Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

The Reaction of O(^{3}P) with Alkynes: A Dynamic and Computational Study Focusing on Formyl Radical Production

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Section S1. Discussion of Benchmarking Results for the Reaction of $O(^3P)$ with Propyne

As mentioned in the article, computational results were obtained for all species on the triplet and singlet state potential energy surfaces in the reaction of $O(^3P)$ with propyne in order to perform benchmarking studies and select a reliable and efficient method for investigations of reactions involving larger alkynes. Full geometry optimizations were carried out for all reactants, intermediates, transition states, and products on the lowest singlet and triplet surfaces at the following levels of theory: CCSD(T)/cc-pVTZ, MP2(full)/6-311++G(d,p), M06-2X/cc-pVTZ, and B3LYP/6-311G(d,p). Single point energies for all of the species also were determined at the CCSD(T)//M06-2X/cc-pVTZ and CCSD(T)//B3LYP/6-311G(d,p) levels. Only a subset of the pathways on the potential energy surfaces for the $O(^3P)$ + propyne reaction, the HCO and CO formation routes, are shown in the article (Figs. 7 and 10); the full potential energy profiles (PEPs) for the triplet and singlet state surfaces obtained at the CCSD(T)/cc-pVTZ level of theory for the reaction of $O(^3P)$ with propyne are presented in Figs. S1 and S2, while those obtained at the CCSD(T)//M06-2X/cc-pVTZ level are presented in Figs. S3 and S4, respectively. In addition, a diagram illustrating the HCO formation pathways on the triplet state surface computed at each of the levels of theory is included as Fig. S5.

Comparisons of optimized geometries and relative energies of all the stable and transition state species on the singlet and triplet potential energy surfaces in the reaction of $O(^3P)$ with propyne were used to assess the reliability of each level of theory for similar reactions, taking the results from the CCSD(T)/cc-pVTZ level as the standard for comparison. For the geometries, selected bond lengths and angles determined using the B3LYP, M06-2X, and MP2 methods as described in Section III of the article were compared with those obtained at the CCSD(T) level. For this comparison, Tables S1 and S2 list selected bond lengths and angles obtained at each level of theory for all the species on the triplet state and singlet state surfaces, respectively. In addition, while overall summaries of the RMS differences for triplet and singlet state species are reported in Table 2 of the article, more detailed comparisons

including RMS differences in selected bond lengths and angles for all the species are reported at each level of theory for the triplet and singlet state species in Tables S3 and S4, respectively. The atom-numbering scheme referred to in the tables is shown in Figure 4 of the article, and images showing the geometry of each species are presented in Appendix S1.

In addition to the geometrical parameters, relative energies computed at each level of theory have been compared with the CCSD(T)/cc-pVTZ results; all relative energies are measured from the separated O(^{3}P) and propyne reactants and include vibrational zero-point energy corrections. A summary of the overall RMS differences in relative energies on the singlet and triplet surfaces is presented in Table 3 of the article. The relative energies for each species along with differences relative to the CCSD(T)/cc-pVTZ results are presented in Tables S5 and S6 for the triplet and singlet surfaces, respectively. The remainder of this section presents a discussion of the geometrical benchmarking studies followed the benchmarking results for the relative energies and finally a summary of the conclusions of the benchmarking study.

Geometry Comparisons

While the bond lengths and angles obtained at different levels of theory are in general similar, there are some significant differences. In order to make more quantitative comparisons, we have determined the RMS differences in key bond lengths and angles for results at the MP2, M06-2X, and B3LYP levels of theory relative to those obtained at the highest level of theory, CCSD(T). The geometrical parameters themselves are given in Tables S1 and S2, while the RMS differences computed for each individual structure are reported in Tables S3 and S4. Table 2 in the article also provides a summary of the average RMS errors in bond lengths and angles.

The average RMS errors in bond lengths are generally small for all levels of theory when compared with the CCSD(T) results. For the triplet state structures, the average RMS errors range from

0.020 Å for the MP2 level to 0.034 Å for the B3LYP level. For the singlet state structures, the average RMS errors are 0.021 Å or lower. For the bond angles, on the triplet surface the average RMS errors range from 1.1° for M06-2X to 1.7° for B3LYP, while on the singlet surface the average RMS errors range from 1.7° for MP2 to 3.8° for M06-2X. From these results, it appears that the M06-2X method does the best job for geometries on the triplet surface, while the MP2 method does the best job for geometries on the singlet surface, though all the methods provide reasonably good agreement with the CCSD(T) results for the optimized geometries.

On the triplet surface, the species that shows by far the greatest deviations in bond lengths relative to the optimized CCSD(T) results is IM-0t. For IM-0t, the MP2 bond lengths are in good agreement with the CCSD(T) results (0.019 Å average RMS error). However, the DFT methods fail to adequately characterize the weakly-bound van der Waals complex IM-0t, with average RMS errors in bond length of 0.23 and 0.33 Å, respectively, for M06-2X and B3LYP; the errors occur primarily in the C1-O8 bond distance. Because the error for the IM-0t species is so large for the DFT methods, it swamps out the otherwise generally good agreement of the DFT methods with respect to bond lengths. Other than IM-0t, no other species on the triplet surface exhibits an RMS error in bond length greater than 0.04 Å for the B3LYP or M06-2X methods, with the exception of TS-5t at the B3LYP level (0.11 Å error). On the other hand, the MP2 method shows errors greater than 0.04 Å for numerous species (TS-1t, TS-4t, TS-5t, TS-8t, and TS-15t). Thus, the generally better agreement attained for the DFT methods compared with the MP2 method tends to be masked in the overall results by one very bad geometrical result (IM-0t).

For the triplet state species, the average RMS errors in bond angles vary from 1.1-1.7° for the MP2, M06-2X, and B3LYP methods. The largest errors for individual species again occur for IM-0t, with RMS errors in bond angles ranging from 2.5° (MP2) to 5.9° (B3LYP). Bond angle errors are below 2.3° for all the other triplet state species for all methods with two exceptions: TS-8t, with errors in bond angle ranging from 2.7-3.0°, and TS-1t, for which the B3LYP method exhibits a 3.6° RMS error in bond angle.

On the singlet surface, the bond lengths predicted by the MP2 and DFT methods all are close to the CCSD(T) results for all structures, with average RMS errors of 0.03 Å or lower for individual species, with a few exceptions. RMS errors for bond lengths in individual species are above 0.03 Å for TS-14s (MP2 and B3LYP), TS-15s and TS-19s (M06-2X), and hydroxyvinylcarbene (MP2 and M06-2X), though none of these errors is larger than 0.07 Å.

Significant deviations, however, are observed for bond angles in some species on the singlet surface. In particular, the average RMS error in bond angle for IM-1s is 10.2° at the B3LYP level, but only 1.6° and 1.7° for the MP2 and M06-2X levels, respectively. The large error from the B3LYP method for IM-1s is a result of large differences in both the C1-C2-C3 and C2-C1-O8 angles. Similarly, large RMS errors of 15.3° and 9.1° are observed at the M06-2X and B3LYP levels, respectively, for the bond angles of TS-8s, whereas the error is only 1.8° at the MP2 level. Finally, the RMS error in bond angle for IM-6s is 8.7° for the M06-2X method, but 0.2-0.3° for the other methods. Average RMS errors for bond angles in the other species are 5° or less for all levels of theory.

Relative Energy Comparisons

Triplet and singlet state PEPs showing relative energies of all species involved in the reaction between O(^{3}P) and propyne are included as Figures S1/S2 and S3/S4, calculated at the CCSD(T)/cc-pVTZ and CCSD(T)//M06-2X/cc-pVTZ levels, respectively. The relative energies at these levels, as well as for the MP2/6-311++G(d,p), B3LYP/6-311G(d,p), CCSD(T)//B3LYP/6-311G(d,p), and M06-2X/cc-pVTZ levels, are presented in Tables S5 and S6 along with differences in energies relative to the CCSD(T)/cc-pVTZ results.

Comparing Figure S1 with S3 and S2 with S4, we see that the qualitative features of the PEPs are similar for the different levels of theory; however, Table 3 of the article shows that RMS errors in relative energies on the singlet and triplet surfaces can be as high as 20-40 kJ/mol in some cases. In

addition, Table S5 includes errors in relative energy for individual species, which may be as high as 60-110 kJ/mol.

An illustration of the differences in relative energies for the various levels of theory is provided by Figure S5, which demonstrates specific trends observed when the PEPs computed at each level of theory are compared with the CCSD(T) results. First, from Fig. S5 and Tables S5 and S6, both DFT methods, M06-2X and B3LYP, tend to underestimate the relative energies for nearly all species. For the both the DFT methods (M06-2X and B3LYP), the relative energies are lower than the CCSD(T) energies for most species by a range of about 2 to 50 kJ/mol. There are only a few exceptions for species in which the DFT relative energies are higher than the CCSD(T) results, in some cases significantly (for example, IM-6s, TS-14s, and TS-15s for the M06-2X method). The average absolute errors in relative energy for the triplet surface are 21 kJ/mol and 33 kJ/mol for the M06-2X and B3LYP methods, respectively. For the singlet surface, the average absolute errors are 29 and 17 kJ/mol for the M06-2X and B3LYP methods, respectively, with the bulk of the difference coming from the three high outliers mentioned above. Thus, the M06-2X method tends to perform somewhat better overall for relative energies than B3LYP when compared with the CCSD(T) results.

While the DFT methods tend to underestimate the relative energies, the MP2 method generally overestimates the energies of species on the triplet surface, with an average absolute error of 32 kJ/mol and the largest errors for individual species in the range of 60-75 kJ/mol. The errors in relative energies for species on the singlet surface exhibit less of a trend, but the MP2 method tends to underestimate energies for singlet state species (with about 2/3 of species with relative energies falling lower in energy than the CCSD(T) results), with an average absolute error of 13 kJ/mol and the largest errors falling in the range of 25-30 kJ/mol.

Finally, the results obtained using CCSD(T) single point energies and DFT-optimized geometries, CCSD(T)//M06-2X and CCSD(T)//B3LYP, provide relative energies that are much closer to the optimized

CCSD(T) results than those provided by the DFT methods alone. However, the results from the CCSD(T)//B3LYP method are generally too high, with average absolute errors of 11 and 28 kJ/mol, respectively, for the triplet and singlet surfaces. Although there is one outlier with a large error in the relative energy (H_2CO + H_2CC product), the vast majority of species exhibit errors in the range of 10-30 kJ/mol for the CCSD(T)//B3LYP method. On the other hand, the CCSD(T)//M06-2X results are in general in very good agreement with the optimized CCSD(T) results, with an average absolute error of 4 kJ/mol for relative energies on the triplet surface and 19 kJ/mol on the singlet surface. The only species at the on the triplet surface at the CCSD(T)//M06-2X level with an error in relative energy greater than 5 kJ/mol is TS-4t (21 kJ/mol error). For the singlet surface at the CCSD(T)//M06-2X level, the largest errors in relative energy for individual species are IM-6s (89 kJ/mol), TS-15s (65 kJ/mol), and TS-8s (12 kJ/mol); errors for the other singlet state species are all lower than 6 kJ/mol.

Summary

To determine the most reliable and efficient computational method for studies of alkyne reactions with $O(^3P)$, we have compared geometries and relative energies from the MP2, M06-2X, and B3LYP methods along with relative energies from the CCSD(T)//M06-2X and CCSD(T)//B3LYP methods (all methods are described in Section III of the article).

For triplet state geometries, all methods perform reasonably well, with fairly low average errors in bond lengths and angles. For the DFT methods, the exception occurs for IM-0t, a weakly-bound intermediate in the entrance channel, which is not well characterized using either the M06-2X or B3LYP methods. On the other hand, the MP2 method yields bond lengths that are too long by 0.04-0.06 Å for a number of transition states on the triplet surface, which corresponds to significantly worse agreement than for the DFT methods in most cases.

For singlet state species, the average RMS error in bond lengths for each method is similar to or slightly lower than the errors in bond lengths for the triplet state species, and thus all are in reasonably good agreement with the CCSD(T) results. The average RMS error in bond angles for the singlet state species for each method, however, increases by 0.2-2.7° compared with the triplet state results. Although the MP2 method exhibits the best overall agreement for the singlet state geometries, certain structures on the singlet surface could not be located using the MP2 method (IM-5s, TS-15s, and TS-20s), which casts doubt on MP2 as a reliable methodology for studies of similar reactions. Of the DFT methods, M06-2X is better overall than B3LYP for triplet state geometries, while B3LYP appears somewhat better overall for singlet state geometries.

Investigation of the differences in relative energies obtained using the various computational methods leads to the conclusion that MP2 should be discarded as the method of choice for further studies because it consistently overestimates the relative energies on the triplet surface, often by a significant amount, especially for transition states. On the other hand, relative energies obtained from the DFT methods also often show significant deviations in relative energies.

The most reliable method for obtaining accurate relative energies for the triplet species is CCSD(T)//M06-2X by a significant margin, with a 4 kJ/mol RMS error vs. a range of 12-33 kJ/mol for the other methods. For the singlet surface, the most reliable method for accurate relative energies is MP2 by a small margin (13 kJ/mol vs. 17 kJ/mol for B3LYP and 19 kJ/mol for CCSD(T)//M06-2X). However, given that certain singlet state species cannot be located using the MP2 method, as well as the significant overestimation of relative energies for the triplet surface, it has been eliminated as a choice for additional studies. Based upon this analysis, the method of choice for reliability and efficiency in the study of reactions of alkynes with O(3P) is CCSD(T)//M06-2X/cc-pVTZ.

Figure S1. Triplet state potential energy profile for the reaction of O(^{3}P) with propyne computed at the CCSD(T)/cc-pVTZ level of theory. The species shown in red was computed at the CCSD(T)//M06-2X/cc-pVTZ level. The two species shown in blue have small second imaginary frequencies at the CCSD(T)/cc-pVTZ level. Energies are in kJ/mol with the reactants set to zero and are corrected for vibrational zero-point energy.

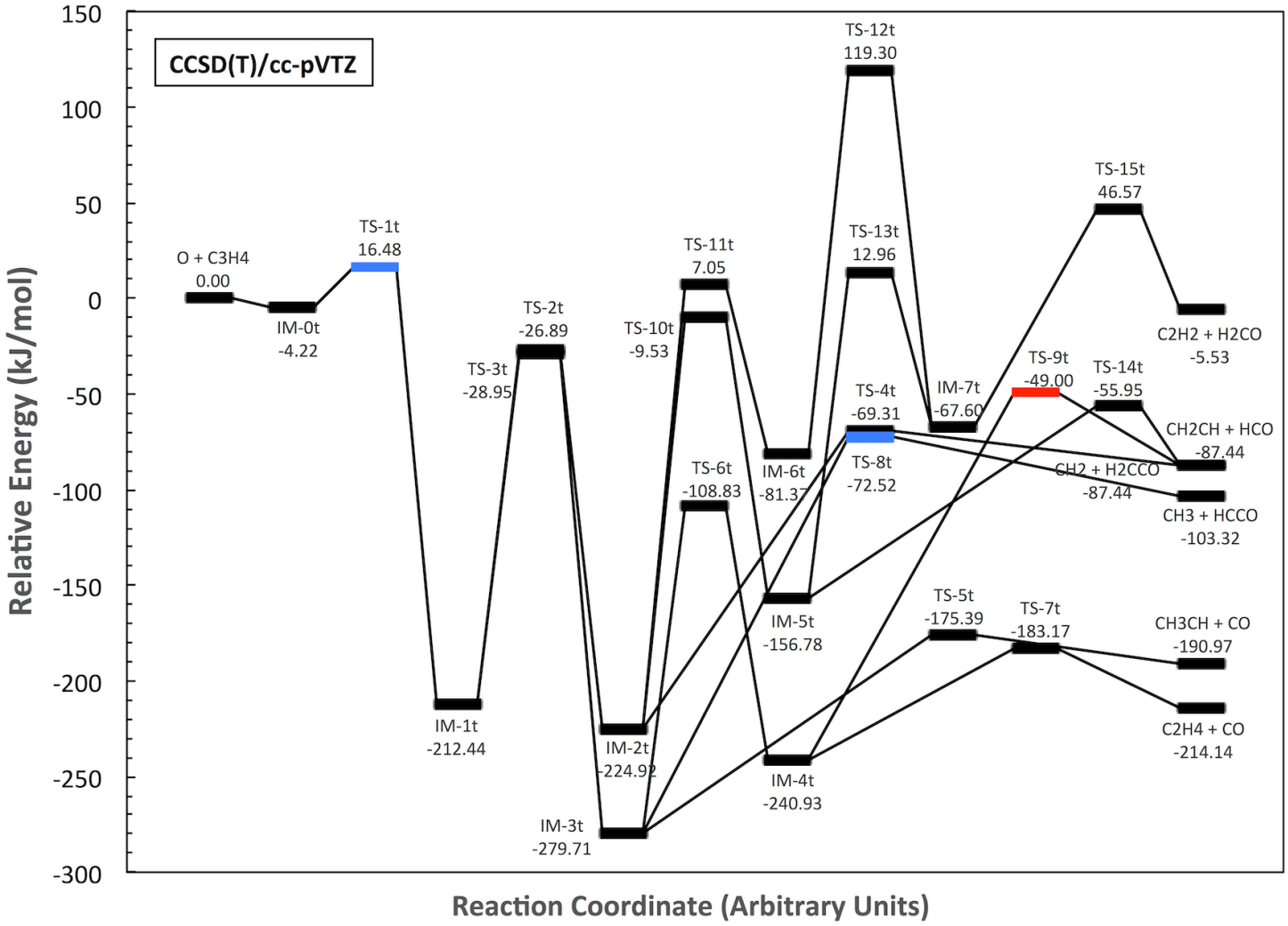


Figure S2. Singlet state potential energy profile for the reaction of O(^{3}P) with propyne computed at the CCSD(T)/cc-PVTZ level of theory. All energies shown are in kJ/mol with the reactants set to zero and are corrected for vibrational zero-point energy.

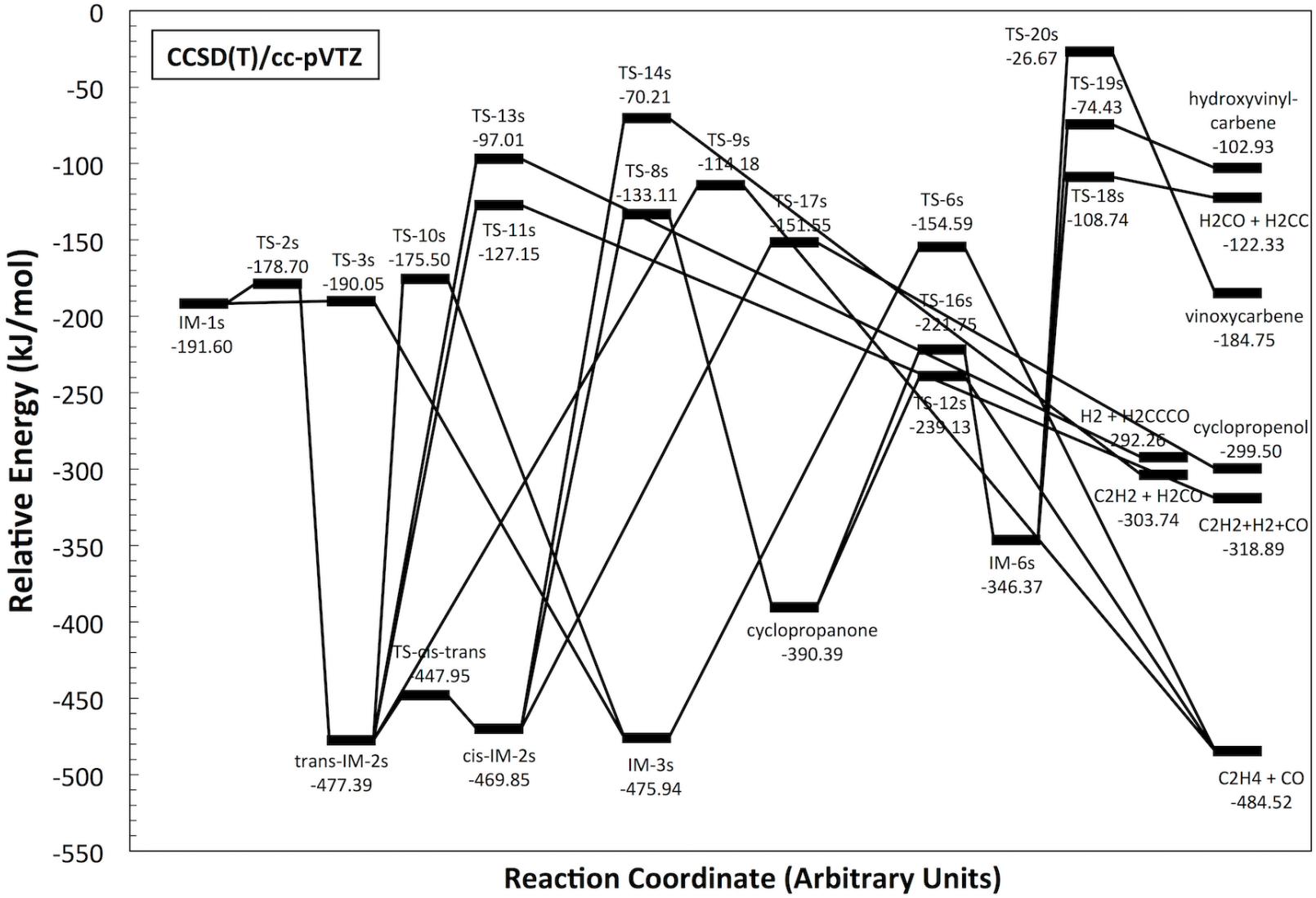


Figure S3. Triplet state potential energy profile for the reaction of O(^{3}P) with propyne computed at the CCSD(T)//M06-2X/cc-pVTZ level of theory.

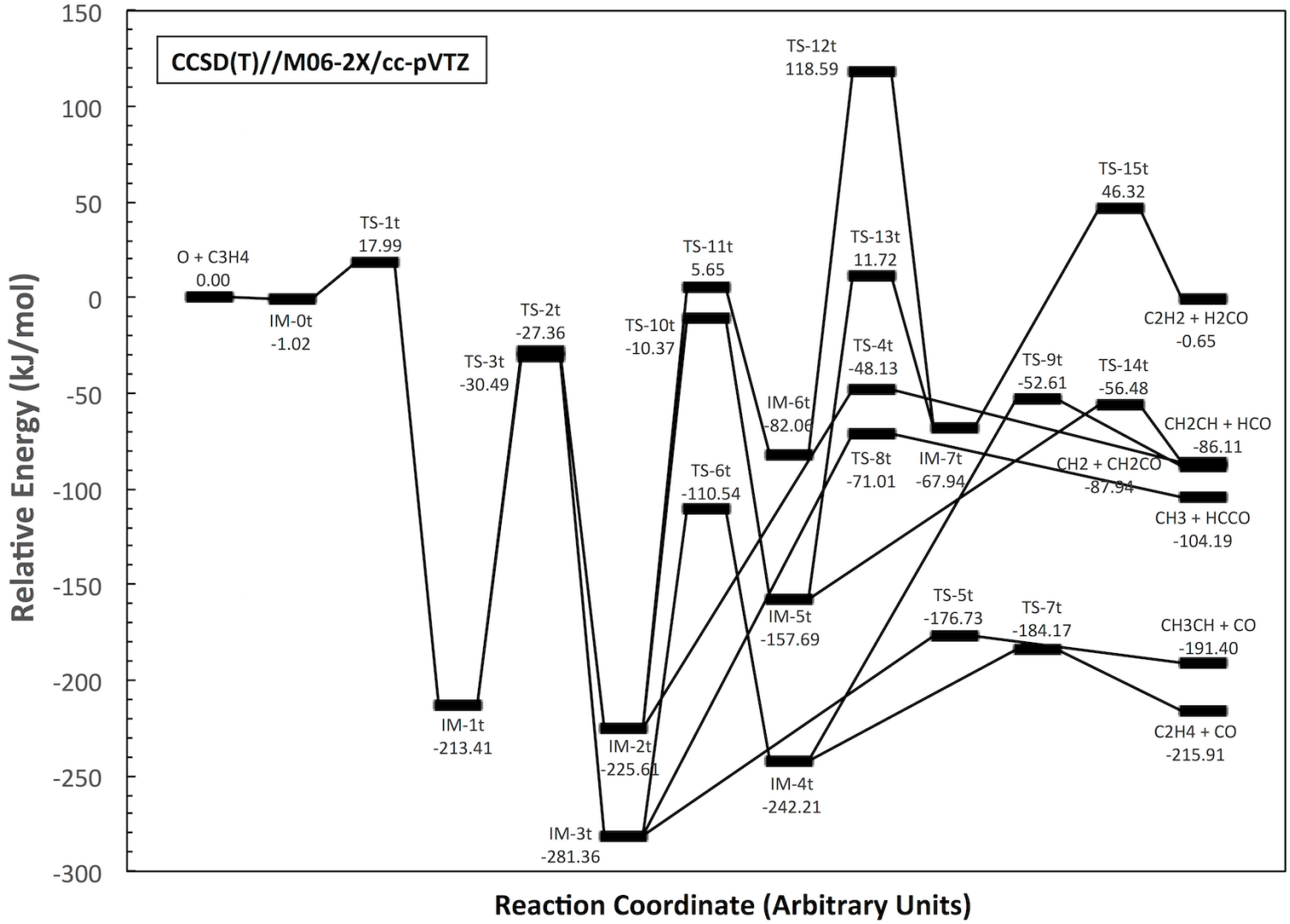


Figure S4. Singlet state potential energy profile for the reaction of O(^{3}P) with propyne computed at the CCSD(T)//M06-2X/cc-pVTZ level of theory.

