68	−12.99
		UCCSD(T) geoms&freqs			
UCCSD(T)/cc-pVDZ	15.17	13.67	2.15	3.82	−11.03
CCSDT/cc-pVDZ	14.56	13.10	1.20	2.96	−11.04
UCCSD(T)/CBS	3.21	1.67	−9.93	−9.84	−10.56
UCCSD(T)-F12a/AVTZ	3.03	1.55	−10.54	−10.34	−10.47
		BH&HLYP geoms&freqs			
G3MP2BH&H	0.74	−0.92	−6.60	−5.35	−8.43

[a] [5,5]-CASPT2 (scale factor 0.958), UCCSD(T) (scale factor 0.975), and BH&HLYP (scale factor 0.935) optimized geometries and frequencies are included.
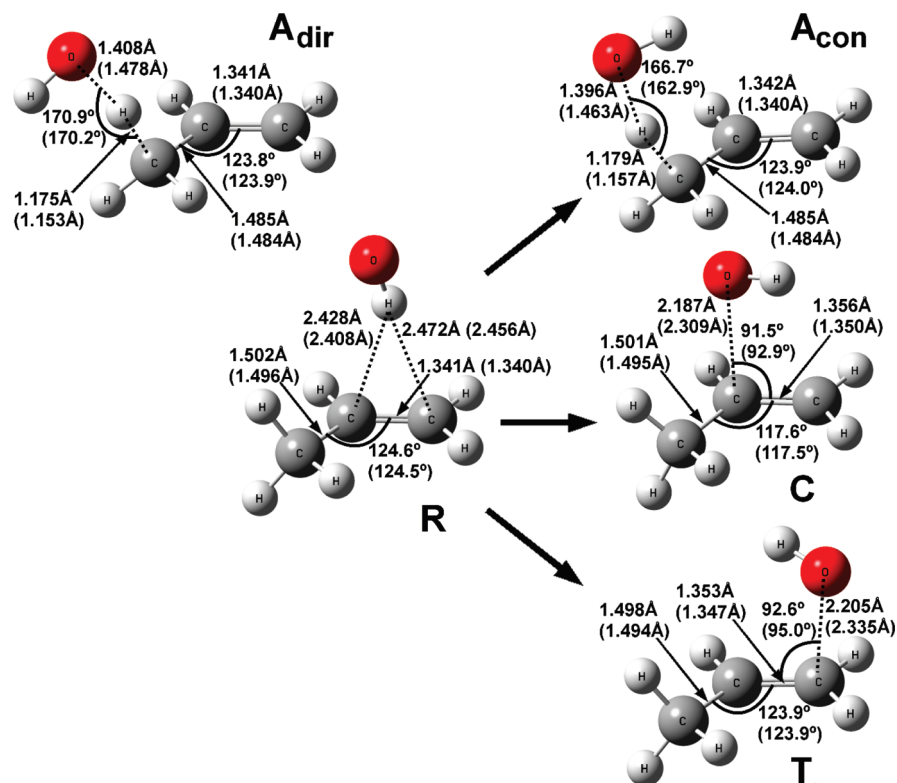
Figure 2. UCCSD(T)/cc-pVTZ geometry parameters followed by [5,5]-CASPT2/cc-pVTZ ones in brackets for the π-complex (**R**) as well as transition state structures of direct (**A**$_{dir}$) and consecutive (**A**$_{con}$) allylic H-abstraction; terminal (**T**) and central (**C**) OH-addition reaction channels.

the C···O distance in **T** and **C** (about 0.12 Å) which is probably due to some neglected correlation contributions rather than spin contamination effects (see above). However, this only yields a difference of about 0.3 kJ/mol between UCCSD(T) and UCCSD(T)//[5,5]-CASPT2 barriers with cc-pVTZ basis. Comparing the extrapolated UCCSD(T) energies at 0 K, they agree within 1 kJ/mol, which is an excellent agreement. At 298.15 K, the maximum difference in enthalpies is a somewhat larger 1.5 kJ/mol, since in this case differences in frequencies also play a role. Allylic abstraction barriers are 1.5 kJ/mol lower at the UCCSD(T) geometries, and the addition barriers are also much closer to each other compared to the results with CASPT2 (0.09 vs 0.65 kJ/mol

difference). From now on, UCCSD(T) geometries will be used by default. Finally, it is also worth mentioning that if we take the extrapolated CASPT2 enthalpy barriers rather than the extrapolated UCCSD(T)//CASPT2 values as above and compare it with optimized UCCSD(T) values, the agreement is still very good (1−2 kJ/mol difference).