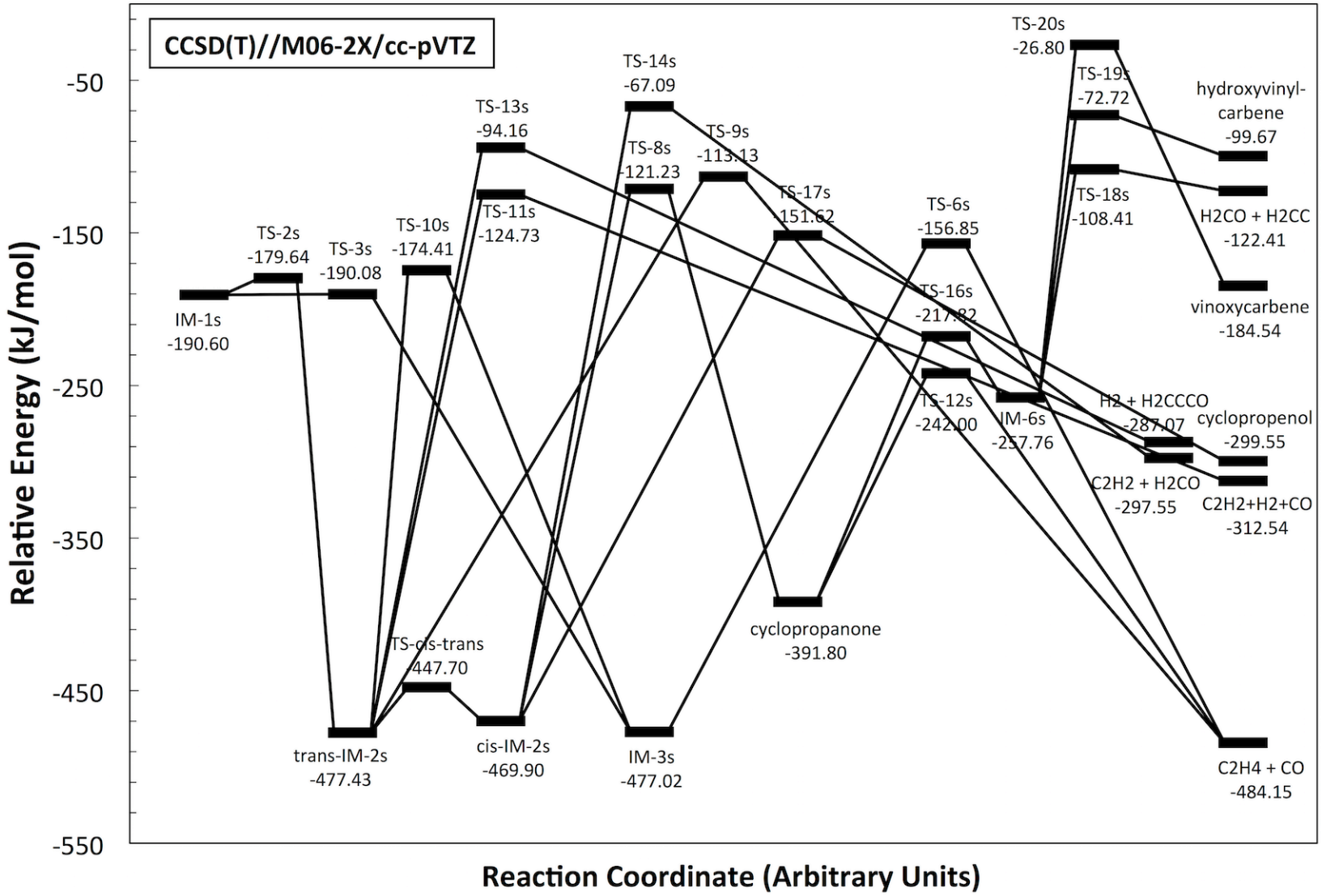


Figure S5. Potential energy profiles of the primary pathway for formation of HCO on the triplet state surface in the O(^{3}P) + propyne reaction calculated at various levels of theory. All energies shown are in kJ/mol with the reactants set to zero and are corrected for vibrational zero-point energy.

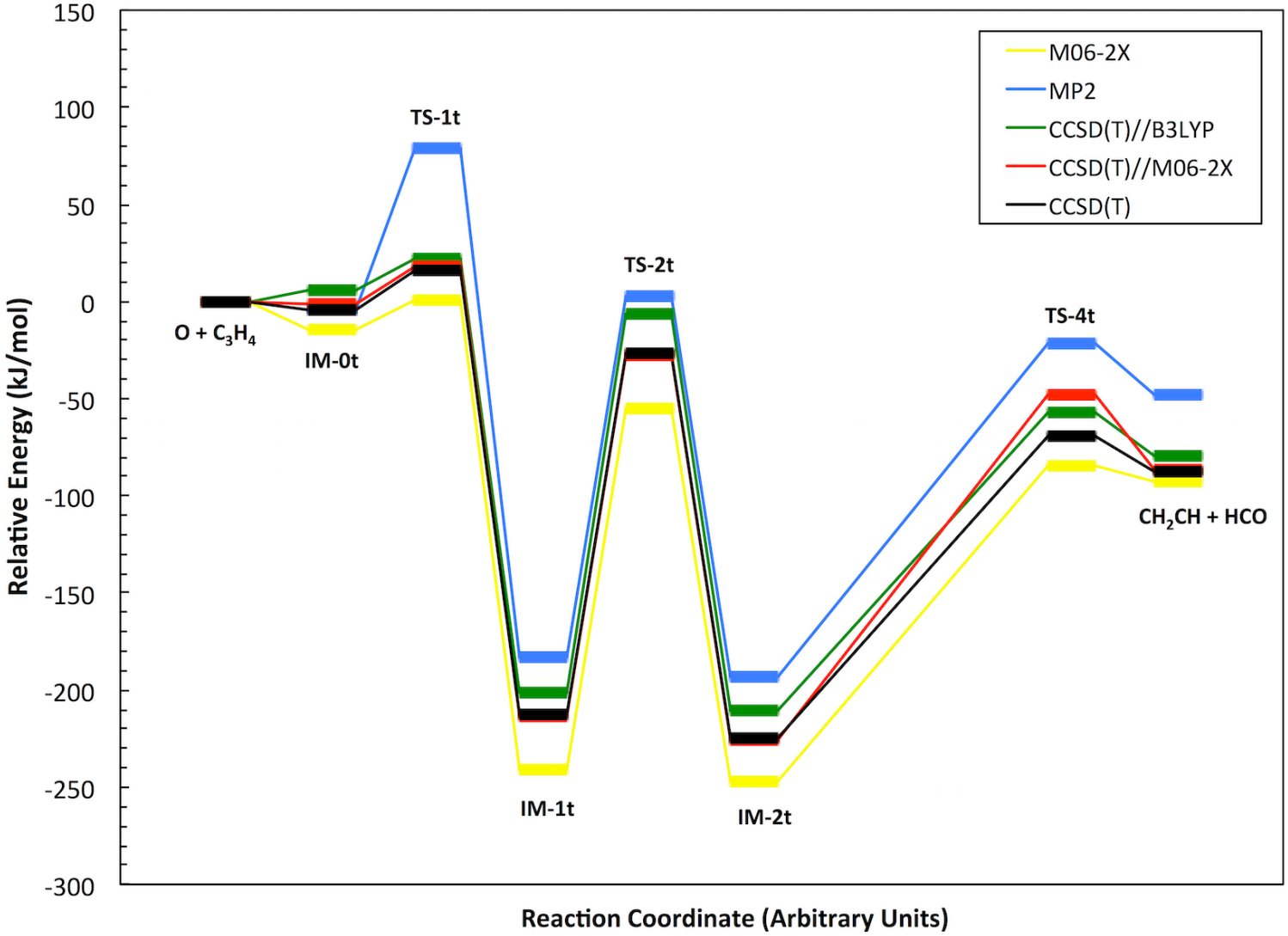
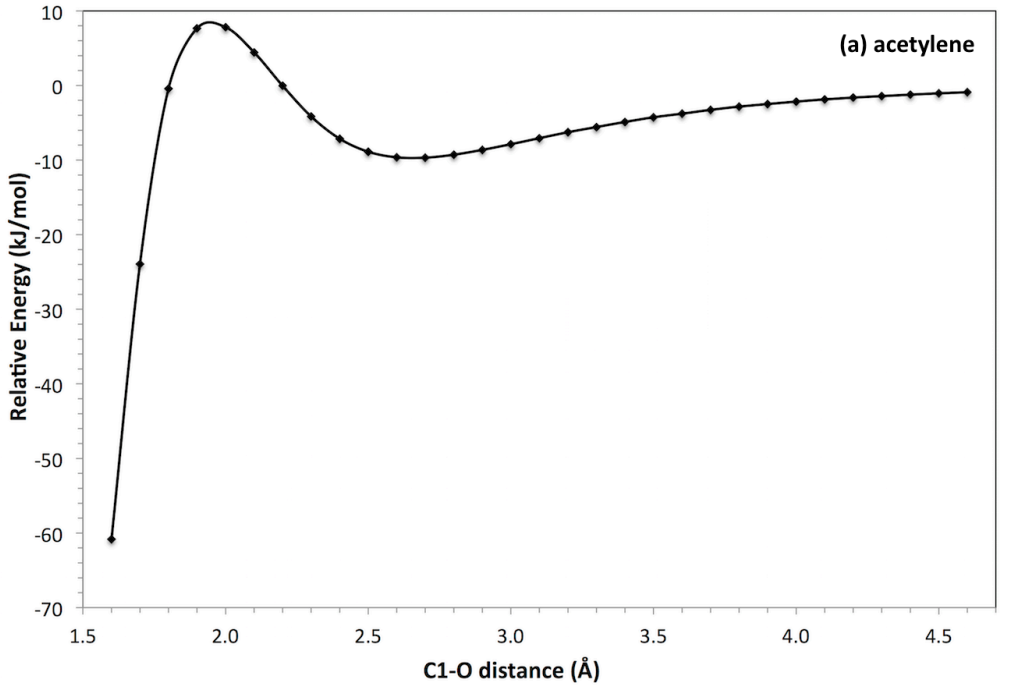


FIgure S6. Relaxed potential surface scans showing the variation of energy with C1-O distance in the reactions of O(^{3}P) with (a) acetylene; (b) propyne; (c) 1-butyne; and (d) 1-pentyne. The electronic energy determined relative to separated O(^{3}P) and alkyne (in kJ/mol) is as a function of the distance between the oxygen atom to the end carbon atom of the triple bond (C1) in angstroms.



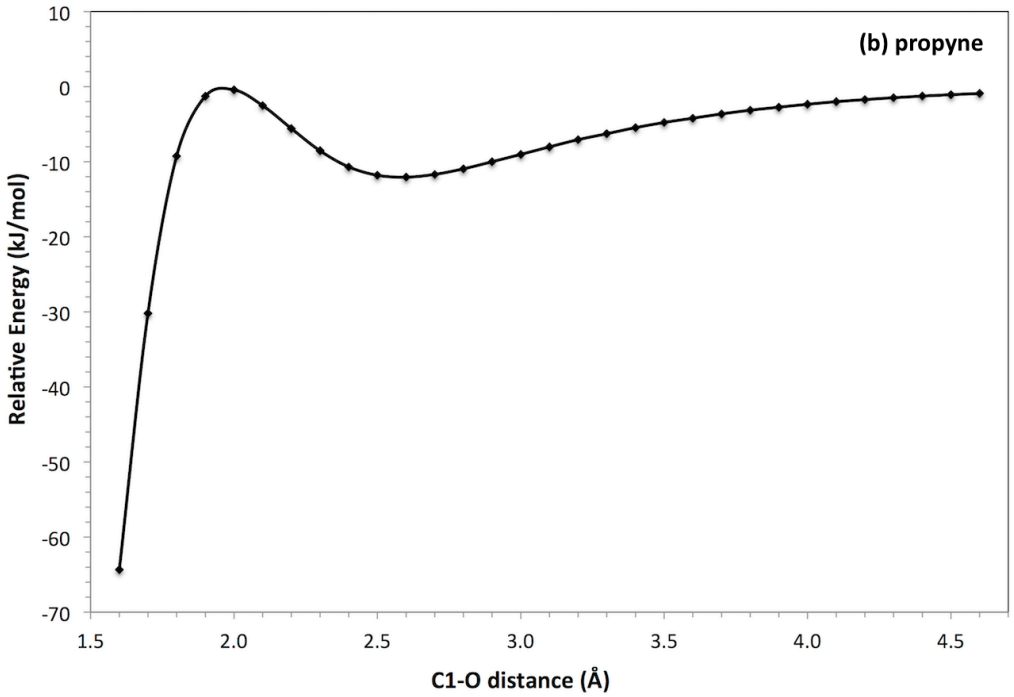
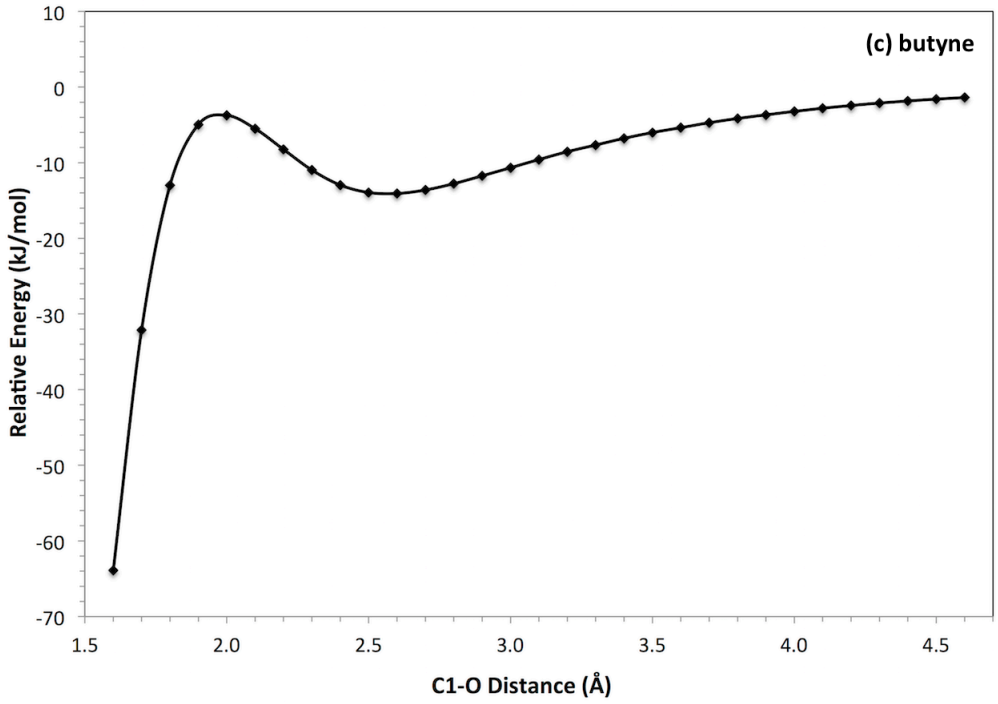


Figure S6 – continued.



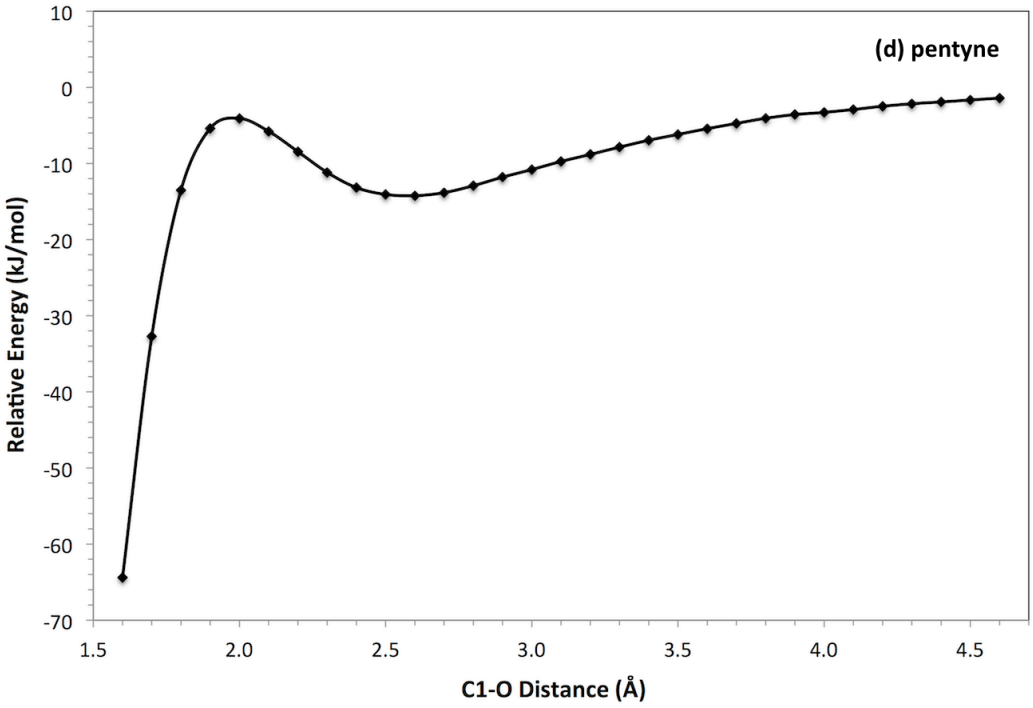


Figure S7. Combined potential energy profile including pathways for HCO formation on the triplet and singlet state surfaces in the reactions of $O(^3P)$ + propyne, 1-butyne, and 1-pentyne, calculated at the CCSD(T)//M06-2x/cc-pVTZ level of theory. All energies shown are in kJ/mol with the reactants set to zero and are corrected for vibrational zero-point energy. Triplet state species are shown in blues and green, singlet state species are shown in red, yellow, and orange, and the approximate locations of the MECPs are shown in black (all three overlap near the same energy).

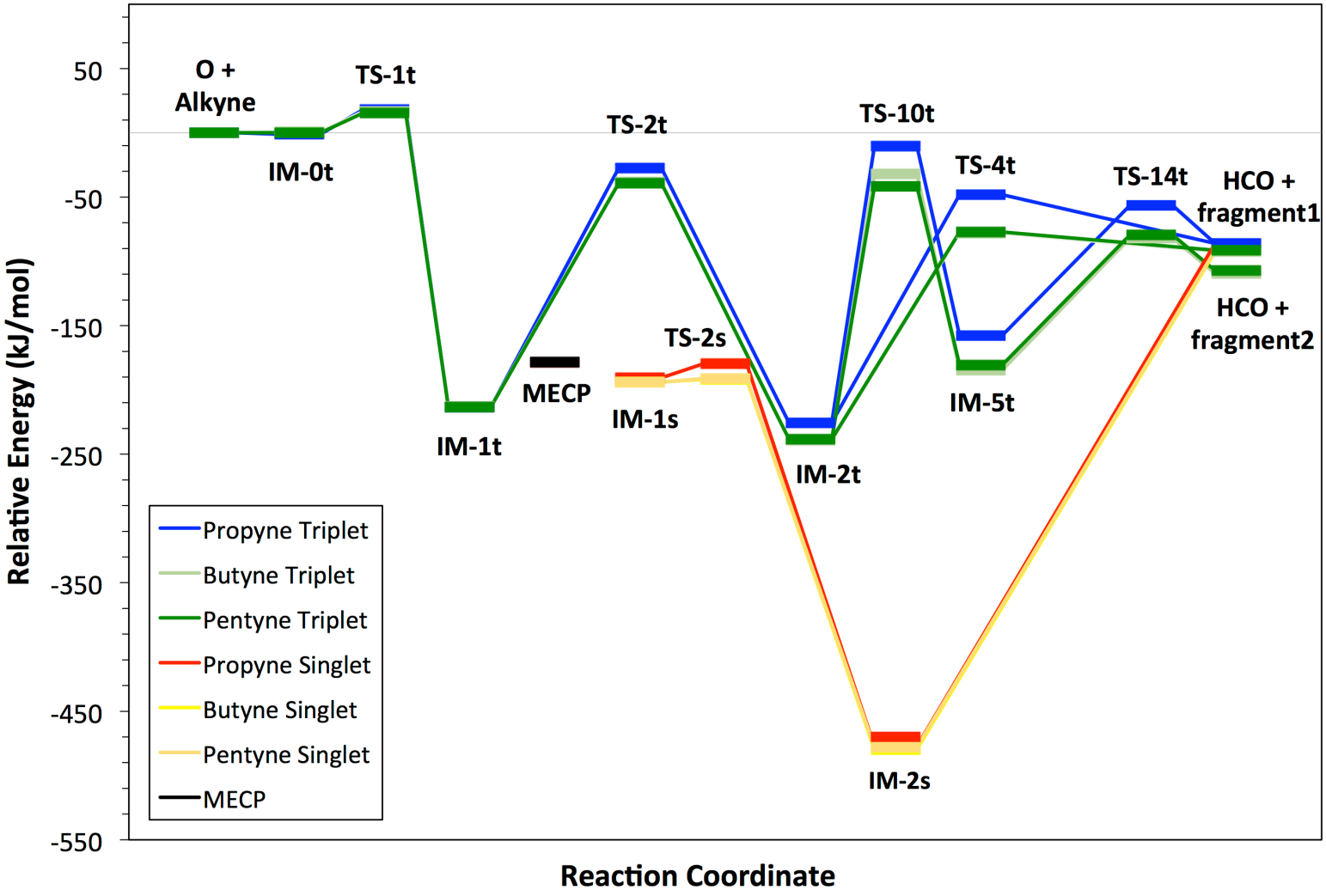


Table S1. Selected bond distances and angles for structures on the triplet state potential energy surface of the O(^{3}P) + propyne reaction. Bond distances are in Angstroms and bond angles are in degrees. The atom-numbering scheme is shown in Figure 4. Values in parentheses correspond to the alternative bond distance (e.g., C2-H4 rather than C2-H6).

Species	Level/Basis Set	r C1-H4	r C2-H6 (C2-H4/7)	r C3-H5 (C3-H7)	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠C2-C1-O8	∠H4-C1-O8
C_3H_4	MP2/6-311++G(d,p)	1.064	---	1.093	1.218	1.462	---	180.0	---	---
	M06-2x/cc-pVTZ	1.062	---	1.089	1.197	1.458	---	180.0	---	---
	CCSD(T)/cc-pVTZ	1.063	---	1.091	1.211	1.467	---	180.0	---	---
	B3LYP/6-311G(d,p)	1.062	---	1.094	1.201	1.457	---	180.0	---	---
IM-0t	MP2/6-311++G(d,p)	1.064	---	1.093	1.218	1.461	3.106	179.7	76.5	103.4
	M06-2x/cc-pVTZ	1.062	---	1.089	1.199	1.457	2.642	179.4	77.2	102.9
	CCSD(T)/cc-pVTZ	1.063	---	1.091	1.212	1.466	3.148	179.7	73.6	106.5
	B3LYP/6-311G(d,p)	1.062	---	1.093	1.207	1.454	2.409	178.8	81.6	100.3
IM-1t	MP2/6-311++G(d,p)	1.108	---	1.091	1.460	1.473	1.195	129.2	122.3	122.4
	M06-2x/cc-pVTZ	1.099	---	1.093	1.417	1.462	1.228	132.2	121.6	121.0
	CCSD(T)/cc-pVTZ	1.098	---	1.093	1.429	1.474	1.237	131.5	121.3	121.2
	B3LYP/6-311G(d,p)	1.102	---	1.097	1.417	1.464	1.238	133.1	121.1	121.2
IM-2t	MP2/6-311++G(d,p)	1.112	1.088	1.084	1.476	1.455	1.192	121.9	124.6	121.7
	M06-2x/cc-pVTZ	1.102	1.086	1.081	1.438	1.450	1.221	122.2	123.3	120.6
	CCSD(T)/cc-pVTZ	1.103	1.088	1.083	1.445	1.459	1.231	122.8	123.6	120.6
	B3LYP/6-311G(d,p)	1.108	1.092	1.085	1.439	1.451	1.229	123.5	124.0	120.7
IM-3t	MP2/6-311++G(d,p)	---	1.083	1.090	1.462	1.491	1.192	122.5	128.1	---
	M06-2x/cc-pVTZ	---	1.080	1.087	1.441	1.485	1.190	122.2	127.6	---
	CCSD(T)/cc-pVTZ	---	1.082	1.089	1.451	1.493	1.200	122.3	127.6	---
	B3LYP/6-311G(d,p)	---	1.084	1.098	1.441	1.490	1.198	123.0	127.9	---
IM-4t	MP2/6-311++G(d,p)	---	1.097	1.081	1.519	1.494	1.186	114.7	128.3	---
	M06-2x/cc-pVTZ	---	1.096	1.078	1.517	1.486	1.173	113.9	127.8	---
	CCSD(T)/cc-pVTZ	---	1.097	1.080	1.524	1.494	1.186	114.0	128.1	---
	B3LYP/6-311G(d,p)	---	1.101	1.081	1.523	1.490	1.180	115.0	128.2	---

Table S1 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H6 (C2-H4/7)	r C3-H5 (C3-H7)	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠C2-C1-O8	∠H4-C1-O8
IM-5t	MP2/6-311++G(d,p)	1.110	1.102	(1.081)	1.515	1.476	1.209	114.5	125.3	121.0
	M06-2x/cc-pVTZ	1.107	1.100	(1.077)	1.512	1.463	1.196	113.5	124.5	121.0
	CCSD(T)/cc-pVTZ	1.107	1.101	(1.080)	1.518	1.474	1.209	114.4	125.1	121.0
	B3LYP/6-311G(d,p)	1.113	1.106	(1.081)	1.524	1.463	1.200	115.5	125.5	121.3
IM-6t	MP2/6-311++G(d,p)	1.100	---	1.091	1.483	1.289	1.387	138.3	114.4	107.3
	M06-2x/cc-pVTZ	1.101	---	1.088	1.480	1.303	1.375	136.5	114.6	107.5
	CCSD(T)/cc-pVTZ	1.100	---	1.090	1.488	1.315	1.384	136.4	114.4	107.5
	B3LYP/6-311G(d,p)	1.108	---	1.092	1.483	1.307	1.373	138.3	115.6	107.6
IM-7t	MP2/6-311++G(d,p)	1.103	1.095	(1.079)	1.509	1.289	1.371	125.5	116.4	107.4
	M06-2x/cc-pVTZ	1.103	1.091	(1.077)	1.508	1.303	1.361	124.0	116.4	107.6
	CCSD(T)/cc-pVTZ	1.040	1.094	(1.078)	1.513	1.315	1.370	124.9	116.7	108.1
	B3LYP/6-311G(d,p)	1.111	1.097	(1.079)	1.516	1.306	1.355	125.5	118.1	107.9
TS-1t	MP2/6-311++G(d,p)	1.066	---	1.093	1.211	1.453	1.846	171.8	102.4	99.2
	M06-2x/cc-pVTZ	1.064	---	1.091	1.217	1.452	1.967	171.4	99.7	98.5
	CCSD(T)/cc-pVTZ	1.065	---	1.092	1.231	1.463	1.987	169.0	100.9	100.0
	B3LYP/6-311G(d,p)	1.063	---	1.094	1.217	1.452	2.079	173.2	97.3	97.3
TS-2t	MP2/6-311++G(d,p)	1.106	1.231	1.085	1.462	1.447	1.203	128.9	122.0	122.9
	M06-2x/cc-pVTZ	1.098	1.232	1.083	1.433	1.434	1.223	132.7	120.9	122.0
	CCSD(T)/cc-pVTZ	1.098	1.248	1.084	1.442	1.448	1.232	132.1	120.5	122.2
	B3LYP/6-311G(d,p)	1.100	1.251	1.086	1.435	1.437	1.233	133.5	119.8	122.4
TS-3t	MP2/6-311++G(d,p)	1.282	(1.479)	1.090	1.394	1.489	1.197	134.9	141.0	131.1
	M06-2x/cc-pVTZ	1.307	(1.440)	1.092	1.380	1.483	1.208	136.1	137.5	131.5
	CCSD(T)/cc-pVTZ	1.302	(1.454)	1.094	1.390	1.494	1.218	136.4	137.7	131.0
	B3LYP/6-311G(d,p)	1.315	(1.446)	1.095	1.382	1.488	1.216	137.1	138.0	131.2

Table S1 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H6 (C2-H4/7)	r C3-H5 (C3-H7)	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠C2-C1-O8	∠H4-C1-O8
TS-4t	MP2/6-311++G(d,p)	1.128	1.080	1.089	2.027	1.283	1.190	114.2	111.1	125.4
	M06-2x/cc-pVTZ	1.119	1.077	1.087	2.154	1.300	1.188	114.2	106.8	123.6
	CCSD(T)/cc-pVTZ	1.121	1.080	1.088	2.145	1.317	1.201	114.7	107.5	123.8
	B3LYP/6-311G(d,p)	1.125	1.079	1.091	2.253	1.304	1.191	114.8	108.2	123.5
TS-5t	MP2/6-311++G(d,p)	---	(1.082)	1.094	2.142	1.479	1.148	116.9	113.9	---
	M06-2x/cc-pVTZ	---	(1.077)	1.092	2.253	1.466	1.132	114.3	110.7	---
	CCSD(T)/cc-pVTZ	---	(1.081)	1.093	2.238	1.478	1.145	115.8	112.3	---
	B3LYP/6-311G(d,p)	---	(1.081)	1.101	2.493	1.465	1.134	116.0	110.2	---
TS-6t	MP2/6-311++G(d,p)	---	(1.238)	1.081	1.454	1.480	1.200	120.9	128.1	---
	M06-2x/cc-pVTZ	---	(1.230)	1.078	1.445	1.476	1.190	120.8	127.8	---
	CCSD(T)/cc-pVTZ	---	(1.247)	1.079	1.455	1.486	1.200	121.0	127.9	---
	B3LYP/6-311G(d,p)	---	(1.245)	1.080	1.451	1.483	1.197	122.3	128.3	---
TS-7t	MP2/6-311++G(d,p)	---	1.089	1.083	2.103	1.466	1.152	106.4	115.7	---
	M06-2x/cc-pVTZ	---	1.087	1.081	2.142	1.455	1.138	105.4	113.8	---
	CCSD(T)/cc-pVTZ	---	1.088	1.083	2.142	1.465	1.150	105.6	114.9	---
	B3LYP/6-311G(d,p)	---	1.090	1.085	2.223	1.455	1.141	106.2	114.4	---
TS-8t	MP2/6-311++G(d,p)	---	(1.078)	1.083	1.324	2.214	1.166	128.5	166.0	---
	M06-2x/cc-pVTZ	---	(1.073)	1.079	1.305	2.321	1.170	126.2	165.5	---
	CCSD(T)/cc-pVTZ	---	(1.076)	1.081	1.326	2.352	1.180	127.6	161.8	---
	B3LYP/6-311G(d,p)	---	(1.075)	1.081	1.307	2.424	1.176	126.8	165.5	---
TS-9t	MP2/6-311++G(d,p)	---	1.083	1.086	1.338	2.129	1.164	115.2	169.9	---
	M06-2x/cc-pVTZ	---	1.080	1.081	1.337	2.186	1.157	115.0	169.4	---
	CCSD(T)/cc-pVTZ	---								---
	B3LYP/6-311G(d,p)	---	1.082	1.085	1.333	2.285	1.162	114.1	171.3	---

Table S1 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H6 (C2-H4/7)	r C3-H5 (C3-H7)	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠C2-C1-O8	∠H4-C1-O8
TS-10t	MP2/6-311++G(d,p)	1.111	1.088	1.295	1.466	1.456	1.204	120.2	124.7	122.2
	M06-2x/cc-pVTZ	1.102	1.086	1.339	1.450	1.449	1.216	121.0	123.4	121.6
	CCSD(T)/cc-pVTZ	1.103	1.087	1.337	1.459	1.460	1.222	122.0	124.1	121.6
	B3LYP/6-311G(d,p)	1.108	1.091	1.356	1.460	1.451	1.220	123.2	124.4	121.8
TS-11t	MP2/6-311++G(d,p)	1.099	1.477	1.089	1.509	1.332	1.236	132.5	120.1	123.8
	M06-2x/cc-pVTZ	1.094	1.441	1.086	1.487	1.336	1.251	133.7	120.1	123.1
	CCSD(T)/cc-pVTZ	1.094	1.458	1.087	1.496	1.352	1.258	132.9	119.7	123.1
	B3LYP/6-311G(d,p)	1.098	1.454	1.089	1.489	1.346	1.257	134.5	119.8	122.8
TS-12t	MP2/6-311++G(d,p)	1.101	(1.257)	1.089	1.501	1.299	1.380	145.6	114.4	107.7
	M06-2x/cc-pVTZ	1.100	(1.271)	1.084	1.499	1.286	1.367	144.4	114.9	108.1
	CCSD(T)/cc-pVTZ	1.101	(1.282)	1.086	1.505	1.300	1.376	144.6	114.8	108.0
	B3LYP/6-311G(d,p)	1.106	(1.280)	1.088	1.506	1.292	1.363	144.2	115.8	108.2
TS-13t	MP2/6-311++G(d,p)	1.103	1.092	(1.079)	1.512	1.330	1.245	124.7	123.7	121.9
	M06-2x/cc-pVTZ	1.099	1.089	(1.076)	1.503	1.341	1.251	123.5	123.0	121.9
	CCSD(T)/cc-pVTZ	1.100	1.091	(1.079)	1.509	1.352	1.255	124.6	123.8	121.9
	B3LYP/6-311G(d,p)	1.105	1.094	(1.079)	1.512	1.347	1.249	125.4	124.4	122.0
TS-14t	MP2/6-311++G(d,p)	1.116	1.086	(1.081)	2.178	1.331	1.186	98.0	119.4	125.9
	M06-2x/cc-pVTZ	1.113	1.084	(1.078)	2.219	1.329	1.174	97.8	118.1	126.0
	CCSD(T)/cc-pVTZ	1.114	1.085	(1.080)	2.186	1.345	1.187	100.0	119.7	126.0
	B3LYP/6-311G(d,p)	1.117	1.087	(1.080)	2.219	1.336	1.180	100.6	119.5	125.8
TS-15t	MP2/6-311++G(d,p)	1.096	1.071	(1.064)	2.106	1.205	1.321	113.9	113.7	111.9
	M06-2x/cc-pVTZ	1.096	1.069	(1.064)	2.210	1.217	1.308	113.1	111.4	112.8
	CCSD(T)/cc-pVTZ	1.097	1.070	(1.066)	2.211	1.234	1.319	114.8	112.6	112.7
	B3LYP/6-311G(d,p)	1.103	1.070	(1.064)	2.272	1.223	1.304	115.0	113.7	113.0

Table S2. Selected bond distances and angles for structures on the singlet state potential energy surface of the O(^{3}P) + propyne reaction. Bond distances are in Angstroms and bond angles are in degrees. The atom numbering scheme is shown in Figure 4. Values in parentheses correspond to the alternative bond distance (e.g., C2-H4 rather than C2-H5).

Species	Level/Basis Set	r C1-H4	r C2-H5 (C2-H4/7)	r C3-H7	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠ C2-C1-O8	∠H4-C1-O8
IM-1s	MP2/6-311++G(d.p)	1.112	---	1.115	1.437	1.457	1.231	116.8	121.0	122.7
	M06-2x/cc-pVTZ	1.112	---	1.109	1.425	1.452	1.216	118.1	122.9	122.5
	CCSD(T)/cc-pVTZ	1.113	---	1.094	1.443	1.462	1.226	115.1	123.3	122.7
	B3LYP/6-311G(d,p)	1.103	---	1.097	1.393	1.459	1.243	125.0	108.6	124.5
trans-IM-2s	MP2/6-311++G(d,p)	1.110	1.086	1.087	1.475	1.343	1.218	120.4	124.1	121.1
	M06-2x/cc-pVTZ	1.108	1.083	1.084	1.475	1.326	1.202	120.4	124.1	121.2
	CCSD(T)/cc-pVTZ	1.108	1.084	1.085	1.478	1.341	1.215	120.3	124.2	121.2
	B3LYP/6-311G(d,p)	1.113	1.086	1.086	1.475	1.334	1.208	121.2	124.3	121.2
cis-IM-2s	MP2/6-311++G(d,p)	1.107	1.087	1.086	1.487	1.343	1.218	121.4	124.2	120.4
	M06-2x/cc-pVTZ	1.105	1.083	1.083	1.486	1.326	1.202	120.8	124.0	120.3
	CCSD(T)/cc-pVTZ	1.105	1.084	1.083	1.489	1.341	1.216	121.1	124.0	120.4
	B3LYP/6-311G(d,p)	1.110	1.086	1.085	1.486	1.333	1.209	121.6	124.5	120.5
IM-3s	MP2/6-311++G(d,p)	---	1.084	1.093	1.321	1.511	1.171	122.5	179.6	---
	M06-2x/cc-pVTZ	---	1.080	1.090	1.307	1.508	1.159	123.1	179.8	---
	CCSD(T)/cc-pVTZ	---	1.081	1.092	1.319	1.512	1.171	122.6	179.7	---
	B3LYP/6-311G(d,p)	---	1.084	1.094	1.310	1.513	1.165	123.8	179.9	---
IM-5s	MP2/6-311++G(d,p)									
	M06-2x/cc-pVTZ	1.105	1.093	---	1.511	1.445	1.196	115.6	123.0	122.7
	CCSD(T)/cc-pVTZ	1.105	1.094	---	1.515	1.464	1.209	115.0	123.2	122.5
	B3LYP/6-311G(d,p)	1.109	1.099	---	1.523	1.453	1.200	115.5	123.2	123.0
IM-6s	MP2/6-311++G(d,p)	1.085	---	1.083	1.437	1.326	1.490	156.3	55.1	113.7
	M06-2x/cc-pVTZ	1.081	---	1.077	1.438	1.308	1.496	141.4	53.9	113.1
	CCSD(T)/cc-pVTZ	1.083	---	1.081	1.439	1.325	1.486	156.3	55.3	113.9
	B3LYP/6-311G(d,p)	1.086	---	1.062	1.437	1.318	1.485	155.8	55.1	114.1

Table S2 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H5 (C2-H4/7)	r C3-H7	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠ C2-C1-O8	∠H4-C1-O8
TS-2s	MP2/6-311++G(d,p)	1.112	1.336	1.096	1.455	1.395	1.226	116.0	125.6	121.5
	M06-2x/cc-pVTZ	1.109	1.311	1.093	1.446	1.380	1.211	117.7	125.4	121.5
	CCSD(T)/cc-pVTZ	1.110	1.321	1.094	1.460	1.394	1.222	115.7	125.3	121.6
	B3LYP/6-311G(d,p)	1.117	1.325	1.097	1.443	1.383	1.218	120.6	125.8	121.8
TS-3s	MP2/6-311++G(d,p)	1.141	1.953	1.105	1.408	1.470	1.220	119.7	137.4	122.7
	M06-2x/cc-pVTZ	1.121	2.068	1.107	1.418	1.454	1.212	119.0	129.0	122.2
	CCSD(T)/cc-pVTZ	1.132	2.009	1.102	1.425	1.476	1.218	117.1	134.3	122.4
	B3LYP/6-311G(d,p)	1.130	2.064	1.110	1.412	1.456	1.221	121.9	129.0	122.6
TS-6s	MP2/6-311++G(d,p)	---	1.084	1.446	1.438	1.503	1.178	120.8	145.8	---
	M06-2x/cc-pVTZ	---	1.081	1.492	1.493	1.446	1.161	122.6	139.4	---
	CCSD(T)/cc-pVTZ	---	1.083	1.449	1.462	1.478	1.183	122.6	139.6	---
	B3LYP/6-311G(d,p)	---	1.085	1.492	1.471	1.467	1.171	123.8	141.0	---
TS-8s	MP2/6-311++G(d,p)	1.498	1.086	1.085	1.449	1.418	1.183	115.9	148.6	142.5
	M06-2x/cc-pVTZ	1.506	1.093	1.078	1.396	1.422	1.153	107.2	168.4	132.5
	CCSD(T)/cc-pVTZ	1.517	1.083	1.083	1.450	1.423	1.181	118.3	146.5	142.7
	B3LYP/6-311G(d,p)	1.541	1.093	1.082	1.420	1.426	1.163	113.0	160.2	137.0
TS-9s	MP2/6-311++G(d,p)	1.106	1.090	1.099	2.051	1.340	1.170	100.8	115.3	163.5
	M06-2x/cc-pVTZ	1.114	1.085	1.095	2.041	1.321	1.155	104.0	114.1	162.8
	CCSD(T)/cc-pVTZ	1.105	1.087	1.094	2.065	1.337	1.170	105.3	113.5	163.4
	B3LYP/6-311G(d,p)	1.102	1.089	1.095	2.085	1.327	1.161	110.4	113.8	163.7
TS-10s	MP2/6-311++G(d,p)	1.379	1.084	1.087	1.389	1.442	1.201	98.0	147.9	120.3
	M06-2x/cc-pVTZ	1.374	1.079	1.082	1.368	1.428	1.189	98.0	149.4	117.7
	CCSD(T)/cc-pVTZ	1.385	1.081	1.084	1.380	1.447	1.200	98.5	149.3	119.0
	B3LYP/6-311G(d,p)	1.397	1.082	1.085	1.372	1.438	1.193	99.4	150.0	118.3

Table S2 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H5 (C2-H4/7)	r C3-H7	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠ C2-C1-O8	∠H4-C1-O8
TS-11s	MP2/6-311++G(d,p)	1.764	1.072	1.652	1.958	1.258	1.153	110.4	129.0	147.9
	M06-2x/cc-pVTZ	1.696	1.068	1.587	1.996	1.234	1.136	107.6	130.7	146.3
	CCSD(T)/cc-pVTZ	1.726	1.070	1.605	1.989	1.250	1.149	108.4	130.2	146.9
	B3LYP/6-311G(d,p)	1.765	1.070	1.643	2.010	1.238	1.142	109.1	129.2	148.3
TS-12s	MP2/6-311++G(d,p)	---	1.093	1.084	1.457	1.475	1.176	91.2	167.9	---
	M06-2x/cc-pVTZ	---	1.089	1.077	1.496	1.444	1.156	91.9	162.2	---
	CCSD(T)/cc-pVTZ	---	1.090	1.080	1.469	1.472	1.176	89.6	168.1	---
	B3LYP/6-311G(d,p)	---	1.094	1.080	1.469	1.463	1.165	92.3	166.6	---
TS-13s	MP2/6-311++G(d,p)	1.554	1.470	1.086	1.422	1.338	1.175	133.8	147.0	117.8
	M06-2x/cc-pVTZ	1.527	1.484	1.083	1.398	1.317	1.163	138.2	148.3	115.5
	CCSD(T)/cc-pVTZ	1.587	1.457	1.083	1.423	1.337	1.170	133.6	147.9	117.4
	B3LYP/6-311G(d,p)	1.636	1.429	1.085	1.408	1.327	1.163	135.0	149.5	116.8
TS-14s	MP2/6-311++G(d,p)	1.094	1.072	1.490	1.842	1.267	1.214	75.3	119.4	133.3
	M06-2x/cc-pVTZ	1.093	1.070	1.561	1.779	1.247	1.215	77.9	117.8	130.6
	CCSD(T)/cc-pVTZ	1.093	1.072	1.584	1.788	1.266	1.222	80.9	118.5	130.3
	B3LYP/6-311G(d,p)	1.090	1.073	1.533	1.870	1.257	1.206	78.9	119.6	132.0
TS-15s	MP2/6-311++G(d,p)									
	M06-2x/cc-pVTZ	1.105	1.086	1.331	1.449	1.454	1.214	123.9	123.3	121.4
	CCSD(T)/cc-pVTZ	1.104	1.093	1.391	1.510	1.416	1.210	117.7	122.4	123.2
	B3LYP/6-311G(d,p)	1.108	1.098	1.409	1.515	1.410	1.202	118.1	122.4	123.4
TS-16s	MP2/6-311++G(d,p)	1.090	---	1.085	1.415	1.390	2.117	126.4	---	---
	M06-2x/cc-pVTZ	1.086	---	1.081	1.424	1.366	2.121	122.7	---	---
	CCSD(T)/cc-pVTZ	1.085	---	1.082	1.443	1.370	2.135	127.3	---	---
	B3LYP/6-311G(d,p)	1.088	---	1.083	1.431	1.372	2.121	124.8	---	---

Table S2 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H5 (C2-H4/7)	r C3-H7	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠ C2-C1-O8	∠H4-C1-O8
TS-17s	MP2/6-311++G(d,p)	1.092	1.092	---	1.416	1.357	1.328	92.3	128.6	110.6
	M06-2x/cc-pVTZ	1.089	1.088	---	1.407	1.346	1.324	92.4	128.9	110.2
	CCSD(T)/cc-pVTZ	1.089	1.089	---	1.420	1.354	1.334	93.0	128.3	110.5
	B3LYP/6-311G(d,p)	1.091	1.093	---	1.420	1.342	1.331	93.0	128.8	110.0
TS-18s	MP2/6-311++G(d,p)	1.100	---	1.080	2.069	1.312	1.237	126.9	86.4	121.6
	M06-2x/cc-pVTZ	1.099	---	1.078	2.066	1.295	1.223	127.8	86.1	121.6
	CCSD(T)/cc-pVTZ	1.098	---	1.079	2.106	1.312	1.234	126.3	86.3	121.7
	B3LYP/6-311G(d,p)	1.104	---	1.081	2.130	1.299	1.226	127.5	88.3	122.0
TS-19s	MP2/6-311++G(d,p)	1.436	---	1.082	1.435	1.325	1.813	153.2	50.2	---
	M06-2x/cc-pVTZ	1.366	---	1.079	1.434	1.312	1.766	152.7	50.4	---
	CCSD(T)/cc-pVTZ	1.397	---	1.080	1.450	1.325	1.837	150.4	48.9	---
	B3LYP/6-311G(d,p)	1.387	---	1.081	1.441	1.319	1.833	149.8	48.9	---
TS-20s	MP2/6-311++G(d,p)									
	M06-2x/cc-pVTZ	1.112	1.162	1.081	1.823	1.318	1.444	169.8	46.6	103.3
	CCSD(T)/cc-pVTZ	1.115	1.183	1.082	1.821	1.332	1.475	168.4	46.4	102.8
	B3LYP/6-311G(d,p)	1.116	1.183	1.083	1.836	1.325	1.472	167.1	45.9	103.0
TS-21s	MP2/6-311++G(d,p)	1.085	---	1.097	1.608	1.323	1.436	141.7	53.7	116.6
	M06-2x/cc-pVTZ	1.082	---	1.094	1.603	1.316	1.413	142.9	54.2	117.1
	CCSD(T)/cc-pVTZ	1.083	---	1.096	1.634	1.329	1.427	140.7	53.6	116.9
	B3LYP/6-311G(d,p)	1.084	---	1.094	1.648	1.316	1.426	141.3	53.1	117.0
cyclopropanone	MP2/6-311++G(d,p)	---	1.085	1.085	1.471	1.577	1.203	57.6	147.6	---
	M06-2x/cc-pVTZ	---	1.082	1.082	1.462	1.562	1.190	57.7	147.7	---
	CCSD(T)/cc-pVTZ	---	1.083	1.083	1.474	1.579	1.201	57.6	147.7	---
	B3LYP/6-311G(d,p)	---	1.086	1.086	1.471	1.573	1.195	57.7	147.7	---

Table S2 - continued.

Species	Level/Basis Set	r C1-H4	r C2-H5 (C2-H4/7)	r C3-H7	r C1-C2	r C2-C3	r C1-O8	∠C1-C2-C3	∠ C2-C1-O8	∠H4-C1-O8
cyclopropenol	MP2/6-311++G(d,p)	1.086	1.080	---	1.486	1.320	1.412	63.6	121.7	107.7
	M06-2x/cc-pVTZ	1.084	1.076	---	1.476	1.299	1.405	63.9	121.9	107.8
	CCSD(T)/cc-pVTZ	1.084	1.078	---	1.490	1.315	1.410	63.8	122.0	107.9
	B3LYP/6-311G(d,p)	1.087	1.079	---	1.487	1.305	1.412	64.0	122.4	107.3
vinoxycarbene	MP2/6-311++G(d,p)	1.125	1.087	1.083	---	1.329	1.304	---	---	106.3
	M06-2x/cc-pVTZ	1.122	1.084	1.080	---	1.315	1.298	---	---	106.3
	CCSD(T)/cc-pVTZ	1.126	1.085	1.081	---	1.329	1.311	---	---	106.1
	B3LYP/6-311G(d,p)	1.129	1.087	1.082	---	1.320	1.305	---	---	106.3
methoxyacetylene	MP2/6-311++G(d,p)	1.092	---	1.062	---	1.215	1.441	---	---	109.9
	M06-2x/cc-pVTZ	1.089	---	1.060	---	1.196	1.435	---	---	109.8
	CCSD(T)/cc-pVTZ	1.091	---	1.061	---	1.210	1.443	---	---	109.9
	B3LYP/6-311G(d,p)	1.092	---	1.060	---	1.201	1.447	---	---	110.0
hydroxyvinyl-	MP2/6-311++G(d,p)	---	---	1.082	1.414	1.327	1.769	158.3	53.4	---
carbene	M06-2x/cc-pVTZ	---	---	1.079	1.408	1.315	1.749	158.5	53.4	---
	CCSD(T)/cc-pVTZ	---	---	1.080	1.430	1/327	1.878	153.0	49.6	---
	B3LYP/6-311G(d,p)	---	---	1.081	1.416	1.322	1.881	152.5	49.8	---

Table S3. RMS differences in selected bond distances (in Å) and angles (in degrees) for species on the triplet state surface. The differences are calculated relative to the CCSD(T)/cc-pVTZ optimized geometries. Note that TS-9t is not listed because the structure could not be located at the CCSD(T)/cc-pVTZ level.

Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)	Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)
Propyne	MP2	0.0044	0.00	IM-7t	MP2	0.0279	0.56
	M06-2x	0.0084	0.00		M06-2x	0.0266	0.60
	B3LYP	0.0072	0.00		B3LYP	0.0299	0.89
IM-0t	MP2	0.0191	2.46	TS-1t	MP2	0.0638	1.89
	M06-2x	0.2264	2.94		M06-2x	0.0120	1.77
	B3LYP	0.3305	5.86		B3LYP	0.0419	3.55
IM-1t	MP2	0.0238	1.61	TS-2t	MP2	0.0163	2.08
	M06-2x	0.0086	0.45		M06-2x	0.0101	0.42
	B3LYP	0.0074	0.93		B3LYP	0.0056	0.91
IM-2t	MP2	0.0207	1.02	TS-3t	MP2	0.0159	2.09
	M06-2x	0.0063	0.39		M06-2x	0.0094	0.34
	B3LYP	0.0050	0.47		B3LYP	0.0075	0.49
IM-3t	MP2	0.0062	0.38	TS-4t	MP2	0.0504	2.29
	M06-2x	0.0074	0.07		M06-2x	0.0096	0.51
	B3LYP	0.0063	0.54		B3LYP	0.0446	0.45
IM-4t	MP2	0.0023	0.51	TS-5t	MP2	0.0430	1.37
	M06-2x	0.0076	0.22		M06-2x	0.0105	1.55
	B3LYP	0.0037	0.71		B3LYP	0.1143	1.49
IM-5t	MP2	0.0020	0.13	TS-6t	MP2	0.0049	0.16
	M06-2x	0.0075	0.62		M06-2x	0.0109	0.16
	B3LYP	0.0071	0.69		B3LYP	0.0028	0.96
IM-6t	MP2	0.0119	1.10	TS-7t	MP2	0.0175	0.80
	M06-2x	0.0077	0.13		M06-2x	0.0071	0.79
	B3LYP	0.0075	1.30		B3LYP	0.0367	0.55

Table S3 - continued.

Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)
TS-8t	MP2	0.0621	3.04
	M06-2x	0.0174	2.80
	B3LYP	0.0334	2.68
TS-10t	MP2	0.0192	1.14
	M06-2x	0.0064	0.70
	B3LYP	0.0090	0.72
TS-11t	MP2	0.0155	0.54
	M06-2x	0.0106	0.52
	B3LYP	0.0045	0.94
TS-12t	MP2	0.0105	0.65
	M06-2x	0.0085	0.14
	B3LYP	0.0067	0.63
TS-13t	MP2	0.0100	0.09
	M06-2x	0.0055	0.79
	B3LYP	0.0042	0.58
TS-14t	MP2	0.0067	1.17
	M06-2x	0.0159	1.57
	B3LYP	0.0143	0.38
TS-15t	MP2	0.0445	0.94
	M06-2x	0.0083	1.21
	B3LYP	0.0261	0.65

Table S4. RMS differences in selected bond distances (in Å) and angles (in degrees) for species on the singlet state surface. The differences are calculated relative to the optimized CCSD(T)/cc-pVTZ geometries.

Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)	Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)
IM-1s		Bond	Angle	TS-3s		Bond	Angle
	MP2	0.0103	1.64		MP2	0.0242	2.36
	M06-2x	0.0123	1.70		M06-2x	0.0265	3.26
	B3LYP	0.0240	10.24		B3LYP	0.0249	4.16
trans-IM-2s	MP2	0.0026	0.12	TS-6s	MP2	0.0158	4.52
	M06-2x	0.0083	0.09		M06-2x	0.0293	0.14
	B3LYP	0.0048	0.52		B3LYP	0.0210	1.30
cis-IM-2s	MP2	0.0023	0.20	TS-8s	MP2	0.0085	1.84
	M06-2x	0.0083	0.17		M06-2x	0.0255	15.32
	B3LYP	0.0049	0.38		B3LYP	0.0177	9.08
IM-3s	MP2	0.0018	0.16	TS-9s	MP2	0.0066	2.81
	M06-2x	0.0079	0.29		M06-2x	0.0140	0.89
	B3LYP	0.0050	0.86		B3LYP	0.0101	3.01
IM-5s	MP2			TS-10s	MP2	0.0053	1.15
	M06-2x	0.0104	0.39		M06-2x	0.0113	0.83
	B3LYP	0.0077	0.42		B2LYP	0.0076	0.81
IM-6s	MP2	0.0023	0.17	TS-11s	MP2	0.0281	1.45
	M06-2x	0.0090	8.66		M06-2x	0.0170	0.69
	B3LYP	0.0090	0.33		B3LYP	0.0243	1.08
TS-2s	MP2	0.0067	0.26	TS-12s	MP2	0.0061	1.13
	M06-2x	0.0102	1.15		M06-2x	0.0197	4.46
	B3LYP	0.0092	2.86		B3LYP	0.0067	2.16

Table S4 - continued.

Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)	Species	Level	RMS Diff in Bond Dist. (Å)	RMS Diff in Bond Angle (°)
TS-13s	MP2	0.0147	0.58	TS-20s	MP2	---	---
	M06-2x	0.0302	2.88		M06-2x	0.0160	0.90
	B3LYP	0.0243	1.29		B3LYP	0.0066	0.80
TS-14s	MP2	0.0448	3.71	TS-21s	MP2	0.0125	0.58
	M06-2x	0.0131	1.79		M06-2x	0.0164	1.30
	B3LYP	0.0403	1.65		B3LYP	0.0087	0.49
TS-15s	MP2	---	---	cyclo-	MP2	0.0023	0.06
	M06-2x	0.0380	3.81	propanone	M06-2x	0.0105	0.06
	B3LYP	0.0089	0.26		B3LYP	0.0043	0.09
TS-16s	MP2	0.0173	0.94	cyclo-	MP2	0.0031	0.25
	M06-2x	0.0105	4.64	propenol	M06-2x	0.0098	0.09
	B3LYP	0.0084	2.57		B3LYP	0.0050	0.41
TS-17s	MP2	0.0039	0.43	vinoxy-	MP2	0.0033	0.19
	M06-2x	0.0083	0.50	carbene	M06-2x	0.0087	0.16
	B3LYP	0.0062	0.41		B3LYP	0.0049	0.17
TS-18s	MP2	0.0165	0.34	methoxy-	MP2	0.0033	0.04
	M06-2x	0.0201	0.89	acetylene	M06-2x	0.0079	0.12
	B3LYP	0.0130	1.38		B3LYP	0.0049	0.07
TS-19s	MP2	0.0215	2.21	hydroxyl-	MP2	0.0547	4.65
	M06-2x	0.0357	1.97	vinylcarbene	M06-2x	0.0656	4.76
	B3LYP	0.0069	0.43		B3LYP	0.0075	0.37

Table S5. Relative energies on the triplet surface for reaction of O(^{3}P) with propyne, computed at different levels of theory. Energy differences (Δ) also are reported between each level and the optimized CCSD(T) results. All energies are in kJ/mol.

Species	B3LYP Rel. E	M06-2X Rel. E	MP2 Rel. E	CCSD(T) //B3LYP Rel. E	CCSD(T) //M06-2X Rel. E	CCSD(T) Rel. E	Δ B3LYP - CCSD(T)	Δ M06-2X - CCSD(T)	Δ MP2 - CCSD(T)	Δ CCSD(T)// B3LYP- CCSD(T)	Δ CCSD(T)// M06-2X - CCSD(T)
Propyne + O(^{3}P)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
IM-0t	-18.43	-14.11	-4.48	6.34	-1.02	-4.22	-14.21	-9.88	-0.25	10.56	3.20
IM-1t	-243.17	-241.21	-182.52	-201.68	-213.41	-212.44	-30.73	-28.77	29.92	10.76	-0.97
IM-2t	-257.14	-246.86	-193.29	-210.81	-225.61	-224.92	-32.22	-21.94	31.63	14.10	-0.69
IM-3t	-312.80	-300.47	-276.05	-270.11	-281.36	-279.71	-33.09	-20.76	3.66	9.60	-1.65
IM-4t	-264.73	-255.97	-243.15	-232.85	-242.21	-240.93	-23.80	-15.04	-2.23	8.08	-1.29
IM-5t	-170.32	-181.40	-161.58	-151.49	-157.69	-156.78	-13.54	-24.62	-4.79	5.29	-0.91
IM-6t	-115.70	-104.85	-28.01	-68.59	-82.06	-81.37	-34.34	-23.48	53.36	12.78	-0.69
IM-7t	-98.18	-91.38	-18.43	-55.45	-67.94	-67.60	-30.57	-23.77	49.18	12.16	-0.34
TS-1t	-17.52	0.40	78.66	22.53	17.99	16.48	-34.00	-16.08	62.18	6.05	1.51
TS-2t	-66.91	-55.04	2.97	-6.33	-27.36	-26.89	-40.02	-28.15	29.86	20.56	-0.47
TS-3t	-71.26	-54.06	-5.32	-16.03	-30.49	-28.95	-42.32	-25.11	23.63	12.92	-1.54
TS-4t	-105.38	-84.18	-21.10	-56.68	-48.13	-69.31	-36.07	-14.86	48.21	12.63	21.18
TS-5t	-192.07	-197.65	-170.01	-187.11	-176.73	-175.39	-16.68	-22.26	5.38	-11.72	-1.34
TS-6t	-143.71	-132.92	-109.20	-92.06	-110.54	-108.83	-34.88	-24.09	-0.37	16.77	-1.71
TS-7t	-207.78	-196.40	-171.84	-183.17	-184.17	-183.17	-24.61	-13.23	11.33	0.00	-1.00
TS-8t	-122.17	-88.28	-39.45	-62.43	-71.01	-72.52	-49.64	-15.76	33.08	10.10	1.51
TS-9t	-92.08	-78.57	-36.10	-46.31	-52.61	-49.00	-43.08	-29.57	12.90	2.69	-3.61
TS-10t	-41.96	-44.14	4.97	6.04	-10.37	-9.53	-32.44	-34.61	14.49	15.56	-0.85
TS-11t	-40.26	-18.47	51.94	25.77	5.65	7.05	-47.30	-25.51	44.89	18.73	-1.39
TS-12t	86.00	95.43	146.73	137.40	118.59	119.30	-33.30	-23.87	27.43	18.10	-0.71
TS-13t	-28.31	-23.11	63.05	29.51	11.72	12.96	-41.27	-36.07	50.08	16.54	-1.25
TS-14t	-92.75	-76.79	-21.17	-46.41	-56.48	-55.95	-36.81	-20.85	34.78	9.54	-0.53

TS-15t	3.94	26.21	121.26	57.99	46.32	46.57	-42.63	-20.36	74.69	11.41	-0.25
$^3C_2H_4$ + CO	-226.67	-217.95	-214.42	-217.69	-215.91	-214.14	-12.53	-3.81	-0.28	-3.55	-1.77
CH_2CH + HCO	-114.74	-92.88	-47.69	-79.63	-86.11	-87.44	-27.31	-5.44	39.75	7.81	1.33
CH_3CH + CO	-194.80	-200.68	-198.25	-200.35	-191.40	-190.97	-3.83	-9.71	-7.28	-9.38	-0.43
CH_3 + HCCO	-144.83	-118.68	-90.23	-92.69	-104.19	-103.32	-41.52	-15.37	13.08	10.63	-0.87
$^3CH_2$ + CH_2CO	-112.37	-110.90	-98.89	-81.84	-87.94	-87.44	-24.94	-23.46	-11.46	5.59	-0.51
C_2H_2 + ^3H_2CO	-32.88	-12.75	14.80	9.92	-0.65	-5.53	-27.35	-7.22	20.33	15.46	4.88

Table S6. Relative energies on the singlet surface for reaction of O(^{3}P) with propyne, computed at different levels of theory. Energy differences (Δ) also are reported between each level and the optimized CCSD(T) results. All energies are in kJ/mol.

Species	B3LYP Rel. E	M06-2X Rel. E	MP2 Rel. E	CCSD(T) //B3LYP Rel. E	CCSD(T) //M06-2X Rel. E	CCSD(T) Rel. E	Δ B3LYP – CCSD(T)	Δ M06-2X – CCSD(T)	Δ MP2 – CCSD(T)	Δ CCSD(T)// B3LYP – CCSD(T)	Δ CCSD(T)// M06-2X – CCSD(T)
IM-1s	-216.44	-208.86	-178.62	-168.75	-190.60	-191.60	-24.84	-17.26	12.98	22.85	1.00
IM-2s-trans	-489.61	-490.07	-482.05	-458.25	-477.43	-477.39	-12.22	-12.68	-4.66	19.14	-0.04
IM-2s-cis	-482.60	-482.43	-473.28	-452.32	-469.90	-469.85	-12.76	-12.58	-3.43	17.53	-0.05
IM-3s	-499.39	-500.79	-488.43	-460.83	-477.02	-475.94	-23.45	-24.85	-12.48	15.12	-1.08
IM-5s	-163.04	-167.04		-137.88	-154.00	-153.43	-9.60	-13.60		15.56	-0.57
IM-6s	-355.50	-290.18	-347.81	-320.56	-257.76	-346.37	-9.13	56.19	-1.44	25.81	88.60
TS-2s	-198.56	-203.23	-179.06	-156.07	-179.64	-178.70	-19.85	-24.53	-0.36	22.63	-0.94
TS-3s	-215.73	-210.17	-178.40	-166.39	-190.08	-190.05	-25.68	-20.12	11.66	23.66	-0.02
TS-6s	-166.25	-143.45	-161.83	-140.45	-156.85	-154.59	-11.67	11.14	-7.24	14.14	-2.26
TS-8s	-154.20	-143.34	-141.58	-107.37	-121.23	-133.11	-21.09	-10.23	-8.47	25.74	11.88
TS-9s	-136.47	-121.90	-116.80	-95.89	-113.13	-114.18	-22.29	-7.72	-2.62	18.29	1.05
TS-10s	-199.56	-188.49	-181.48	-154.76	-174.41	-175.50	-24.06	-12.99	-5.98	20.74	1.10
TS-11s	-146.22	-140.15	-149.08	-116.07	-124.73	-127.15	-19.07	-13.00	-21.93	11.07	2.41
TS-12s	-257.86	-252.71	-248.36	-221.31	-242.00	-239.13	-18.72	-13.58	-9.23	17.82	-2.87
TS-13s	-126.91	-108.29	-103.62	-78.31	-94.16	-97.01	-29.90	-11.28	-6.62	18.70	2.84
TS-14s	-94.47	-96.16	-81.06	-43.40	-67.09	-70.21	-24.26	-25.95	-10.85	26.81	3.11
TS-15s	-160.72	-40.53		-133.41	-89.19	-151.66	-9.07	111.13		18.25	62.47
TS-16s	-226.07	-188.74	-191.43	-196.28	-217.82	-221.75	-4.32	33.02	30.32	25.47	3.94
TS-17s	-168.41	-177.00	-144.78	-129.36	-151.62	-151.55	-16.86	-25.44	6.77	22.19	-0.07
TS-18s	-124.02	-119.23	-88.46	-89.84	-108.41	-108.74	-15.28	-10.49	20.27	18.89	0.33
TS-19s	-80.83	-89.01	-62.20	-47.38	-72.72	-74.43	-6.40	-14.58	12.23	27.05	1.70
TS-20s	-30.57	-52.46		-0.23	-26.80	-26.67	-3.90	-25.80		26.43	-0.14

TS-21s	70.39	47.88	93.46	113.69	84.46	83.80	-13.41	-35.93	9.65	29.88	0.66
TS-cis-trans-IM-2s	-455.60	-458.79	-452.26	-429.98	-447.70	-447.95	-7.65	-10.84	-4.31	17.97	0.25
cyclopropanone	-405.48	-420.92	-403.42	-375.59	-391.80	-390.39	-15.09	-30.53	-13.03	14.81	-1.40
cyclopropenol	-301.32	-337.79	-315.06	-275.69	-299.55	-299.50	-1.82	-38.29	-15.57	23.81	-0.05
vinoxycarbene	-191.69	-202.20	-157.95	-162.72	-184.54	-184.75	-6.94	-17.45	26.80	22.03	0.21
methoxyacetylene	-312.76	-331.79	-304.79	-276.42	-299.00	-300.01	-12.75	-31.78	-4.78	23.59	1.01
hydroxyvinylcarbene	-114.79	-123.87	-82.35	-73.86	-99.67	-102.93	-11.87	-20.94	20.58	29.07	3.25
$C_2H_4 + CO$	-482.23	-484.33	-487.72	-481.72	-484.15	-484.52	2.29	0.19	-3.20	2.80	0.37
$C_2H_2 + H_2 + CO$	-309.06	-313.25	-337.48	-316.78	-312.54	-318.89	9.83	5.64	-18.59	2.11	6.35
$H_2 + H_2CCCO$	-326.69	-307.30	-304.63	-278.33	-287.07	-292.26	-34.42	-15.04	-12.37	13.93	5.19
$C_2H_2 + H_2CO$	-306.90	-306.03	-316.62	-284.97	-297.55	-303.74	-3.15	-2.28	-12.88	18.77	6.19
$H_2CO + H_2CC$	-133.76	-126.99	-104.78	-236.48	-122.41	-122.33	-11.44	-4.66	17.55	-114.16	-0.09

Table S7. RMS differences for selected bond lengths and bond angles taken from available stable and transition state structures on the triplet and singlet state surfaces in the reaction of O(^{3}P) with propyne, calculated relative to the CASPT2/aug-cc-pVTZ results from Ref. 43. Bond length differences are reported in Angstroms and bond angle differences in degrees. The atom-numbering scheme is shown in Figure 4.

		Triplet State RMS errors		
Bond/Angle	**MP2**	**M06-2X**	**CCSD(T)**	**B3LYP**
C1-H4	0.020	0.018	0.019	0.022
C2-H6	0.013	0.012	0.002	0.005
C3-H5	0.010	0.011	0.002	0.018
C1-C2	0.068	0.028	0.041	0.009
C2-C3	0.018	0.013	0.007	0.010
C1-O8	0.074	0.038	0.045	0.011
∠ C1-C2-C3	2.65	0.85	1.79	1.60
∠ C2-C1-O8	3.30	2.65	2.30	2.52
∠ H4-C1-O8	1.56	1.89	0.44	1.98
avg bond error (Å)	**0.034**	**0.020**	**0.020**	**0.012**
avg angle error (deg.)	**2.51**	**1.77**	**1.51**	**2.03**

		Singlet State RMS errors		
Bond/Angle	**MP2**	**M06-2X**	**CCSD(T)**	**B3LYP**
C1-H4	0.008	0.038	0.024	0.011
C2-H5	0.011	0.057	0.033	0.054
C3-H7	0.015	0.037	0.022	0.026
C1-C2	0.012	0.023	0.020	0.030
C2-C3	0.007	0.021	0.010	0.013
C1-O8	0.007	0.017	0.005	0.013
∠ C1-C2-C3	0.97	1.98	1.36	4.54
∠ C2-C1-O8	3.29	3.98	2.17	7.75
∠ H4-C1-O8	0.32	0.91	0.69	1.10
avg bond error (Å)	**0.010**	**0.032**	**0.019**	**0.025**
avg angle error (deg.)	**1.53**	**2.29**	**1.41**	**4.46**

Table S8. Energy barriers for transition states on the triplet and singlet surfaces in the reaction of $O(^3P)$ with propyne, computed at the CCSD(T)/cc-pVTZ and CCSD(T)//M06-2X/cc-pVTZ levels of theory and compared with the CASPT2/aug-cc-pVTZ results from Ref. 43. Energy differences (Δ) are reported between each level and the CASPT2 results.

Transition State	Barrier Relative To:	CASPT2/ aTZ [a] Barrier (kJ/mol)	CCSD(T)/ cc-pVTZ Barrier (kJ/mol)	CCSD(T) – CASPT2 Δ (kJ/mol)	CCSD(T)// M06-2X Barrier kJ/mol	CCSD(T)// M06-2X – CASPT2 Δ (kJ/mol)
TS-1t (TS1)[b]	O + propyne	7.11	16.48	9.37	17.99	10.88
TS-2t cis (TS3 cis)	IM-1t cis	177.82	185.55	7.73	186.05	8.23
TS-2t trans (TS3 trans)	IM-1t trans	182.84			187.94	5.10
TS-3t cis (TS4 cis)	IM-1t cis	183.68	183.49	-0.19	182.92	-0.76
TS-3t trans (TS4 trans)	IM-1t trans	208.36			215.53	7.17
TS-4t (TS10)	CH_2CH + HCO	10.04	18.13	8.09	37.98	27.94
TS-2s (TS17)	IM-1s	7.53	12.9	5.37	10.96	3.43
TS-3s (TS14)	IM-1s	-1.26	1.55	2.81	0.52	1.78
TS-6s (TS16)	IM-3s	311.29	321.35	10.06	320.17	8.88
TS-11s (TS19)	IM-2s trans	351.50	350.24	-1.26	352.7	1.20
			RMS Error:	**6.64**	**RMS Error:**	**10.68**

[a] CASPT2/aug-cc-pVTZ results are taken from Ref. 43.

[b] The labeling scheme from Ref. 43 is listed in parentheses.

Table S9a. Natural atomic charges for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with propyne, computed at the M06-2X/cc-pVTZ level of theory. The atom-numbering scheme is shown in Figure 4 of the manuscript.

Atom	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_2CH + HCO
C1	-0.2475	-0.1855	0.1769	0.2431	0.2817	0.2294	0.3338
C2	0.0177	0.0988	0.2499	-0.0863	-0.1424	-0.0663	-0.0432
C3	-0.6690	-0.6778	-0.7590	-0.5420	-0.3101	-0.4866	-0.5316
H4	0.2371	0.2461	0.1281	0.1261	0.1144	0.1588	0.1200
H5	0.2394	0.2452	0.2444	0.2389	0.1880	0.2192	0.2042
H6	0.2315	0.2361	0.2341	0.3291	0.1845	0.1915	0.1622
H7	0.2318	0.2361	0.2335	0.2268	0.1880	0.2271	0.2084
O8	-0.0410	-0.1990	-0.5079	-0.5356	-0.5041	-0.4731	-0.4538

Table S9b. Natural spin densities for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with propyne, computed at the M06-2X/cc-pVTZ level of theory.

Atom	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_2CH + HCO
C1	0.0213	-0.1433	-0.0783	0.0147	-0.0573	0.5820	0.6132
C2	0.0267	0.4132	1.6405	1.1719	0.7423	0.7726	1.0420
C3	-0.0023	-0.0196	-0.0453	0.5697	1.0032	-0.0837	-0.1572
H4	-0.0008	0.0128	-0.0017	-0.0069	0.0003	0.1402	0.1326
H5	0.0025	0.0249	0.0529	0.0345	-0.0004	0.0536	0.0004
H6	0.0000	0.0077	0.0357	-0.0713	0.0131	0.0039	0.0418
H7	-0.0001	0.0076	0.0339	0.0021	-0.0004	0.0359	0.0731
O8	1.9527	1.6968	0.3624	0.2852	0.2991	0.4955	0.2543

Table S9c. Natural bond orders for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with propyne, computed at the M06-2X/cc-pVTZ level of theory.

Bond	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_2CH + HCO
C1-C2	2.9141	2.7722	1.2878	1.1871	1.2400	0.2863	0.0000
C2-C3	1.0463	1.0515	1.0525	1.1697	1.0545	2.0378	2.0509
C1-H4	0.9911	0.9831	0.9609	0.9609	0.9612	0.9624	0.9783
C2-H6	0.0000	0.0000	0.0000	0.4753	0.9778	0.9876	0.9907
C3-H5	0.9814	0.9788	0.9781	0.9775	0.9845	0.9730	0.9763
C3-H6	0.9821	0.9819	0.9804	0.3276	0.0000	0.0000	0.0000
C3-H7	0.9821	0.9819	0.9815	0.9905	0.9845	0.9770	0.9715
C1-O8	0.0151	0.1014	1.7385	1.7840	1.7817	1.5960	2.0892
C2-O8	0.0144	0.0790	0.0106	0.0000	0.0000	0.0113	---

Table S10a. Natural atomic charges for species in the HCO pathway on the singlet state surface for the reaction of O(^{3}P) with propyne, computed at the M06-2X/cc-pVTZ level of theory. The atom-numbering scheme is shown in Figure 4 of the manuscript.

Atom	IM-1s	TS-2s	cis-IM-2s	TS-4s (cis-trans)	trans-IM-2s	CH_2CH + HCO
C1	0.2340	0.3373	0.4060	0.4184	0.4028	0.3338
C2	0.2179	-0.2341	-0.3258	-0.2895	-0.2965	-0.0432
C3	-0.7437	-0.3870	-0.2687	-0.3450	-0.2993	-0.5316
H4	0.1223	0.1167	0.1049	0.1063	0.0984	0.1200
H5	0.2247	0.3324	0.2021	0.2156	0.2152	0.1622
H6	0.2267	0.2090	0.1948	0.1988	0.2011	0.2042
H7	0.2785	0.1944	0.2068	0.1918	0.1886	0.2084
O8	-0.5604	-0.5687	-0.5201	-0.4963	-0.5103	-0.4538

Table S10b. Natural bond order for species in the HCO pathway on the singlet state surface for the reaction of O(^{3}P) with propyne, computed at the M06-2X/cc-pVTZ level of theory.

Bond	IM-1s	TS-2s	cis-IM-2s	TS-4s (cis-trans)	trans-IM-2s	CH_2CH + HCO
C1-C2	1.0979	1.0632	1.0161	0.9895	1.0235	0.0000
C2-C3	1.0743	1.3904	1.9688	2.0025	1.9654	2.0509
C1-H4	0.9482	0.9552	0.9607	0.9575	0.9588	0.9783
C2-H5	0.0000	0.2663	0.9813	0.9575	0.9801	0.9907
C3-H5	0.9738	0.3878	0.0000	0.0000	0.0000	0.0000
C3-H6	0.9809	0.9917	0.9891	0.9883	0.9904	0.9763
C3-H7	0.9519	0.9700	0.9867	0.9869	0.9854	0.9715
C1-O8	1.9408	1.9749	2.0120	2.0401	2.0060	2.0892
C2-O8	0.0126	0.0000	0.0000	0.0000	0.0000	---

Table S11a. Natural atomic charges for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with 1-butyne, computed at the M06-2X/cc-pVTZ level of theory. The atom-numbering scheme is shown in Figure 4 of the manuscript.