In the following, our results will be compared with structural data available in the literature. The UCCSD(T) geometry of the π-complex is in good agreement with the previously published MP2/6-31+G(d) geometry.[16] Most geometry parameters of transition state structures corresponding to addition channels calculated with UCCSD(T)/cc-pVTZ, CASPT2/cc-pVTZ, MP2/6-31+G(d),[16] and MP2/
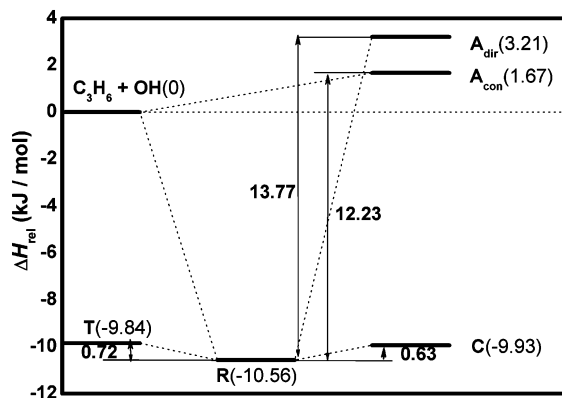
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Figure 3. Energetics of the examined structures at the UCCSD(T)/CBS//[5,5]-CASPT2/cc-pVTZ level of theory.

cc-pVTZ[17] are also close to each other. The only exceptions are the bonds being formed (C−O) in **T** and **C**, where the CASPT2 bond lengths are about 0.13 Å larger, whereas the MP2 results are about the same value shorter compared to UCCSD(T) with cc-pVTZ basis. In general CASPT2 predicts earlier transition states than those obtained by single reference methods. Our previous BH&HLYP/6-31G(d) and CCSD/6-31G(d) results[12] on the transition states of allylic hydrogen abstraction channels are consistent with the corresponding UCCSD(T) geometries. Here, while the bonds being broken (C−H) are somewhat larger in the case of the BH&HLYP (1.22 Å) or CCSD (1.23 Å) geometries compared to UCCSD(T) transition states (1.18 Å).

In the second section of Table 3, some single point calculations on UCCSD(T) geometries are shown to further investigate some of the problems which occurred so far. Since it has been concluded above that the triples contribution is of great importance, results gained at the (unrestricted) CCSDT/cc-pVDZ level are included, together with the perturbative CCSD(T) results for comparison. The good agreement (within 1 kJ/mol) between CCSDT and UCCSD(T) results suggests that we can indeed rely on the latter as a good approximation for triples contribution.

Finally, the convergence of the basis set extrapolation using the CCSD(T) results is tested. An explicitly correlated theory, UCCSD(T)-F12a[34] - as implemented in MOLPRO - was utilized with the recommended AVTZ basis set. This improves basis set convergence, so that we can obtain accurate results with relatively small bases (differences from UCCSD(T)/CBS are within 0.7 kJ/mol). This procedure yields very similar results from what we had from extrapolation. It is also worth noting that using the G3MP2BH&H extrapolation scheme also gives quasi-quantitative answers, the differences being in the worst cases around 3−4 kJ/mol.

The UCCSD(T)/CBS result for **R** as shown in Figure 3 is −10.56 kJ/mol relative to the infinitely separated species. The addition barriers - as suggested by earlier theoretical works lie very close to each other; actually our calculations show that they are within 0.09 kJ/mol (the virtual activation enthalpies are −9.93 kJ/mol for **C** and −9.84 kJ/mol for **T**). The allylic H-abstraction enthalpy barriers are (about 12 kJ/mol) higher and have a larger difference, 1.54 kJ/mol, making the consecutive reaction energetically favored (enthalpy barriers: 3.21 kJ/mol for **A_dir** and 1.67 kJ/mol for **A_con**).