Atom	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_3CHCH + HCO
C1	-0.2530	-0.1911	0.1785	0.2189	0.2801	0.2343	0.3338
C2	0.0180	0.1000	0.2542	-0.0760	-0.1261	-0.0766	-0.0567
C3	-0.4615	-0.4717	-0.5491	-0.3202	-0.1225	-0.2832	-0.3210
C4	-0.5615	-0.5595	-0.5713	-0.6160	-0.6534	-0.6027	-0.6081
H5	0.2394	0.2472	0.1282	0.1264	0.1151	0.1577	0.1200
H6	0.2239	0.2280	0.2215	0.2251	0.1888	0.2239	0.1577
H7	0.2239	0.2277	0.2312	0.3257	0.1835	0.1880	0.2047
H8	0.2073	0.2120	0.1986	0.2268	0.2284	0.2153	0.2095
H9	0.2043	0.2076	0.2164	0.2265	0.2067	0.2161	0.2095
H10	0.1990	0.1997	0.2051	0.2079	0.2132	0.2062	0.2044
O11	-0.0396	-0.1998	-0.5135	-0.5449	-0.5137	-0.4789	-0.4538

Table S11b. Natural spin densities for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with 1-butyne, computed at the M06-2X/cc-pVTZ level of theory.

Atom	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_3CHCH + HCO
C1	-0.0015	-0.1364	-0.0712	0.0213	-0.0524	0.5867	0.6132
C2	0.0471	0.4062	1.6421	1.1519	0.7463	0.7798	1.0491
C3	-0.0029	-0.0191	-0.0443	0.5031	0.9380	-0.0798	-0.1453
C4	0.0038	0.0218	0.0434	0.0264	-0.0212	0.0495	0.0663
H5	0.0003	0.0123	-0.0026	-0.0070	0.0016	0.14023	0.1326
H6	0.0008	0.0063	0.0240	0.0066	-0.0005	0.0350	0.0005
H7	0.0012	0.0101	0.0491	-0.0702	0.0081	0.0036	0.0401
H8	-0.0003	-0.0008	-0.0009	0.0328	0.0551	-0.0017	-0.0041
H9	-0.0004	-0.0009	-0.0015	0.0082	0.0177	-0.0012	-0.0041
H10	-0.0006	0.0007	0.0045	0.0040	0.0083	-0.0019	-0.0027
O11	1.9524	1.6998	0.3574	0.3228	0.2990	0.4896	0.2543

Table S11c. Natural bond orders for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with 1-butyne, computed at the M06-2X/cc-pVTZ level of theory.

Bond	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_3CHCH + HCO
C1-C2	2.9152	2.7756	1.2854	1.3310	1.3878	0.4261	---
C2-C3	1.0354	1.0398	1.0388	1.1231	1.0424	2.0197	2.0171
C3-C4	1.0123	1.0087	1.0094	1.0285	1.0371	0.9941	1.0089
C1-H5	0.9909	0.9837	0.9623	0.9624	0.9615	0.9640	0.9783
C2-H5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0068	---
C2-H6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C2-H7	0.0000	0.0000	0.0000	0.4516	0.9794	0.9893	0.9905
C3-H6	0.9734	0.9729	0.9774	0.9793	0.9754	0.9716	0.9679
C3-H7	0.9733	0.9726	0.9684	0.4138	0.0000	0.0000	0.0000
C4-H8	0.9909	0.9909	0.9905	0.9768	0.9768	0.9931	0.9861
C4-H9	0.9909	0.9910	0.9903	0.9852	0.9856	0.9930	0.9861
C4-H10	0.9901	0.9899	0.9898	0.9916	0.9886	0.9963	0.9930
C1-O11	0.0153	0.0884	1.7399	1.6190	1.6299	1.4427	2.0892
C2-O11	0.0146	0.0910	0.0121	0.0098	0.0000	0.0104	---

Table S12a. Natural atomic charges for species in the HCO pathway on the singlet state surface for the reaction of O(^{3}P) with 1-butyne, computed at the M06-2X/cc-pVTZ level of theory. The atom-numbering scheme is shown in Figure 4 of the manuscript.

Atom	IM-1s	TS-2s	cis-IM-2s	TS-4s (cis-trans)	trans-IM-2s	CH_3CHCH + HCO
C1	0.2311	0.2748	0.3988	0.4167	0.4090	0.3338
C2	0.2040	0.0222	-0.3480	-0.3143	-0.3206	-0.0567
C3	-0.5345	-0.4057	-0.0482	-0.1314	-0.0856	-0.3210
C4	-0.5993	-0.6165	-0.6480	-0.6295	-0.6270	-0.6081
H5	0.1227	0.1119	0.1049	0.1054	0.0958	0.1200
H6	0.2270	0.2210	0.1939	0.2202	0.1878	0.1577
H7	0.2839	0.3046	0.2048	0.1953	0.2111	0.2047
H8	0.2086	0.2114	0.2368	0.2065	0.2206	0.2095
H9	0.2064	0.2144	0.2376	0.2138	0.2206	0.2095
H10	0.2185	0.2270	0.2040	0.2200	0.2102	0.2044
O11	-0.5685	-0.5650	-0.5367	-0.5027	-0.5219	-0.4538

Table S12b. Natural bond orders for species in the HCO pathway on the singlet state surface for the reaction of O(^{3}P) with 1-butyne, computed at the M06-2X/cc-pVTZ level of theory.

Bond	IM-1s	TS-2s	cis-IM-2s	TS-4s (cis-trans)	trans-IM-2s	CH_3CHCH + HCO
C1-C2	1.1043	1.1942	1.0330	0.9913	1.0297	---
C2-C3	1.0769	1.3380	1.9188	1.9646	1.9245	2.0171
C3-C4	1.0120	0.9943	1.0281	1.0292	1.0296	1.0089
C1-H5	0.9496	0.9539	0.9629	0.9588	0.9586	0.9783
C2-H5	0.0000	0.0000	0.0000	0.0000	0.0000	---
C2-H6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C2-H7	0.0000	0.0000	0.9813	0.9738	0.9792	0.9905
C3-H6	0.9699	0.9790	0.9807	0.9784	1.0296	0.9679
C3-H7	0.9264	0.6855	0.0000	0.0000	0.0000	0.0000
C4-H8	0.9906	0.9946	0.9822	0.9897	0.9845	0.9861
C4-H9	0.9918	0.9938	0.9818	0.9850	0.9845	0.9861
C4-H10	0.9894	0.9912	0.9961	0.9839	0.9911	0.9930
C1-O11	1.9319	1.8108	1.9986	2.0413	2.0027	2.0892
C2-O11	0.0177	0.0082	0.0000	0.0000	0.0000	---

Table S13a. Natural atomic charges for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with 1-pentyne, computed at the M06-2X/cc-pVTZ level of theory. The atom-numbering scheme is shown in Figure 4 of the manuscript.

Atom	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_3CH_2CHCH + HCO
C1	-0.2529	-0.1907	0.1788	0.2204	0.2811	0.2353	0.3338
C2	0.0218	0.1045	0.2592	-0.0730	-0.1240	-0.0745	-0.0549
C3	-0.4684	-0.4790	-0.5571	-0.3257	-0.1261	-0.2878	-0.3242
C4	-0.3548	-0.3517	-0.3606	-0.4145	-0.4475	-0.3949	-0.4008
C5	-0.5851	-0.5860	-0.5829	-0.5781	-0.5760	-0.5748	-0.5762
H6	0.2393	0.2470	0.1282	0.1263	0.1153	0.1573	0.1200
H7	0.2225	0.2264	0.2203	0.2244	0.1878	0.2232	0.1585
H8	0.2225	0.2264	0.2302	0.3262	0.1841	0.1883	0.2036
H9	0.1969	0.2039	0.1923	0.2201	0.2221	0.1986	0.1973
H10	0.2035	0.2038	0.2087	0.2214	0.2006	0.2077	0.2014
H11	0.1931	0.1935	0.1930	0.1942	0.1969	0.1997	0.1993
H12	0.1935	0.1935	0.1971	0.1961	0.1961	0.1976	0.1944
H13	0.2060	0.2081	0.2068	0.2076	0.2039	0.2042	0.2016
O14	-0.0379	-0.1996	-0.5139	-0.5454	-0.5143	-0.4799	-0.4538

Table S13b. Natural spin densities for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with 1-pentyne, computed at the M06-2X/cc-pVTZ level of theory.

Atom	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_3CH_2CHCH + HCO
C1	-0.0016	-0.1351	-0.0713	0.0212	-0.0519	0.5881	0.6132
C2	0.0454	0.4028	1.6407	1.1509	0.7446	0.7774	1.0469
C3	-0.0028	-0.0194	-0.0450	0.5013	0.9382	-0.0802	-0.1467
C4	0.0029	0.0219	0.0428	0.0290	-0.0178	0.0490	0.0656
C5	-0.0004	0.0016	0.0066	0.0061	0.0093	-0.0001	-0.0022
H6	0.0003	0.0121	-0.0024	-0.0069	0.0015	0.1400	0.1326
H7	0.0014	0.0081	0.0241	0.0072	0.0002	0.0348	0.0004
H8	0.0006	0.0081	0.0496	-0.0698	0.0078	0.0036	0.0404
H9	-0.0003	-0.0009	-0.0015	0.0309	0.0518	-0.0019	-0.0029
H10	0.0000	-0.0009	-0.0016	0.0066	0.0185	-0.0009	-0.0035
H11	0.0000	0.0000	-0.0002	-0.0003	-0.0003	0.0006	0.0008
H12	0.0001	-0.0001	-0.0002	0.0003	-0.0002	-0.0001	0.0000
H13	0.0001	0.0006	0.0014	0.0013	-0.0006	0.0012	0.0011
O14	1.9543	1.7011	0.3571	0.3222	0.2989	0.4885	0.2543

Table S13c. Natural bond orders for species in the HCO pathway on the triplet state surface for the reaction of O(^{3}P) with 1-pentyne, computed at the M06-2X/cc-pVTZ level of theory.

Bond	IM-0t	TS-1t	IM-1t	TS-2t	IM-2t	TS-4t	CH_3CH_2CHCH + HCO
C1-C2	2.9156	2.7758	1.2856	1.3320	1.2440	0.4336	---
C2-C3	1.0343	1.0395	1.0392	1.1740	1.0424	1.9972	2.0201
C3-C4	1.0054	1.0026	1.0005	1.0186	1.0251	1.0071	0.9984
C4-C5	1.0183	1.0175	1.0180	1.0105	1.0191	1.0129	1.0164
C1-H6	0.9910	0.9838	0.9624	0.9611	0.9631	0.9540	0.9783
C2-H6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0077	---
C2-H7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C2-H8	0.0000	0.0000	0.0000	0.2985	0.9791	0.9849	0.9904
C3-H7	0.9726	0.9723	0.9765	0.9759	0.9747	0.9682	0.9670
C3-H8	0.9730	0.9723	0.9677	0.5171	0.0000	0.0000	0.0000
C4-H9	0.9814	0.9814	0.9814	0.9711	0.9674	0.9814	0.9842
C4-H10	0.9814	0.9814	0.9812	0.9800	0.9760	0.9757	0.9768
C5-H11	0.9908	0.9910	0.9913	0.9944	0.9908	0.9903	0.9900
C5-H12	0.9906	0.9910	0.9909	0.9936	0.9906	0.9910	0.9896
C5-H13	0.9908	0.9901	0.9897	0.9929	0.9906	0.9925	0.9914
C1-O14	0.0152	0.1071	1.7400	1.6210	1.7762	2.0708	2.0892
C2-O14	0.0140	0.0724	0.0122	0.0060	0.0000	0.0104	---

Table S14a. Natural atomic charges for species in the HCO pathway on the singlet state surface for the reaction of O(^{3}P) with 1-pentyne, computed at the M06-2X/cc-pVTZ level of theory. The atom-numbering scheme is shown in Figure 4 of the manuscript.

Atom	IM-1s	TS-2s	cis-IM-2s	TS-4s (cis-trans)	trans-IM-2s	CH_3CH_2CHCH + HCO
C1	0.2303	0.2777	0.4003	0.4171	0.3980	0.3338
C2	0.2140	0.0145	-0.3437	-0.3115	-0.32070	-0.0549
C3	-0.5436	-0.3992	-0.0507	-0.1337	-0.0832	-0.3242
C4	-0.3900	-0.4110	-0.4481	-0.4221	-0.4285	-0.4008
C5	-0.5824	-0.5818	-0.5796	-0.5743	-0.5722	-0.5762
H6	0.1228	0.1114	0.1052	0.1054	0.1016	0.1200
H7	0.2259	0.2189	0.1920	0.1941	0.2166	0.1585
H8	0.2829	0.3044	0.2051	0.2204	0.1926	0.2036
H9	0.2108	0.2196	0.2310	0.2114	0.2123	0.1973
H10	0.1991	0.2074	0.2310	0.1995	0.1994	0.2014
H11	0.1974	0.1982	0.1941	0.1954	0.1966	0.1993
H12	0.1930	0.1947	0.1941	0.1972	0.2010	0.1944
H13	0.2100	0.2113	0.2065	0.2043	0.2058	0.2016
O14	-0.5702	-0.5661	-0.5372	-0.5027	-0.5193	-0.4538

Table S14b. Natural bond orders for species in the HCO pathway on the singlet state surface for the reaction of O(^{3}P) with 1-pentyne, computed at the M06-2X/cc-pVTZ level of theory.

Bond	IM-1s	TS-2s	cis-IM-2s	TS-4s (cis-trans)	trans-IM-2s	CH_3CH_2CHCH + HCO
C1-C2	1.1047	1.0855	1.0325	0.9918	1.0296	---
C2-C3	1.0777	1.1896	1.9216	1.9654	1.9259	2.0201
C3-C4	1.0005	1.0054	1.0223	1.0201	1.0206	0.9984
C4-C5	1.0176	1.0167	1.0228	1.0150	1.0145	1.0164
C1-H6	0.9487	0.9511	0.9626	0.9586	0.9613	0.9783
C2-H6	0.0000	0.0000	0.0000	0.0000	0.0000	---
C2-H7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C2-H8	0.0000	0.0000	0.9806	0.9737	0.9783	0.9904
C3-H7	0.9696	0.9678	0.9812	0.9776	0.9782	0.9670
C3-H8	0.9288	0.8223	0.0000	0.0000	0.0000	0.0000
C4-H9	0.9795	0.9764	0.9740	0.9746	0.9744	0.9842
C4-H10	0.9821	0.9823	0.9740	0.9809	0.9819	0.9768
C5-H11	0.9902	0.9904	0.9892	0.9908	0.9912	0.9900
C5-H12	0.9917	0.9900	0.9892	0.9906	0.9899	0.9896
C5-H13	0.9914	0.9898	0.9904	0.9909	0.9905	0.9914
C1-O14	1.9324	1.9428	1.9980	2.0409	2.0021	2.0892
C2-O14	0.0154	0.0183	0.0000	0.0000	0.0000	---

Table S15. Relative energies in kJ/mol for the species involved in the ~~entrance barrier~~ the primary HCO formation pathways on the triplet and singlet surfaces for reactions of $O(^3P)$ with alkenes. Results are reported at the CCSD(T)//M06-2X/cc-pVTZ level.

Species	**ethylene**	**propene**	**1-butene**	**1-pentene**
alkene + $O(^3P)$	0.0	0.0	0.0	0.0
IM-0t	1.6	1.9	-1.0	-1.1
TS-1t	17.6	11.8	10.6	11.2
IM-1t	-87.7	-88.6	-88.4	-88.5
TS-2t	48.0	42.9	41.0	40.4
IM-2t	-123.1	-113.3	-114.7	-114.7
TS-4t	-64.5	-66.8	-67.4	-66.8
MECP	-88.4	-110.9	-111.5	-113.0
IM-1s	-325.9	-336.3	-338.2	-337.7
TS-2s	-75.9	-100.7	-102.9	-103.3
IM-2s	-443.8	-429.3	-431.6	-423.9
HCO + fragment	-106.8 (CH_3)	-98.3 (CH_3CH_2)	-97.1 ($CH_3CH_2CH_2$)	-95.6 ($CH_3CH_2CH_2CH_2$)

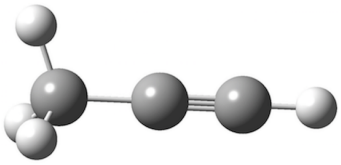
Appendix S1. Cartesian coordinates in Å computed at the CCSD(T)/cc-pVTZ level for species on the triplet and singlet state surfaces in the reaction of O(^{3}P) with propyne. Electronic energies (E_{el}) and vibrational zero-point energies (E_{VZP}), both in hartrees, also are reported. For transition states, the imaginary frequency is reported in cm^{-1}. Also included are the Cartesian coordinates of the MECP near IM-1t and IM-1s, obtained at the CCSD/cc-pVTZ level.

Cartesian Coordinates of Species on the Triplet State Surface in the O(^{3}P) + Propyne Reaction

Propyne

E_{el} = -116.4354728 E_{VZP} = 0.0553088

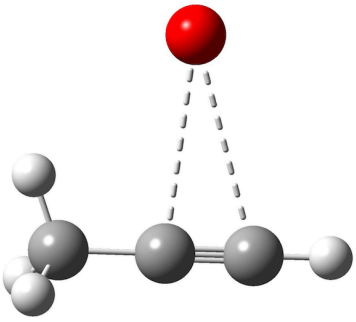
C	0.000000	-0.000003	1.429552
C	0.000000	-0.000005	0.218364
C	0.000000	-0.000011	-1.248151
H	0.000000	0.000001	2.492325
H	0.000000	1.021284	-1.631559
H	0.884439	-0.510638	-1.631541
H	-0.884439	-0.510638	-1.631541



IM-0t

E_{el} = -191.4113566 E_{VZP} = 0.0556229

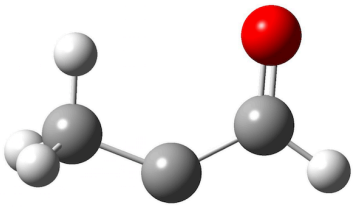
C	0.218567	-1.502857	0.000867
C	0.708505	-0.394645	-0.001697
C	1.294791	0.949494	0.000192
H	-0.210397	-2.475381	-0.000031
H	0.508078	1.704160	-0.026330
H	1.939662	1.087852	-0.868712
H	1.893164	1.103973	0.899196
O	-2.182710	0.533431	-0.000037



IM-1t

E_{el} = -191.4941089 E_{VZP} = 0.0590701

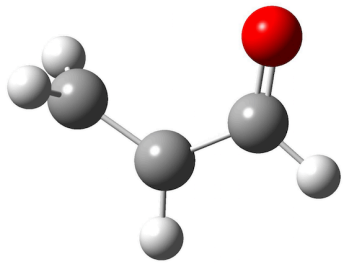
C	-0.921438	0.479410	0.000002
C	0.492263	0.687328	0.000350
C	1.619447	-0.262759	0.000140
H	-1.566018	1.368821	0.000322
H	1.231281	-1.286121	-0.001227
H	2.248326	-0.123858	0.883347
H	2.249627	-0.121954	-0.881831
O	-1.402587	-0.660098	-0.000634



IM-2t

E_{el} = -191.4966834 E_{VZP} = 0.0568910

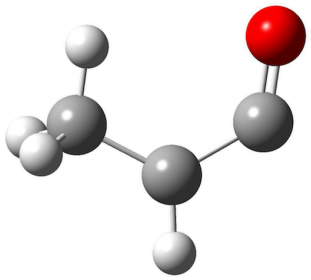
C	0.825299	0.466898	0.013753
C	-0.608641	0.640940	0.049122
C	-1.541754	-0.476226	-0.043650
H	1.422165	1.390859	0.092795
H	-1.868245	-0.847118	-1.006984
H	-0.981449	1.657970	0.149767
H	-1.843747	-1.021111	0.841827
O	1.377022	-0.628352	-0.096618



IM-3t

E_{el} = -191.5198433 E_{VZP} = 0.0591805

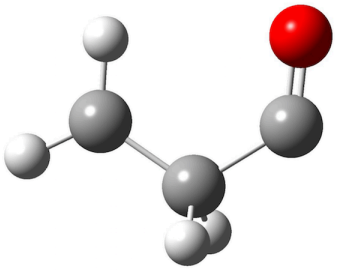
C	0.926532	0.523187	0.000003
C	-0.513698	0.699458	-0.000074
C	-1.459268	-0.456296	-0.000067
H	-0.892364	1.712798	0.000135
H	-0.916277	-1.400215	-0.001903
H	-2.113061	-0.417372	-0.877160
H	-2.109600	-0.419304	0.879760
O	1.538738	-0.509250	-0.000001



IM-4t

E_{el} = -191.5030684 E_{VZP} = 0.0571791

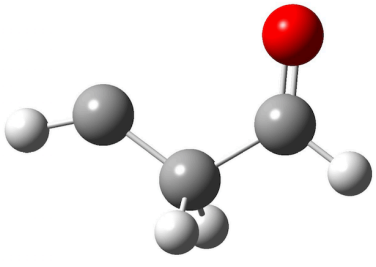
C	-0.872662	0.519731	0.000373
C	0.642974	0.675483	-0.000205
C	1.387224	-0.619587	0.000098
H	0.885672	1.299176	-0.869414
H	0.851879	-1.557027	-0.000846
H	0.886267	1.300000	0.868164
H	2.467867	-0.621417	0.001003
O	-1.504613	-0.484311	-0.000063



IM-5t

E_{el} = -191.4710874 E_{VZP} = 0.0572458

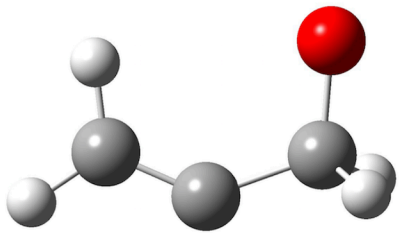
C	-0.811690	0.422210	-0.000041
C	0.695786	0.601869	0.000058
C	1.458614	-0.659657	-0.000024
H	-1.377726	1.373645	-0.000188
H	0.937470	1.225960	0.874823
H	0.937427	1.225994	-0.874712
H	2.517386	-0.873894	-0.000120
O	-1.383853	-0.642279	0.000030



IM-6t

E_{el} = -191.4418989 E_{VZP} = 0.0567825

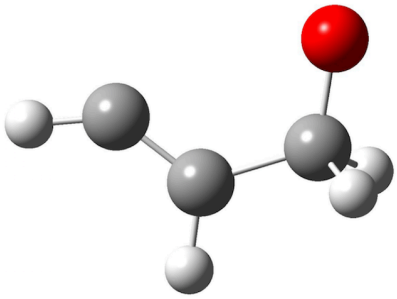
C	0.810130	-0.547968	0.000362
C	-0.677011	-0.585311	-0.000126
C	-1.651801	0.297577	-0.000836
H	1.220956	-1.081458	-0.870711
H	-1.433158	1.365399	0.001451
H	1.222152	-1.081922	0.869970
H	-2.694762	0.002347	0.003094
O	1.349613	0.726231	-0.000025



IM-7t

E_{el} = -191.4358588 E_{VZP} = 0.0559842

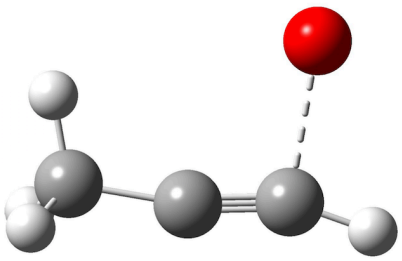
C	-0.742298	0.515667	-0.001927
C	0.770761	0.513633	0.001486
C	1.522419	-0.565543	-0.001917
H	-1.124657	1.090324	-0.863046
H	-1.124510	1.072889	0.872168
H	1.238568	1.502738	0.001805
H	2.577479	-0.788736	0.003638
O	-1.359021	-0.707470	-0.000052



TS-1t

E_{el} = -191.4032174 E_{VZP} = 0.0553682
Imag freq = 497.6*i*
[CCSD(T)/cc-pVTZ result includes second imaginary frequency of 87*i*, although the other levels do not.]

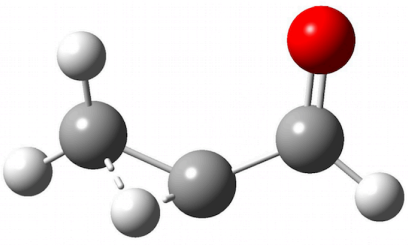
C	0.690979	0.877132	-0.001328
C	-0.467976	0.462188	-0.001353
C	-1.726377	-0.283733	-0.000338
H	1.500059	1.569546	-0.002757
H	-1.518024	-1.355586	-0.003722
H	-2.317956	-0.039901	-0.883766
H	-2.313477	-0.044596	0.887344
O	1.701412	-0.833381	0.005948



TS-2t

E_{el} = -191.4177592 E_{VZP} = 0.0533919
Imag freq = 1877.5*i*

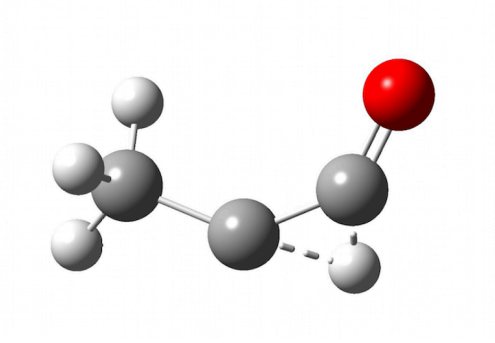
C	-0.909020	0.475589	-0.056977
C	0.525680	0.618134	-0.035243
C	1.597665	-0.354889	-0.036312
H	-1.506855	1.390447	0.045578
H	1.366994	-1.387887	0.197349
H	1.218264	0.487344	0.994651
H	2.578704	-0.075162	-0.391652
O	-1.425842	-0.639896	-0.141844



TS-3t

E_{el} = -191.4185814 E_{VZP} = 0.0534302
Imag freq = 1737.9*i*

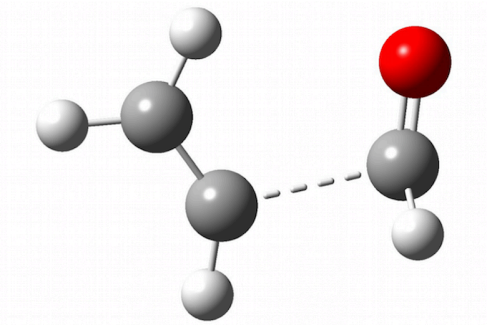
C	−0.878468	0.414050	0.126543
C	0.500985	0.583132	0.103588
C	1.696758	−0.302400	−0.029310
H	−0.457795	1.345757	−0.680078
H	1.458655	−1.138377	−0.694288
H	1.957486	−0.708227	0.951288
H	2.551485	0.240145	−0.430017
O	−1.678185	−0.488499	−0.043979



TS-4t

E_{el} = -191.4337223 E_{VZP} = 0.0531968
Imag freq = 337.1*i*

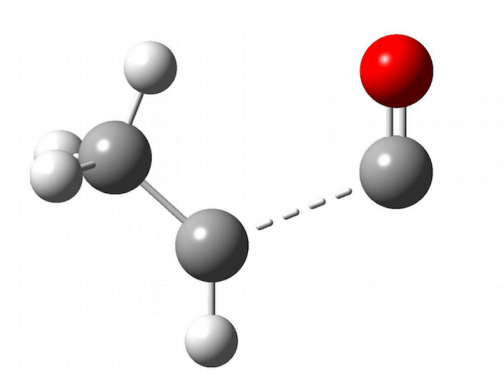
C	−1.178373	0.579172	−0.079723
C	0.965612	0.639823	−0.058005
C	1.548242	−0.538230	0.032913
H	−1.085370	1.229473	0.828435
H	2.628701	−0.632874	−0.054166
H	1.273118	1.661438	−0.222813
H	0.969479	−1.441331	0.192725
O	−1.506528	−0.575472	−0.043697



TS-5t

E_{el} = -191.4747274 E_{VZP} = 0.0538004
Imag freq = 315.2*i*

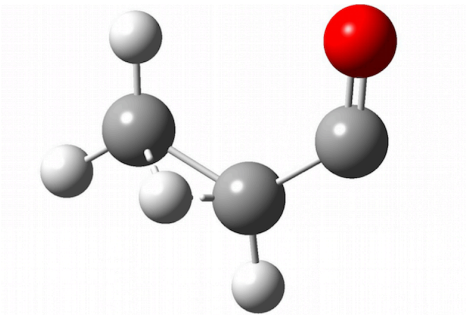
C	1.358925	0.560990	0.000586
C	−0.868973	0.768052	−0.000809
C	−1.632033	−0.497247	0.000202
H	−1.185401	1.801482	0.000637
H	−0.956472	−1.356623	0.000948
H	−2.274017	−0.580882	−0.884918
H	−2.273758	−0.578898	0.885707
O	1.692767	−0.534480	−0.000280



TS-6t

E_{el} = -191.4503852 E_{VZP} = 0.0548084
Imag freq = 1725.2*i*

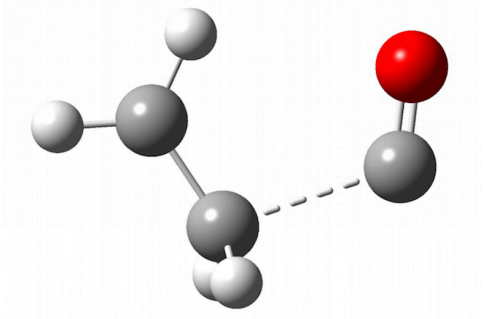
C	−0.884498	0.529413	−0.031855
C	0.564574	0.664209	−0.024910
C	1.443675	−0.533393	−0.055610
H	0.999747	1.640928	−0.173092
H	0.983682	−1.509654	−0.057009
H	1.009564	0.166676	1.027895
H	2.511364	−0.411726	−0.148608
O	−1.530858	−0.480950	0.003133



TS-7t

E_{el} = -191.4773470 E_{VZP} = 0.0534553
Imag freq = 411.4*i*

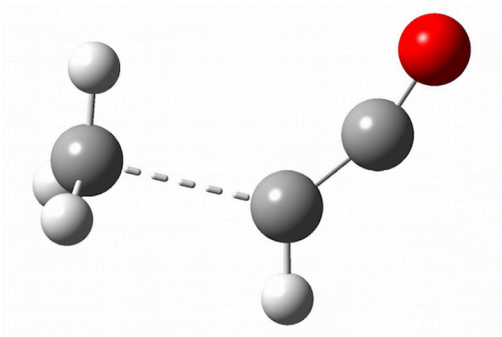
C	−1.177342	0.576010	−0.000839
C	0.959901	0.714891	0.000295
C	1.445029	−0.667466	−0.000543
H	1.057580	1.306740	−0.907442
H	0.761149	−1.506644	−0.001681
H	1.056284	1.305167	0.909196
H	2.508511	−0.877029	0.001938
O	−1.593631	−0.496105	0.000563



TS-8t

E_{el} = -191.4335932 E_{VZP} = 0.0518444
Imag freq = 441.5*i*
[CCSD(T)/cc-pVTZ result includes second imaginary frequency of 57*i*, although the other levels do not.]

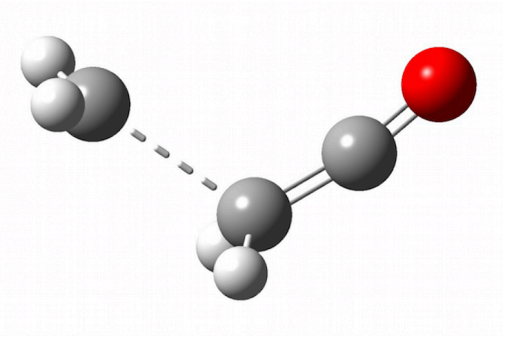
C	1.050524	0.257520	0.000518
C	−0.173023	0.767385	−0.000415
C	−2.214442	−0.401599	0.000069
H	−0.461607	1.803790	0.000033
H	−1.841096	−1.415565	−0.003110
H	−2.613727	−0.007456	−0.924516
H	−2.610161	−0.011645	0.927976
O	1.943530	−0.513620	−0.000177



TS-9t

E_{el} = -191.4260054 E_{VZP} = 0.053216
Imag freq = 519.7*i*
[CCSD(T)//M06-2X/cc-pVTZ results are reported. This structure was not found at the CCSD(T)/cc-pVTZ level.]

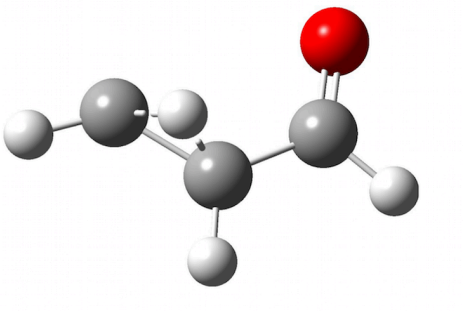
C	0.901412	0.187978	0.001430
C	−0.275657	0.821149	0.014080
C	−2.028159	−0.486168	−0.005450
H	−0.534337	1.303970	0.945000
H	−2.411750	−0.826537	0.945590
H	−0.540297	1.328940	−0.901740
H	−2.513590	−0.638417	−0.958880
O	1.801801	−0.538214	−0.011290



TS-10t

E_{el} = -191.4112276 E_{VZP} = 0.0534734
Imag freq = 1804.5*i*

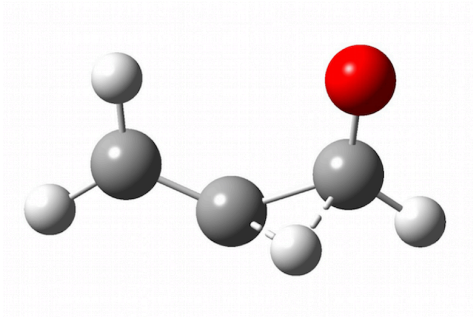
C	−0.826413	0.441130	−0.026715
C	0.625859	0.581400	−0.017605
C	1.515504	−0.575745	−0.059522
H	−1.374142	1.398881	−0.033060
H	1.124353	0.082280	1.036390
H	1.070888	1.561710	−0.164775
H	2.578708	−0.671791	−0.216414
O	−1.411188	−0.631474	0.000114



TS-11t

E_{el} = -191.4043329 E_{VZP} = 0.0528905
Imag freq = 1483.0*i*

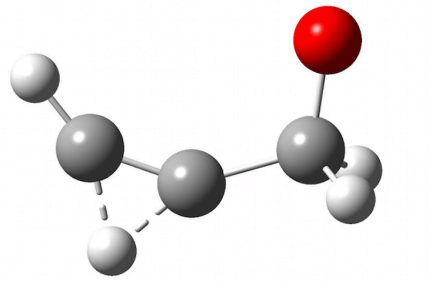
C	0.847827	−0.474236	−0.047902
C	−0.643126	−0.593752	−0.075443
C	−1.641490	0.315955	−0.008630
H	1.394888	−1.377310	−0.335989
H	−1.412431	1.377688	−0.046728
H	0.261449	−0.802824	1.048667
H	−2.677456	0.008284	0.043829
O	1.381786	0.663295	0.010259



TS-12t

E_{el} = -191.3591352 E_{VZP} = 0.0504483
Imag freq = 2085.4*i*

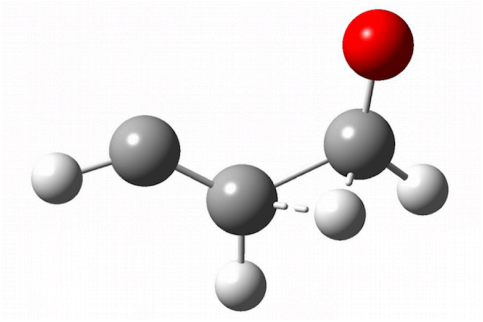
C	0.796575	−0.528934	−0.000110
C	−0.706703	−0.452172	0.000395
C	−1.727042	0.354002	0.000090
H	1.151409	−1.099621	−0.871705
H	−2.075609	1.382528	−0.000684
H	1.151958	−1.100221	0.870865
H	−1.896273	−0.931150	−0.000973
O	1.436441	0.688886	0.000031



TS-13t

E_{el} = -191.4019724 E_{VZP} = 0.052784
Imag freq = 1520.9*i*

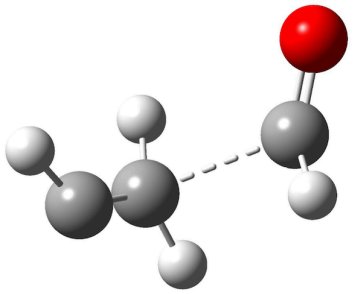
C	−0.771147	0.438901	−0.035328
C	0.736487	0.503853	−0.054714
C	1.551623	−0.574126	−0.019909
H	−1.240453	1.400524	−0.291062
H	−0.227958	0.666154	1.089379
H	1.143417	1.514899	−0.098268
H	2.616675	−0.728700	0.050945
O	−1.424182	−0.633080	−0.011411



TS-14t

E_{el} = -191.4283826 E_{VZP} = 0.0529479
Imag freq = 542.5*i*

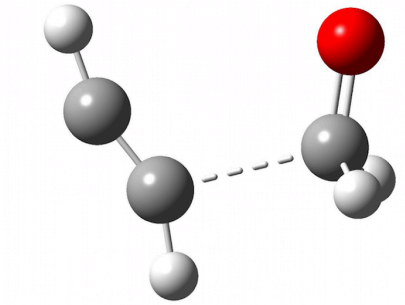
C	−0.945889	0.127276	0.462772
C	1.096902	0.607606	−0.149665
C	1.696507	−0.572734	0.088011
H	−0.860481	−0.297503	1.489099
H	1.231084	1.442610	0.529913
H	0.756734	0.863285	−1.153305
H	1.768461	−1.519327	−0.427088
O	−1.747614	−0.182744	−0.355666



TS-15t

E_{el} = -191.3880850 E_{VZP} = 0.0516985
Imag freq = 570.9*i*

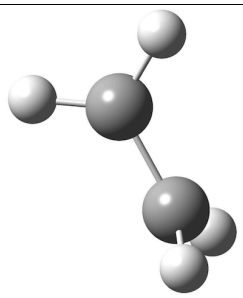
C	−0.571195	−0.993580	0.000000
C	−0.519814	1.216908	0.000000
C	0.611959	1.708440	0.000000
H	−1.132265	−1.215431	−0.916443
H	−1.132265	−1.215431	0.916443
H	−1.583040	1.337779	0.000000
H	1.675362	1.781725	0.000000
O	0.633970	−1.529032	0.000000



$^3C_2H_4$

E_{el} = -78.3307418 E_{VZP} = 0.0457300

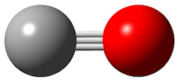
C	−0.728276	0.000055	−0.000087
C	0.728264	−0.000097	−0.000034
H	−1.294557	−0.837600	−0.392500
H	−1.294405	0.837551	0.392907
H	1.294621	0.392879	−0.837365
H	1.294417	−0.392577	0.837679



^1CO

E_{el} = -113.1555787 E_{VZP} = 0.0049040

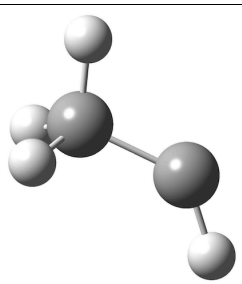
C	0.000000	0.000000	−0.649263
O	0.000000	0.000000	0.486513



$^3CH_3CH$

E_{el} = -78.3236483 E_{VZP} = 0.0474600

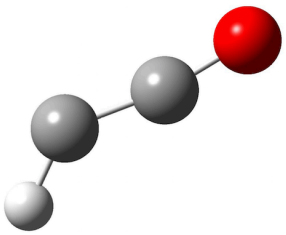
C	-0.812181	0.019083	-0.251861
C	0.615803	0.026675	0.121672
H	-1.627916	0.701718	-0.057400
H	1.122444	-0.856338	-0.274715
H	0.750444	0.021375	1.210211
H	1.134076	0.908198	-0.275147



^2HCCO

E_{el} = -151.6810022 E_{VZP} = 0.0187215

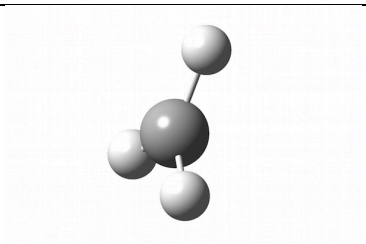
C	-0.023175	0.054162	-0.000062
C	1.269691	-0.146362	0.000016
H	2.094591	0.542205	0.000062
O	-1.196710	0.001374	0.000027



$^2CH_3$

E_{el} = -39.7609764 E_{VZP} = 0.0297807

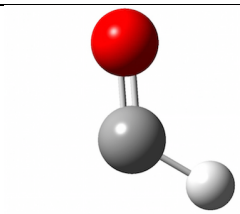
C	0.000002	0.000013	0.000000
H	-0.917474	0.567507	0.000000
H	-0.032803	-1.078291	0.000000
H	0.950263	0.510703	0.000000



^2HCO

E_{el} = -113.6841865 E_{VZP} = 0.0129884

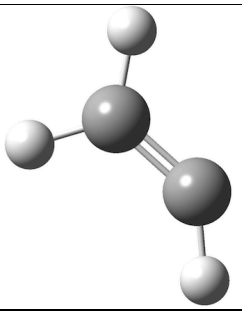
C	0.112360	0.613351	0.000000
H	-0.746223	1.333940	0.000000
O	-0.004067	-0.563491	0.000000

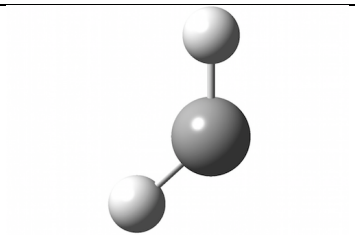
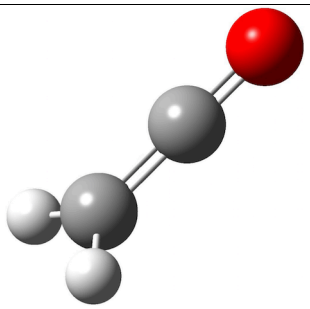
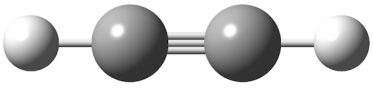
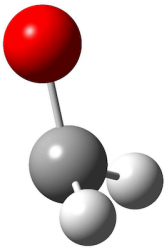


$^2CH_2CH$

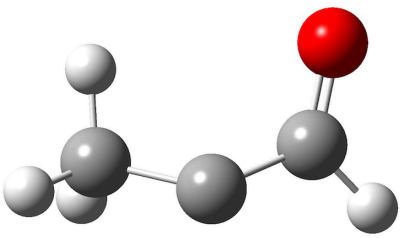
E_{el} = -77.7527401 E_{VZP} = 0.0365090

C	0.714665	-0.151392	-0.000163
C	-0.590107	0.031437	-0.000025
H	-1.022600	1.032435	-0.000014
H	1.598175	0.468769	0.000131
H	-1.285473	-0.801358	0.000092



$^3CH_2$ E_{el} = -39.0778538 E_{VZP} = 0.0173453 C 0.000000 0.106218 0.000000 H 0.990830 -0.318633 0.000000 H -0.990830 -0.318672 0.000000	
$^1CH_2CO$ E_{el} = -152.3583728 E_{VZP} = 0.0314531 C -0.102925 0.000357 -0.000224 C 1.216154 0.000027 -0.000022 H 1.738815 -0.942553 0.000315 H 1.741650 0.940704 0.000316 O -1.269980 -0.000056 0.000106	
$^1C_2H_2$ E_{el} = -77.1876481 E_{VZP} = 0.0250277 C 0.604840 0.000040 0.000000 C -0.604844 -0.000052 0.000000 H 1.668394 -0.000063 0.000000 H -1.668373 0.000136 0.000000	
^3H_2CO E_{el} = -114.2170385 E_{VZP} = 0.0234261 C -0.595466 -0.000003 -0.106894 H -1.069606 0.925801 0.235429 H -1.069631 -0.925777 0.235437 O 0.714004 -0.000001 0.021312	

MECP in the Vicinity of IM-1t and IM-1s in the O(^{3}P) + Propyne Reaction (CCSD/cc-pVTZ level)

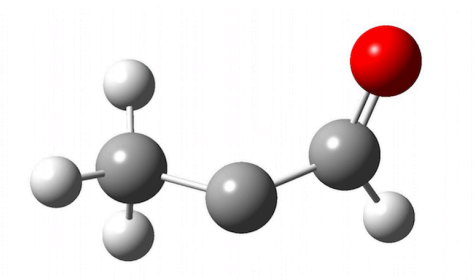
MECP for *O(^{3}P) + propyne* E_{el} = -191.447999 E_{VZP} (est.) = 0.058087 C 1.589241 -0.234829 0.089866 C 0.415502 0.472358 0.624792 H 2.447428 -0.217245 0.755962 H 1.874565 0.180006 -0.883931 H 1.283591 -1.272371 -0.097767 C -0.874469 0.419862 -0.025111 H -1.302006 1.379010 -0.360297 O -1.498742 -0.625712 -0.106033	

Cartesian Coordinates of Species on the Singlet State Surface in the O(^{3}P) + Propyne Reaction

IM-1s

E_{el} = -191.4841039 E_{VZP} = 0.0570007

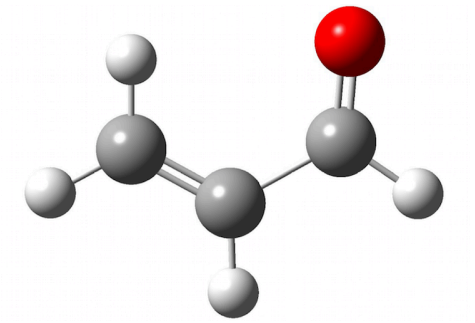
C	-0.705557	0.824872	0.066602
C	0.436951	0.526816	-0.762913
C	1.544316	-0.138523	-0.078813
H	-0.798025	1.901081	0.333211
H	1.720504	0.116414	0.970680
H	1.057708	-1.141840	-0.064841
H	2.462421	-0.225786	-0.654014
O	-1.556129	-0.006094	0.364268



cis-IM-2s

E_{el} = -191.5941817 E_{VZP} = 0.0611006

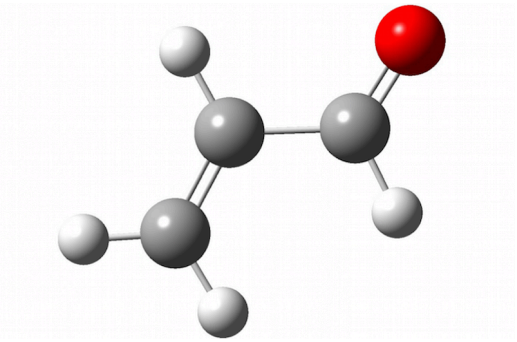
C	0.816140	0.442711	0.000115
C	-0.662860	0.611866	0.000156
C	-1.481879	-0.450044	-0.000217
H	1.403507	1.378479	0.000612
H	-1.047563	1.625518	0.000512
H	-1.065883	-1.450496	-0.000559
H	-2.558179	-0.338521	-0.000189
O	1.377356	-0.635652	-0.000420



trans-IM-2s

E_{el} = -191.5970577 E_{VZP} = 0.0611038

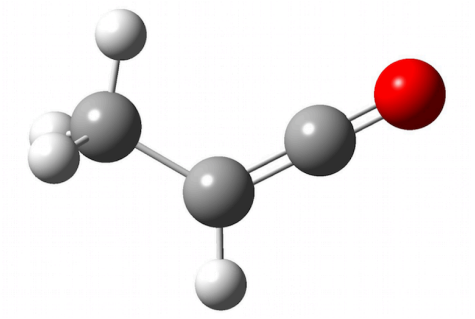
C	0.675114	0.349684	0.000185
C	-0.563389	-0.456138	0.000130
C	-1.762412	0.145211	-0.000109
H	0.511698	1.445296	0.000417
H	-0.449686	-1.533663	0.000330
H	-1.834593	1.227946	-0.000257
H	-2.687599	-0.415877	-0.000245
O	1.795538	-0.119531	-0.000185



IM-3s

E_{el} = -191.5963193 E_{VZP} = 0.0609160

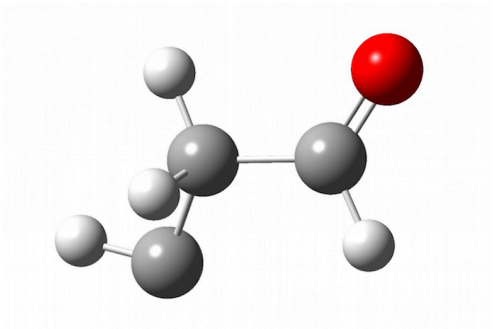
C	0.763224	0.134508	-0.000024
C	-0.477510	0.581141	0.000060
C	-1.676369	-0.340649	0.000012
H	-0.592590	1.656011	0.000162
H	-1.364164	-1.385558	-0.000100
H	-2.295697	-0.176481	-0.883960
H	-2.295636	-0.176655	0.884059
O	1.862872	-0.268217	-0.000099



IM-5s

E_{el} = -191.4692482 E_{VZP} = 0.0566833

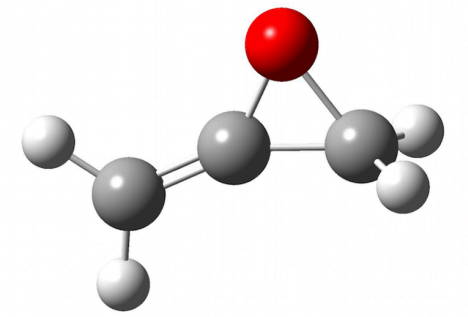
C	0.683704	-0.361571	0.125184
C	-0.621337	0.407220	0.158047
C	-1.804601	-0.366453	-0.222545
H	0.587245	-1.431889	0.381991
H	-0.493981	1.451398	-0.143205
H	-0.958541	0.407814	1.231064
H	-2.607208	0.373611	-0.400982
O	1.740736	0.140486	-0.179123



IM-6s

E_{el} = -191.5475883 E_{VZP} = 0.0615386

C	-1.073278	-0.596437	-0.000288
C	0.264857	-0.065935	0.001265
C	1.588984	-0.112851	-0.000629
H	-1.521913	-0.943006	0.922904
H	-1.519248	-0.943737	-0.924482
H	2.085982	-1.070958	0.001416
H	2.173104	0.796283	-0.000750
O	-0.737663	0.851594	-0.000147