Conventional transition state theory (cTST) might provide a rough estimation for the rate constants of these channels by means of our UCCSD(T) results. We assume a 4-fold electronic degeneracy (g) for OH (g = 4, ignoring spin−orbit splitting), g = 2 for the transition states, and g = 1 for propene. A 2-fold degeneracy of reaction paths was considered in the case of the addition transition states, since they have nonsuperimposable mirror images (the OH can come from either side of the propene plain). In the case of direct H-abstraction, a 3-fold rotational degeneracy is assumed (although the conformer with the OH in the propene plain is expected to be energetically a bit different), whereas in the consecutive case the same degeneracy is two. Propene also has a 3-fold conformational degeneracy because of the methyl group (this only affects the abstraction cases). At room temperature, the rate constants are 4.86×10^{-14} (for **A_dir**), 4.49×10^{-14} (for **A_con**), 4.23×10^{-12} (for **C**), and 8.33×10^{-12} (for **T**) in cm^3 molecule^{-1} s^{-1} which in total (1.27×10^{-11} cm^3 molecule^{-1} s^{-1}) agrees within a factor of 2 with the value recommended by IUPAC at this temperature (3.02×10^{-11} cm^3 molecule^{-1} s^{-1}).[47] This latter experimental value is derived from a temperature dependent formula recommended by IUPAC and is partially based on work of Zellner and Lorenz,[48] who suggest a value of $(3.0 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. Similarly, in Atkinson's review,[49] the suggested 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} with a 15% error is again in good agreement with our results. The above-mentioned factor of 2 corresponds to a 1.7 kJ/mol change in the barriers. However, in our estimation, the error of the energy calculations is only around 1 kJ/mol or perhaps even less in some cases (see Table 3 for CCSDT benchmarks for triples errors and also for basis set convergence). The rest of the discrepancy must come from sources like the choice of cTST for our estimations, the quality of the calculated frequencies (e.g., ignoring anharmonicity), and some other issues which a more thorough kinetic study should deal with. Since this was not our goal here, we consider our results in good agreement with experiment. To further support this point, the branching ratio for terminal addition (**T**, 65.8%) was calculated and was found to be in near perfect agreement with Cvetanović's data (65%)[19] with a calculated contribution of 0.4% for direct and consecutive allylic abstraction channels each. These results may also prove the accuracy of our quantum chemical results. It is also worth noting that the cTST overall rate constant obtained from UCCSD(T)/CBS//CASPT2/cc-pVTZ values (2.26×10^{-11} cm^3 molecule^{-1} s^{-1}) is closer to Atkinson's experimental one, whereas the calculated branching ratio for **T** (57.8%) is in a less good agreement with the above data (Cvetanović).

In their recent paper, Zhou et al.[17] have explored the propene + OH potential energy surface with projected MP2 methodology using the PMP2/aug-cc-pVQZ//MP2/cc-pVTZ level of theory and CCSD(T) methodology at the same geometries using the 6-311+G(3df,2p) basis and extrapolation from cc-pVDZ and cc-pVTZ bases. Their aim was to give an overall kinetic description at a broad temperature range, whereas our report focuses on species relevant around room temperature. In at least some of their cases, Zhou finds