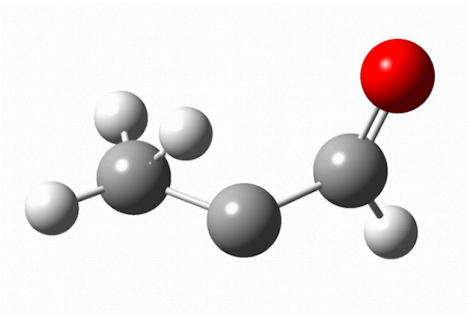


TS-2s

E_{el} = -191.4781260 E_{VZP} = 0.0559359

Imag freq = 912.5*i*

C	-0.751783	0.407370	0.183439
C	0.586516	0.555238	-0.380897
C	1.573587	-0.249775	0.186540
H	-1.032991	1.243331	0.856915
H	0.958428	-0.613108	-0.873741
H	1.432732	-0.859164	1.083908
H	2.582706	-0.231128	-0.218416
O	-1.540695	-0.482633	-0.095779

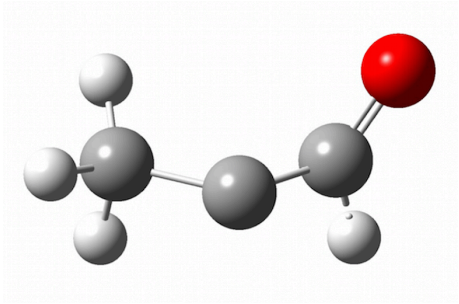


TS-3s

E_{el} = -191.4823795 E_{VZP} = 0.0558661

Imag freq = 226.2*i*

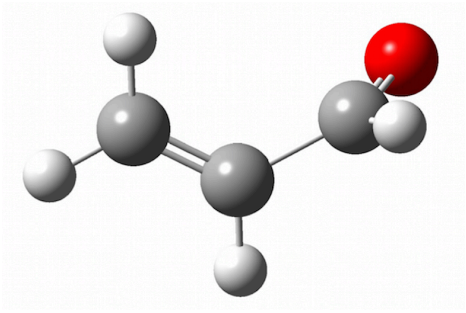
C	-0.667175	0.414022	0.152537
C	0.490333	0.306631	-0.671866
C	1.664368	-0.376150	-0.094795
H	-0.500654	1.393210	0.696367
H	2.000663	0.273929	0.728986
H	2.489333	-0.489691	-0.793865
H	1.394859	-1.330515	0.375598
O	-1.699856	-0.223667	0.256407



TS-4s

E_{el} = -191.5849652 E_{VZP} = 0.060224
Imag freq = 205.4*i*

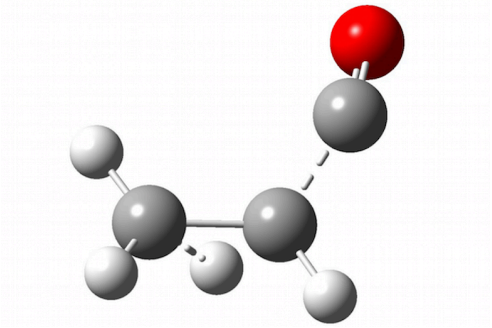
C	−0.760259	0.195069	0.371119
C	0.622057	0.500820	−0.125137
C	1.641113	−0.353347	0.014299
H	−0.973623	0.475674	1.419982
H	0.758854	1.462107	−0.610530
H	1.511021	−1.313453	0.500223
H	2.628048	−0.116984	−0.361758
O	−1.617721	−0.320325	−0.313701



TS-6s

E_{el} = -191.4680114 E_{VZP} = 0.0550066
Imag freq = 1703.2*i*

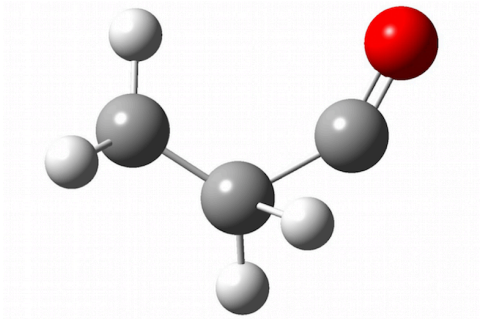
C	0.823183	0.284122	−0.286549
C	−0.555312	0.559957	0.115228
C	−1.645902	−0.422350	−0.055801
H	−0.836295	1.601051	0.020230
H	−1.397854	−1.470013	0.039086
H	−2.589610	−0.139290	−0.502084
H	−1.023930	0.120090	1.135505
O	1.764484	−0.330276	0.083749



TS-8s

E_{el} = -191.4588433 E_{VZP} = 0.0540196
Imag freq = 1615.6*i*

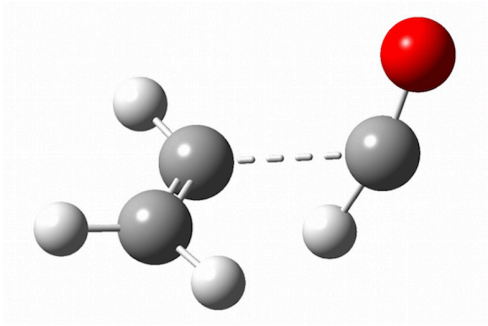
C	−0.761714	0.369659	0.034502
C	0.660938	0.591614	−0.135128
C	1.533907	−0.528205	−0.038064
H	0.899124	1.574565	−0.521895
H	0.180950	1.075150	0.991672
H	1.115461	−1.513767	−0.198782
H	2.397403	−0.463360	0.613072
O	−1.648966	−0.408874	−0.006491



TS-9s

E_{el} = -191.4519343 E_{VZP} = 0.0543194
Imag freq = 1763.9*i*

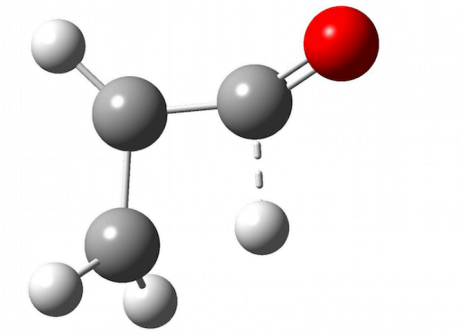
C	−0.985668	−0.290443	0.419178
C	0.848416	0.626173	0.170968
C	1.687453	−0.354603	−0.178597
H	−0.132971	−0.304454	1.121483
H	1.039052	1.685680	0.020957
H	2.655116	−0.204451	−0.650455
H	1.408114	−1.397669	−0.003456
O	−1.783814	0.041766	−0.369728



TS-10s

E_{el} = -191.4765064 E_{VZP} = 0.0555353
Imag freq = 1941.3*i*

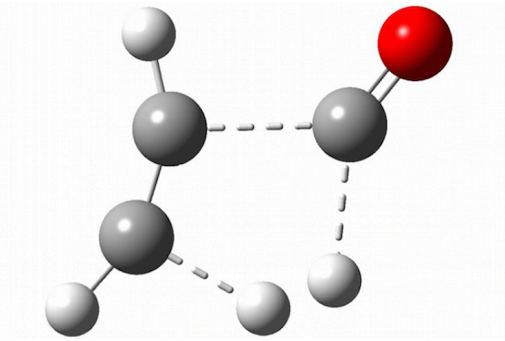
C	0.584066	-0.041910	-0.120382
C	-0.566659	0.717541	-0.058304
C	-1.525797	-0.358254	0.067673
H	-0.217539	-1.169884	-0.061331
H	-0.716376	1.787850	-0.063228
H	-2.319608	-0.305586	0.817235
H	-1.771546	-0.998082	-0.772304
O	1.759426	-0.152320	0.093214



TS-11s

E_{el} = -191.4506122 E_{VZP} = 0.0480588
Imag freq = 1046.2*i*

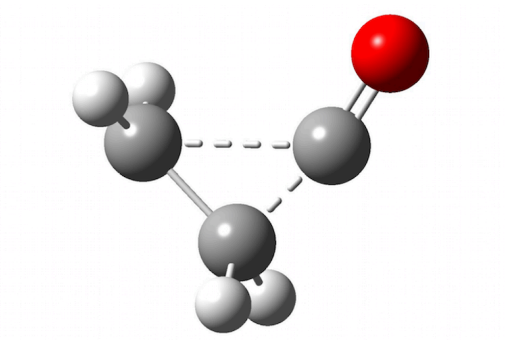
C	-0.854025	0.309750	-0.000566
C	0.870211	-0.682543	-0.000202
C	1.804657	0.148064	0.000210
H	0.183726	1.689007	-0.000475
H	0.525609	-1.695673	-0.000479
H	2.826492	0.459635	0.001021
H	1.015691	1.546214	-0.000109
O	-1.934572	-0.081351	0.000424



TS-12s

E_{el} = -191.5031580 E_{VZP} = 0.0579509
Imag freq = 698.9*i*

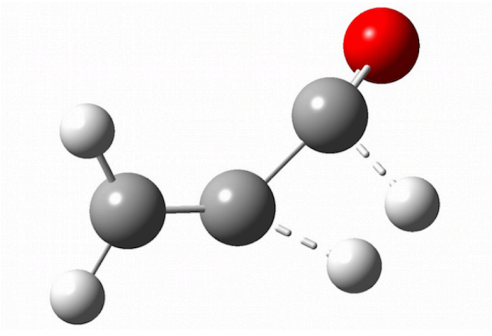
C	0.589774	0.311676	0.000519
C	-0.826489	0.703474	0.000207
C	-1.210086	-0.717409	0.000388
H	-1.050990	1.286219	-0.892826
H	-1.053065	1.290062	0.890220
H	-1.147018	-1.261478	-0.930681
H	-1.141637	-1.263852	0.929685
O	1.634190	-0.229675	-0.000385



TS-13s

E_{el} = -191.4404659 E_{VZP} = 0.0493919
Imag freq = 1977.1*i*

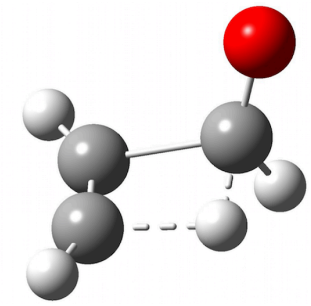
C	-0.715270	0.074946	0.155556
C	0.623721	0.276421	-0.282158
C	1.795585	-0.272762	0.052036
H	-0.605341	1.550441	0.730110
H	0.077397	1.597350	0.002386
H	2.704637	0.127089	-0.376971
H	1.884228	-1.088035	0.759782
O	-1.785642	-0.332309	-0.083489



TS-14s

E_{el} = -191.4342745 E_{VZP} = 0.0534079
Imag freq = 1407.5*i*

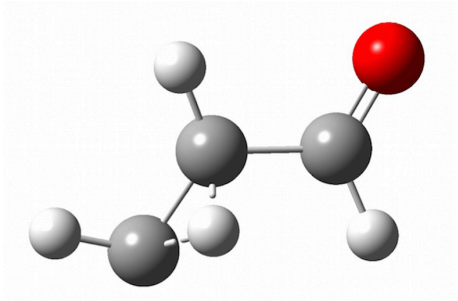
C	−0.599219	−0.099694	0.411443
C	0.934310	0.711934	−0.018526
C	1.309400	−0.492093	−0.125628
H	−0.525416	0.161892	1.469735
H	1.138173	1.746504	−0.211778
H	1.818065	−1.362807	−0.494021
H	0.038279	−1.177853	0.525573
O	−1.542006	−0.011077	−0.361656



TS-15s

E_{el} = -191.4674153 E_{VZP} = 0.0555259
Imag freq = 589.4*i*

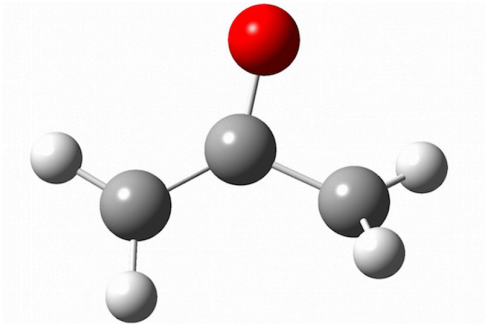
C	0.687862	−0.371952	0.073593
C	−0.608757	0.401453	0.090498
C	−1.800005	−0.305445	−0.204973
H	0.568685	−1.463010	0.191276
H	−0.484448	1.487174	0.127753
H	−2.614918	0.434322	−0.220626
H	−1.206281	−0.096621	1.035369
O	1.757795	0.161725	−0.111060



TS-16s

E_{el} = -191.4953246 E_{VZP} = 0.0567371
Imag freq = 687.3*i*

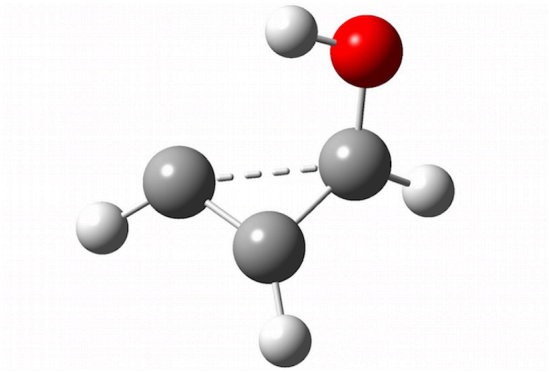
C	−1.040637	−0.843949	0.042498
C	0.096748	0.043252	0.017529
C	1.422001	−0.303920	0.040500
H	−1.244665	−1.563240	−0.744290
H	−1.841357	−0.575841	0.719237
H	1.694217	−1.337407	−0.126870
H	2.193622	0.450232	0.118956
O	−0.458811	1.206744	−0.071274



TS-17s

E_{el} = -191.4709586 E_{VZP} = 0.0591100
Imag freq = 598.6*i*

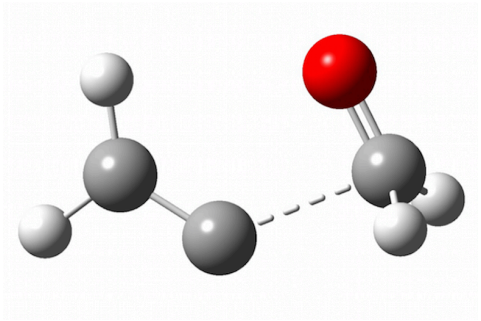
C	0.431741	0.508379	0.226422
C	−0.889405	0.523091	−0.294480
C	−1.149370	−0.733178	0.139022
H	0.772936	1.283278	0.911347
H	−1.480493	1.417318	−0.489200
H	−2.164859	−0.981430	0.457508
H	1.012638	−1.046976	−0.563110
O	1.437748	−0.307743	−0.092791



TS-18s

E_{el} = -191.4505185 E_{VZP} = 0.0549763
Imag freq = 322.3*i*

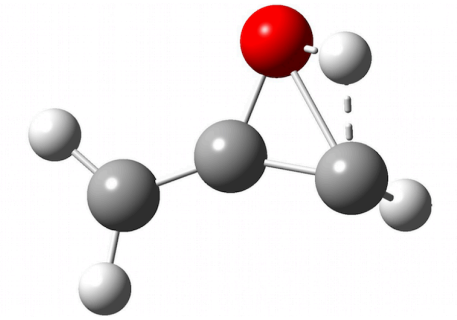
C	−1.300057	−0.420335	0.000158
C	0.785179	−0.714865	−0.000144
C	1.702437	0.223806	0.000123
H	−1.507392	−0.966222	−0.930264
H	−1.507241	−0.966888	0.930256
H	2.708548	−0.196469	−0.000550
H	1.569535	1.294230	0.000650
O	−1.048601	0.787964	−0.000115



TS-19s

E_{el} = -191.4373995 E_{VZP} = 0.0549252
Imag freq = 1456.9*i*

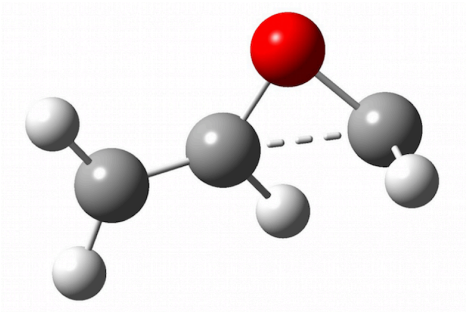
C	−1.018902	−0.876736	−0.119112
C	0.214742	−0.118468	−0.042505
C	1.538004	−0.072957	0.001250
H	−1.504741	0.368172	−0.526248
H	−1.310446	−1.241308	0.873354
H	2.104306	−0.991613	−0.029324
H	2.053003	0.873927	0.069343
O	−0.718148	0.924974	0.071884



TS-20s

E_{el} = -191.4200419 E_{VZP} = 0.0557593
Imag freq = 565.6*i*

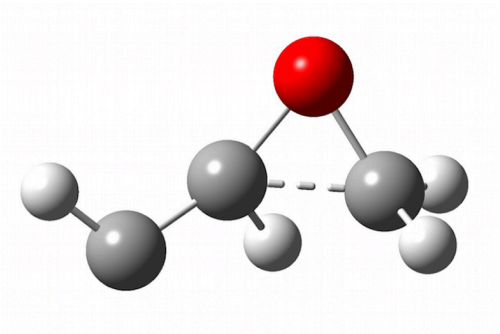
C	1.481680	−0.466490	−0.048642
C	−0.308860	−0.137106	−0.099166
C	−1.629703	−0.081633	0.060248
H	1.480131	−0.779564	1.021246
H	0.199699	−1.142468	−0.458419
H	−2.224688	−0.974568	−0.050196
H	−2.109945	0.868477	0.252298
O	0.674512	0.767437	−0.029946



TS-21s

E_{el} = -191.3773386 E_{VZP} = 0.0551320
Imag freq = 1199.5*i*

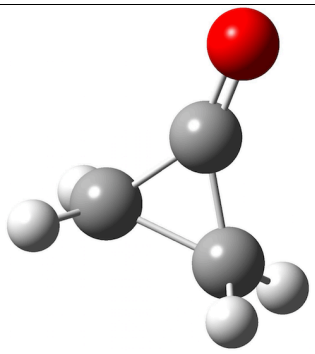
C	1.086472	−0.527729	0.094491
C	−0.425893	0.034351	−0.163101
C	−1.695071	−0.281389	0.073144
H	1.173643	−0.956482	1.085002
H	1.814551	−0.829734	−0.654362
H	−0.006008	−0.903980	−0.793797
H	−2.335702	0.597887	0.202309
O	0.695058	0.842614	0.016705



Cyclopropanone

E_{el} = -191.5637711 E_{VZP} = 0.0609519

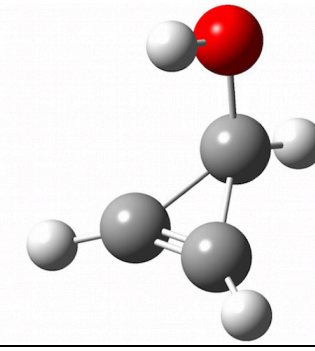
C	0.384017	0.000222	0.000923
C	-0.861438	0.789172	-0.000269
C	-0.861430	-0.789342	-0.000302
H	-1.159686	1.283814	-0.916344
H	-1.164382	1.282942	0.914993
H	-1.161526	-1.283712	-0.916151
H	-1.164381	-1.281872	0.915614
O	1.585386	-0.000185	-0.000028



Cyclopropenol

E_{el} = -191.5289992 E_{VZP} = 0.0608011

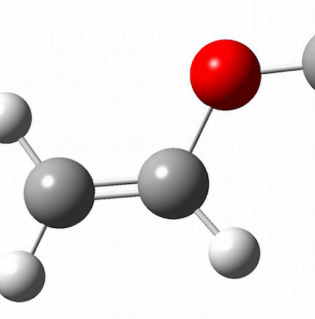
C	-0.220884	-0.000037	0.484242
C	0.983129	-0.657706	-0.096605
C	0.983130	0.657727	-0.096518
H	-0.412118	-0.000170	1.551504
H	1.474044	-1.575536	-0.375593
H	1.474092	1.575547	-0.375428
H	-1.282138	0.000179	-1.122816
O	-1.465767	0.000009	-0.178048



Vinoxycarbene

E_{el} = -191.4835172 E_{VZP} = 0.0590238

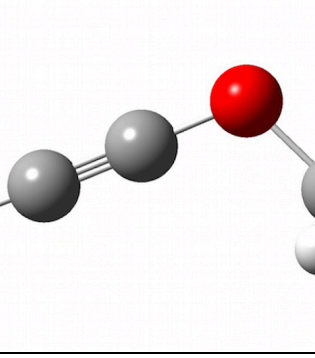
C	1.850591	-0.002593	0.000351
C	-0.485408	0.400341	-0.000246
C	-1.714238	-0.105314	0.000210
H	1.762339	1.120043	0.000346
H	-0.216776	1.451148	-0.000414
H	-2.565322	0.559558	0.000346
H	-1.874989	-1.174396	0.000366
O	0.623635	-0.463870	-0.000317



Methoxyacetylene

E_{el} = -191.5286837 E_{VZP} = 0.0602901

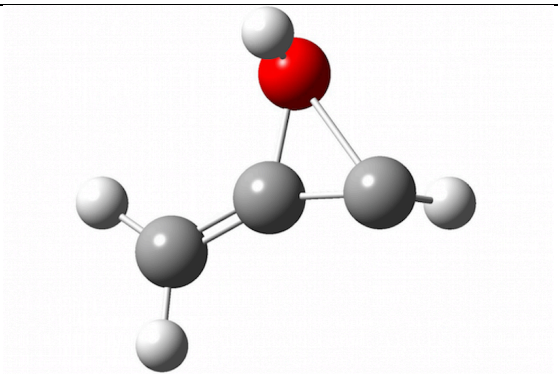
C	1.502212	0.394480	0.000015
C	-0.718650	-0.179802	-0.000282
C	-1.854969	0.234552	0.000140
H	1.400881	1.006405	-0.896994
H	2.462492	-0.113889	0.006360
H	1.392906	1.014023	0.890816
H	-2.858948	0.577878	-0.000005
O	0.503889	-0.647474	0.000073



Hydroxyvinylcarbene

E_{el} = -191.4518517 E_{VZP} = 0.0585235

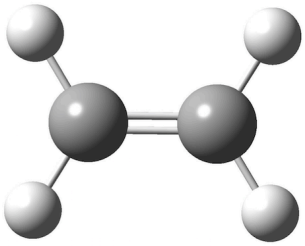
C	-1.002459	-0.948042	-0.168942
C	0.198095	-0.188619	-0.001895
C	1.517833	-0.049931	0.003797
H	-0.966725	1.181793	-0.781486
H	-1.383575	-1.201203	0.831275
H	2.150500	-0.922935	-0.059345
H	1.960966	0.931693	0.087604
O	-0.755248	0.891275	0.115523



$^1C_2H_4$

E_{el} = -78.4388032 E_{VZP} = 0.0508085

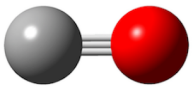
C	0.668385	0.000000	-0.000028
C	-0.668385	0.000000	0.000008
H	1.233484	-0.924119	0.000066
H	1.233486	0.924118	0.000050
H	-1.233484	-0.924116	-0.000007
H	-1.233483	0.924117	0.000008



^1CO

E_{el} = -113.1555787 E_{VZP} = 0.0049040

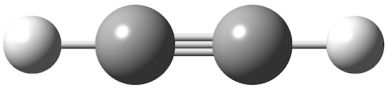
C	0.000000	0.000000	-0.649263
O	0.000000	0.000000	0.486513



C_2H_2

E_{el} = -77.1876481 E_{VZP} = 0.0250277

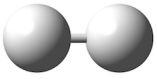
C	0.604840	0.000040	0.000000
C	-0.604844	-0.000052	0.000000
H	1.668394	-0.000063	0.000000
H	-1.668373	0.000136	0.000000



H_2

E_{el} = -1.1723367 E_{VZP} = 0.0100470

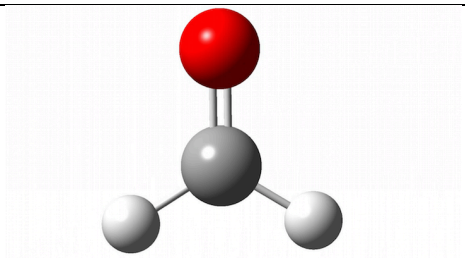
H	0.000000	0.000000	0.371322
H	0.000000	0.000000	-0.371322



H_2CO

E_{el} = -112.5043207 E_{VZP} = 0.0276323

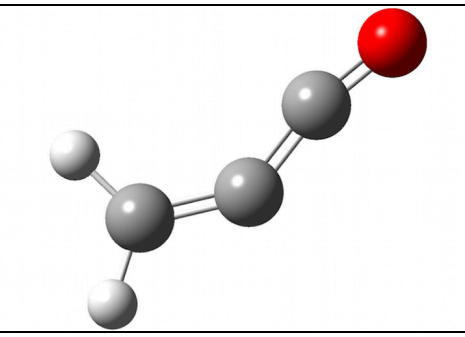
C	0.557633	0.000000	-0.000002
O	-0.710848	0.000000	0.000000
H	1.170492	-0.947199	0.000004
H	1.170493	0.947199	0.000004



H_2CCCO

E_{el} = -190.3403774 E_{VZP} = 0.0372247

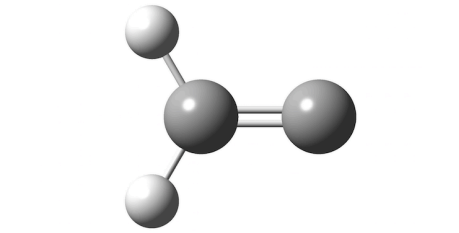
C	0.687198	0.006148	-0.000199
C	-0.572905	-0.372147	-0.000153
C	-1.808576	0.138499	0.000094
H	-2.676227	-0.513273	0.000522
H	-2.004223	1.207503	-0.000206
O	1.855769	0.083847	0.000154



H_2CC

E_{el} = -77.1170417 E_{VZP} = 0.0235193

C	0.824672	-0.000107	0.000000
C	-0.482319	-0.000021	-0.000001
H	-1.026392	0.940269	0.000001
H	-1.027730	-0.939499	0.000001



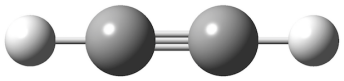
Appendix S2. Cartesian coordinates at the M06-2X/cc-pVTZ level for species in the HCO pathways on the triplet and singlet state surfaces in the reaction of O(^{3}P) with acetylene. Electronic energies (E_{el}, hartrees) are reported at the CCSD(T)//M06-2X/cc-pVTZ level with vibrational zero-point energies (E_{VZP}, hartrees) at the M06-2X/cc-pVTZ level. For transition states, the imaginary frequency is reported in cm^{-1}. Also included are the Cartesian coordinates of the MECP near IM-1t and IM-1s, obtained at the CCSD/cc-pVTZ level.