that PMP2 results are closer to experimental values than CCSD(T) ones. It might be justified to choose their PMP2 methodology over an elaborate CCSD(T) optimization with so many species examined. However, the inclusion of higher excitations is known to be important with radical transition states,[44,45] which is particularly true for the studied system as we pointed out in the previous discussion. The good results with the PMP2 methodology are probably due to a cancellation of errors,[15] and the inferior behavior of CCSD(T) observed by these authors might be a problem of inadequate extrapolation and simply the fact that CCSD(T) single points are not calculated at their optimized geometries. Both of these issues have been addressed here by using larger bases, using CCSD(T) optimized geometries and by comparing those results with ones from a wider choice of ab initio models. The authors were also able to reasonably reproduce the kinetic behavior of the system based on weak collision master equation/microcanonical variational RRKM theory by lowering the barrier heights of central OH-addition (TS11) and terminal OH-addition (TS12) with 1 kcal/mol. However, in Figure 11 of Zhou's article, the branching ratio for these is around 50−50% at room temperature versus the experimental 65% preference for the terminal case, which is well predicted by our CCSD(T) model (65.8%). If cTST branching is calculated with their results it turns out to be 54% for the central case, indicating that the difference between their calculations and the ones presented here (and also the experimental results) is not due to the choice of the kinetic model but to the fact that the optimized CCSD(T) results yield better and more consistent results compared to PMP2/aug-cc-pVQZ//MP2/cc-pVTZ.

In another recent paper, Huynh et al.[18] describes the kinetics of the enol formation based on CCSD(T)/cc-pVDZ//B3LYP/cc-pVTZ results. In our experience, results with cc-pVDZ basis are still roughly 10 kJ/mol away from the CBS limit. In addition, the pathologic behavior of the B3LYP in relevant cases is also known for a while.[12]

4. Conclusions

Barrier heights for different possible reaction paths were calculated for the propene + OH system with the most accurate models available for general use. The results could be summarized in the following points:

1. The use of single reference methods are sufficient and accurate in this case, and in fact they yield more accurate results than multireference methods due to computational limitations for the latter. On the other hand, the advantage of using a multireference CASPT2 in this case is that if active orbitals are carefully selected, it is able to approximate UCCSD(T) within 1−2 kJ/mol with considerably less computational effort.

2. The RHF-UCCSD(T)/CBS method is expected to yield the most accurate results. Triples contributions are substantial (typically around 10 kJ/mol for barriers). The restricted coupled cluster variant exhibits a slight difference to these results (around 2 kJ/mol), which is, however, unlikely to effect geometry optimizations.

3. G3MP2BH&H yields a result within 3−4 kJ/mol to the extrapolated UCCSD(T). As another way of approximating

the complete basis set limit, the explicitly correlated UCCSD(T)-F12a model was utilized giving results within 0.7 kJ/mol maximum difference compared to extrapolated values.

4. Consecutive allylic abstraction and addition mechanisms go through a π-complex (**R**), which lies at −10.56 kJ/mol with respect to the enthalpy level of the infinite separation of the species.

5. The addition mechanisms have negative enthalpy barriers relative to infinite separation (−9.93 kJ/mol for **C** and −9.84 kJ/mol for **T**). There is only a marginal 0.09 kJ/mol energetic difference between the two.

6. The allylic abstraction mechanisms have slightly positive enthalpy barriers relative to infinite separation (3.21 kJ/mol for $\mathbf{A_{dir}}$ and 1.67 kJ/mol for $\mathbf{A_{con}}$), with the consecutive mechanism favored by 1.54 kJ/mol. Although they have significantly higher barriers, they may contribute to the overall reaction system at higher temperatures.

7. Using conventional transition state theory, our UCCSD(T) results were able to reproduce the experimental overall high pressure rate constant within a factor of 2. Calculated branching ratios show the preference of **T** (65.8%) in good agreement with experiment. Allylic abstraction channels have a small contribution of 0.4% each. UCCSD(T)/CBS//CASPT2/cc-pVTZ values show similar good agreement supporting its use as an alternative to more expensive methods.

8. For higher 1-alkene homologues, where UCCSD(T) becomes too demanding to compute, a CASPT2 with similar active space structure may still be an option. Another possibility is to use the G3MP2BH&H method, which is found to be somewhat less accurate compared to CASPT2, but does not require constructing an active space.

Supporting Information Available: Optimized geometries and harmonic frequency analysis results with rotational constants at both the [5,5]-CASPT2/cc-pVTZ and UCCSD(T)/cc-pVTZ levels, energies used for extrapolation for our final results, and additional calculated thermochemical data for both geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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