Species in the HCO Formation Pathways on the Triplet State Surface for O(^{3}P) + Acetylene

Acetylene

E_{el} = -77.3244964 E_{VZP} = 0.0275154

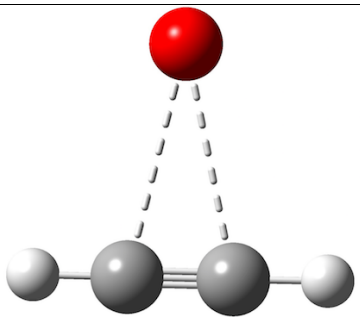
C	0.00000	0.00000	-0.59690
C	0.00000	0.00000	0.59690
H	0.00000	0.00000	-1.65949
H	0.00000	0.00000	1.65949



IM-0t

E_{el} = -152.3931674 E_{VZP} = 0.0280224

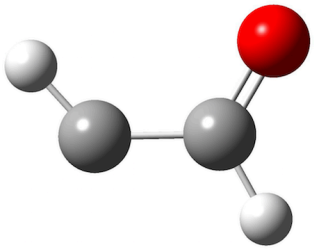
C	0.95952	-0.59779	0.00000
C	0.95950	0.59781	0.00000
H	0.95520	-1.66059	-0.00000
H	0.95506	1.66061	0.00001
O	-1.67805	-0.00002	-0.00000



cis-IM-1t

E_{el} = -152.4795525 E_{VZP} = 0.0306953

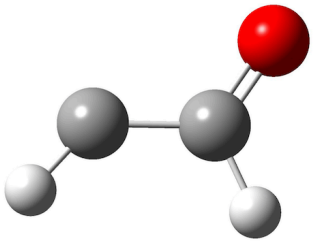
C	0.00000	0.43933	0.00000
C	1.20765	-0.30796	0.00000
H	0.07873	1.53534	0.00000
H	1.38395	-1.37304	0.00000
O	-1.08858	-0.11882	0.00000



trans-IM-1t

E_{el} = -152.4781056 E_{VZP} = 0.0302548

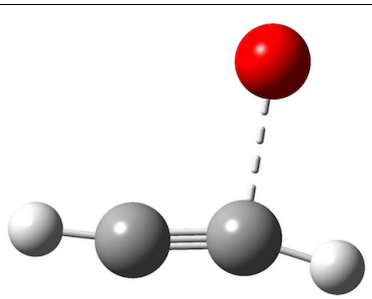
C	0.06155	0.34704	0.00005
C	-1.20583	-0.29362	0.00009
H	0.01962	1.45347	0.00000
H	-2.21768	0.08092	-0.00048
O	1.13296	-0.23186	-0.00005



TS-1t

E_{el} = -152.3855426 E_{VZP} = 0.0274827
Imag freq = 531.7*i*

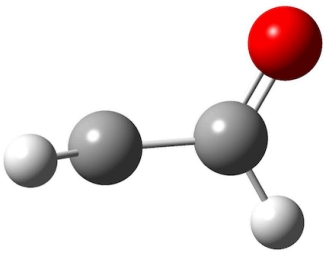
C	1.12594	-0.33697	-0.00000
C	0.38645	0.62634	0.00000
H	1.65726	-1.25849	0.00000
H	0.04107	1.63328	0.00000
O	-1.34658	-0.26388	0.00000



TS-2t

E_{el} = -152.469259 E_{VZP} = 0.0284570
imag freq = 608.8*i*

C	-0.09390	0.38724	0.01114
C	1.22700	-0.14373	-0.08707
H	-0.17584	1.48591	0.06213
H	2.13574	-0.52275	0.33708
O	-1.09481	-0.30303	0.00705



^{2}CH

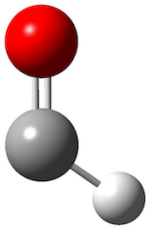
E_{el} = -38.4725438 E_{VZP} = 0.0065539

C	0.00000	0.00000	0.15962
H	0.00000	0.00000	-0.95770

^{2}HCO

E_{el} = -113.6841865 E_{VZP} = 0.0129884

C	0.11236	0.61335	0.00000
H	-0.74622	1.33394	0.00000
O	-0.00407	-0.56349	0.00000

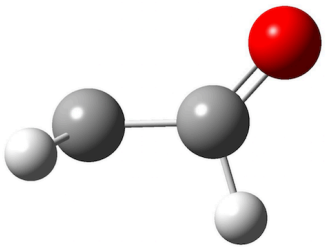


MECP in the Vicinity of IM-1t and IM-1s in the O(^{3}P) + Acetylene Reaction (M06-2x/cc-pVTZ level)

MECP for *O(^{3}P) + acetylene*

E_{el} = -152.459792 E_{VZP} (est.) = 0.028240

C	-0.08585	0.26119	0.004722
C	1.21925	-0.17964	-0.314883
H	0.02696	1.36812	0.189710
H	2.00449	-0.27395	0.430467
O	-1.16666	-0.27207	0.020313



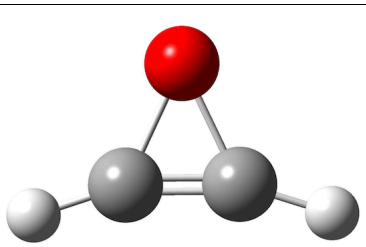
Species in the HCO Formation Pathways on the Singlet State Surface for O(^{3}P) + Acetylene

Note that ^{2}HCO and ^{2}CH are listed in the triplet section but also appear as products on the singlet surface.

IM-1s

E_{el} = -152.4714822 E_{VZP} = 0.0303712

C	0.62749	0.45914	-0.00009
C	-0.63122	0.45442	-0.00034
H	1.64387	0.79023	0.00075
H	-1.65048	0.77619	0.00132
O	0.00363	-0.88097	0.00006



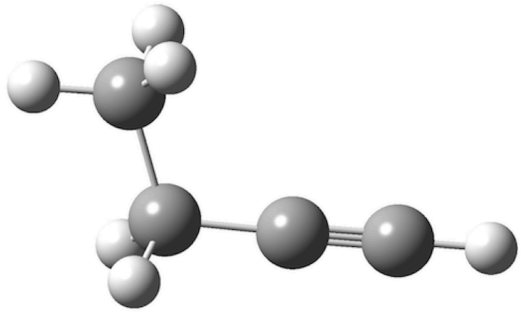
Appendix S3. Cartesian coordinates at the M06-2X/cc-pVTZ level for species in the HCO formation pathways on the triplet and singlet state surfaces in the reaction of O(^{3}P) with 1-butyne. Electronic energies (E_{el}, hartrees) are reported at the CCSD(T)//M06-2X/cc-pVTZ level with vibrational zero-point energies (E_{VZP}, hartrees) at the M06-2X/cc-pVTZ level. For transition states, the imaginary frequency is reported in cm^{-1}. Also included are the Cartesian coordinates of the MECP near IM-1t and IM-1s, obtained at the CCSD/cc-pVTZ level.

Species in the HCO Formation Pathways on the Triplet State Surface for O(^{3}P) + 1-Butyne

1-butyne

E_{el} = -155.6741384 E_{VZP} = 0.0849069

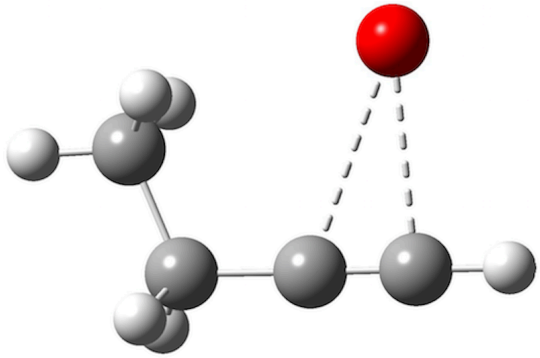
C	1.35472	-1.16629	-0.04444
C	1.94529	-0.26254	-0.00005
H	2.93930	-0.63612	0.00015
C	0.82689	0.16508	0.00004
C	-0.55044	0.65238	-0.00001
H	-0.69923	1.28709	-0.87523
C	-1.56823	-0.49004	0.00000
H	-1.43943	-1.11630	0.88098
H	-1.43956	-1.11620	-0.88107
H	-2.58289	-0.09487	0.00013
H	-0.69927	1.28712	0.87519



IM-0t

E_{el} = -230.6490669 E_{VZP} = 0.086212

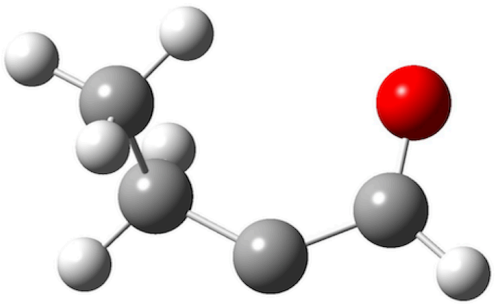
C	1.35472	-1.16629	-0.04444
C	0.17830	-0.93407	0.00318
C	-1.25124	-0.63946	0.05781
C	-1.54814	0.85766	-0.05133
H	2.39471	-1.37784	-0.08508
H	-1.65189	-1.03473	0.99281
H	-1.74765	-1.18049	-0.74962
H	-1.07296	1.40203	0.76177
H	-1.16069	1.25720	-0.98672
H	-2.62255	1.03009	-0.01333
O	1.68240	1.39959	0.03610



IM-1t

E_{el} = -230.7330048 E_{VZP} = 0.0887018

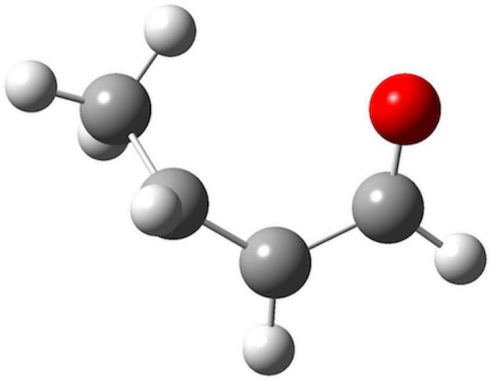
C	1.41452	0.18217	0.25863
C	0.15792	0.05780	-0.38273
C	-1.18130	0.59456	-0.12901
C	-2.21393	-0.50857	0.13564
H	1.40785	0.84137	1.15091
H	-1.49830	1.19081	-0.98993
H	-1.13366	1.28011	0.72606
H	-2.27215	-1.18748	-0.71328
H	-1.94039	-1.08872	1.01545
H	-3.19841	-0.07392	0.29952
O	2.44647	-0.36474	-0.09798



IM-2t

E_{el} = -230.7407415 E_{VZP} = 0.0864818

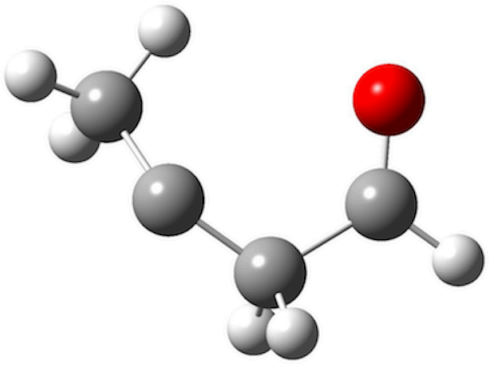
C	-1.41856	0.19510	-0.19053
H	-2.29526	0.68382	-0.64652
C	-0.22442	0.98840	-0.08721
C	0.99974	0.45434	0.48849
H	1.12311	0.50988	1.56325
C	1.83675	-0.50346	-0.28951
H	1.98958	-0.15602	-1.31295
H	1.33528	-1.47639	-0.35198
H	2.80855	-0.65188	0.17743
H	-0.25924	2.00077	-0.48000
O	-1.48288	-0.96457	0.19042



IM-5t

E_{el} = -230.7205393 E_{VZP} = 0.0870053

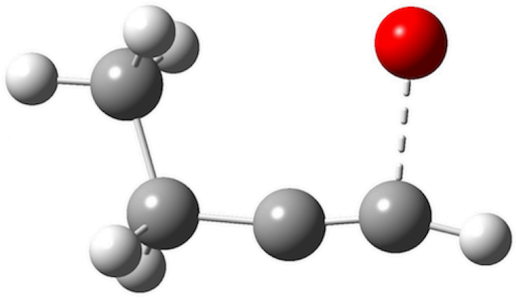
C	-1.00483	0.56746	-0.39589
C	0.29495	1.08672	0.03566
C	-1.87541	-0.48533	0.13654
H	0.25011	1.55393	1.03374
H	0.65008	1.88207	-0.62892
C	1.40313	0.05210	0.11126
O	1.26690	-1.11397	-0.12417
H	2.38707	0.45527	0.42242
H	-2.80450	-0.54793	-0.43139
H	-2.14368	-0.29586	1.18350
H	-1.38129	-1.46149	0.08866



TS-1t

E_{el} = -230.6425147 E_{VZP} = 0.0856090
imag freq = 469.2*i*

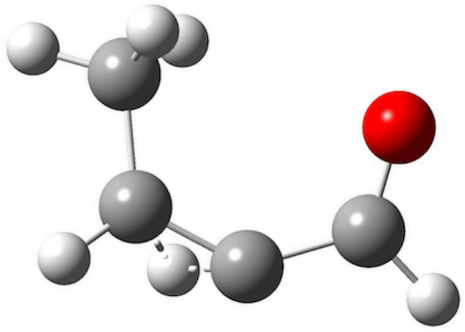
C	1.41541	-0.81683	-0.05055
H	2.43482	-1.11490	-0.10671
C	0.19978	-0.85581	-0.00294
C	-1.24250	-0.66900	0.05763
H	-1.61204	-1.09022	0.99416
C	-1.62701	0.81185	-0.04863
H	-1.27100	1.22899	-0.98825
H	-1.17137	1.37998	0.75885
H	-2.70937	0.91934	0.00143
H	-1.70568	-1.23833	-0.75050
O	1.69507	1.13674	0.04474



TS-2t

E_{el} = -230.6604580 E_{VZP} = 0.0826687
imag freq = 1803.3*i*

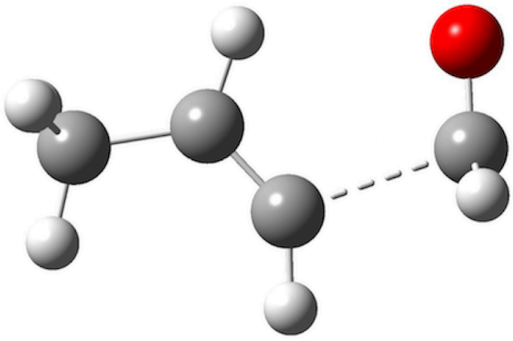
C	1.45312	-0.29724	-0.04554
H	2.35271	-0.88542	-0.26877
C	0.21921	-1.00866	0.02508
C	-1.16325	-0.64787	0.14779
H	-1.82069	-1.38070	0.59821
C	-1.63603	0.75634	-0.08712
H	-1.06379	1.23202	-0.88105
H	-1.47358	1.35437	0.81372
H	-2.69471	0.77463	-0.33793
H	-0.54004	-1.29779	-0.91225
O	1.50023	0.92343	0.09335



TS-4t

E_{el} = -230.6758347 E_{VZP} = 0.0829315
imag freq = 304.2*i*

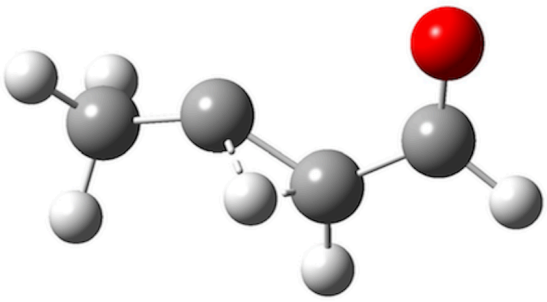
C	0.92367	-0.22407	0.07156
C	2.42566	-0.21724	-0.01689
H	0.43835	-1.18448	0.22819
C	0.17212	0.83492	-0.03550
H	0.29727	1.89281	-0.20142
C	-1.94964	0.42626	-0.08967
H	-1.97012	1.09144	0.81049
O	-2.07768	-0.75430	-0.03758
H	2.81319	0.78663	-0.17605
H	2.75480	-0.85395	-0.83883
H	2.85710	-0.61729	0.90128



TS-10t

E_{el} = -230.6581573 E_{VZP} = 0.0827951
imag freq = 1629.6*i*

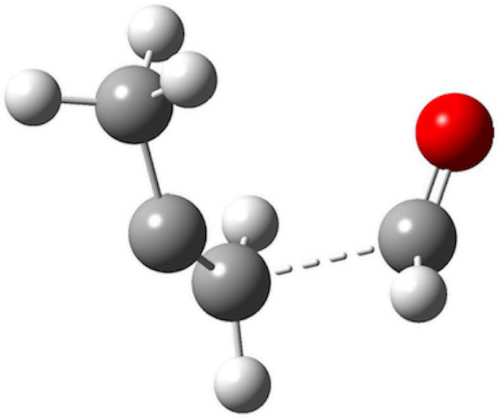
C	0.89602	-0.25406	0.11751
C	-0.16116	0.73323	0.01591
C	2.35046	-0.21682	-0.09220
H	0.12656	1.76613	-0.15663
H	0.29290	0.39645	1.13612
C	-1.55548	0.34967	-0.07949
O	-1.94432	-0.80147	-0.01490
H	-2.26139	1.19089	-0.17944
H	2.84802	-1.01950	0.45107
H	2.77678	0.73188	0.25130
H	2.59267	-0.32619	-1.15360



TS-14t

E_{el} = -230.6770867 E_{VZP} = 0.0826737
imag freq = 392.3*i*

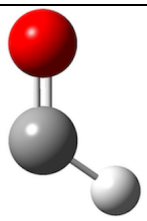
C	-1.13528	0.46363	-0.30372
C	-0.27311	1.29879	0.27560
C	-1.69887	-0.85494	0.00654
H	-0.01681	1.18258	1.32758
H	-0.02224	2.25135	-0.17480
C	1.46907	0.15279	-0.35647
O	1.74834	-0.79384	0.28872
H	1.40647	0.17823	-1.46756
H	-1.29903	-1.61833	-0.66491
H	-2.78468	-0.86045	-0.09249
H	-1.44129	-1.14424	1.03075



^{2}HCO

E_{el} = -113.6837609 E_{VZP} = 0.0132749

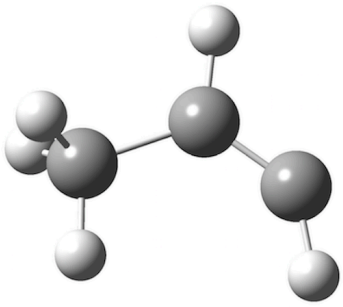
H	-0.86747	1.20854	0.00000
C	0.06196	0.58132	0.00000
O	0.06196	-0.58706	0.00000



$^2CH_3CHCH$

E_{el} = -116.9944237 E_{VZP} = 0.0665246

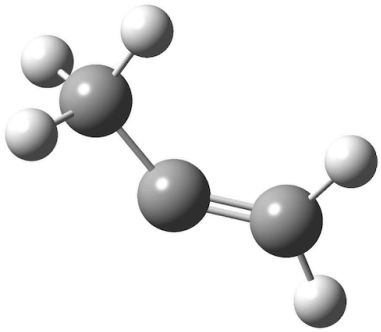
C	1.35591	-0.15660	0.00000
C	0.21255	0.47145	-0.00000
H	0.21049	1.55948	0.00000
C	-1.13888	-0.19697	0.00000
H	-1.04018	-1.28059	0.00006
H	-1.71153	0.10054	-0.87945
H	-1.71157	0.10063	0.87940
H	1.67528	-1.18735	-0.00001



$^2CH_3CCH_2$

E_{el} = -117.2055935 E_{VZP} = 0.0660122

C	-0.12684	-0.39544	0.00001
C	-1.33214	0.10295	0.00005
C	1.26252	0.07963	-0.00002
H	-1.49659	1.18094	-0.00009
H	-2.21611	-0.52387	-0.00020
H	1.29596	1.17486	-0.00020
H	1.79784	-0.27756	-0.88032
H	1.79767	-0.27724	0.88053

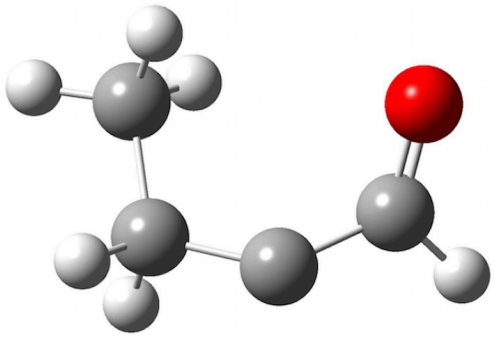


MECP in the Vicinity of IM-1t and IM-1s in the O(^{3}P) + 1-Butyne Reaction (M06-2x/cc-pVTZ level)

MECP for *O(^{3}P) + 1-butyne*

E_{el} = -231.090855 E_{VZP} (est.) = 0.087008

C	-1.30036	-0.24347	0.35820
C	-0.18071	-0.97128	-0.12762
C	1.23947	-0.64584	-0.03483
C	1.54379	0.85597	0.06552
H	-1.89934	-0.71870	1.15603
H	1.79781	-1.11707	-0.84609
H	1.58092	-1.14999	0.88353
H	1.16998	1.38076	-0.81084
H	1.06229	1.28891	0.94005
H	2.61875	1.01164	0.13991
O	-1.63826	0.81290	-0.15431



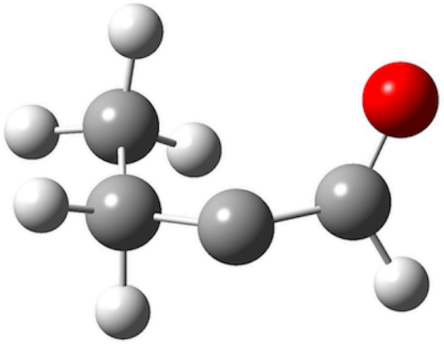
Species in the HCO Formation Pathways on the Singlet State Surface for O(^{3}P) + 1-Butyne

Note that ^{2}HCO and ^{2}CH$_3$CHCH are listed in the triplet section but also appear as products on the singlet surface.

IM-1s

E_{el} = -230.723308 E_{VZP} = 0.0863121

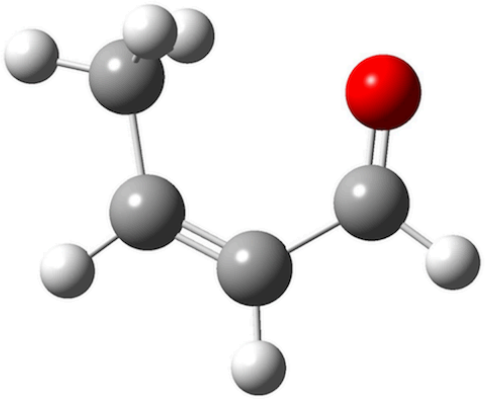
C	1.18677	-0.61003	-0.12056
C	-0.19364	-1.02893	-0.23220
H	1.83387	-1.10306	-0.84661
H	1.35434	-1.20046	0.81528
C	1.52933	0.86234	0.09781
C	-1.22201	-0.23041	0.34213
H	-1.54178	-0.53273	1.36277
O	-1.78523	0.64733	-0.28648
H	1.22042	1.44677	-0.76678
H	2.60128	0.99055	0.23651
H	1.01098	1.26245	0.96768



cis-IM-2s

E_{el} = -230.8362950 E_{VZP} = 0.0903623

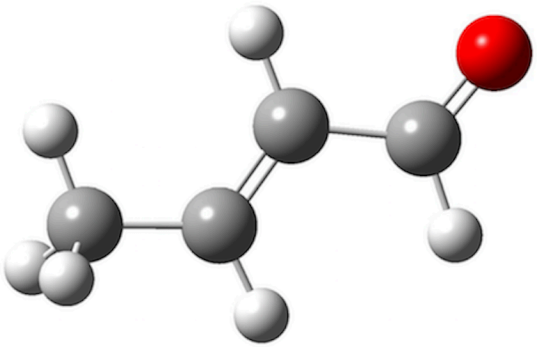
C	-1.35461	0.20073	-0.00888
H	1.08622	-1.30078	-0.84430
C	-0.18423	1.09324	0.00342
C	1.08041	0.66300	0.00411
H	1.85774	1.42018	0.01402
C	1.52999	-0.76230	-0.00714
H	2.61341	-0.83022	-0.06306
H	-0.39129	2.15599	0.00869
H	1.18347	-1.27950	0.88858
H	-2.33479	0.71145	-0.03834
O	-1.30552	-1.00565	0.01066



trans-IM-2s

E_{el} = -230.8420696 E_{VZP} = 0.0902298

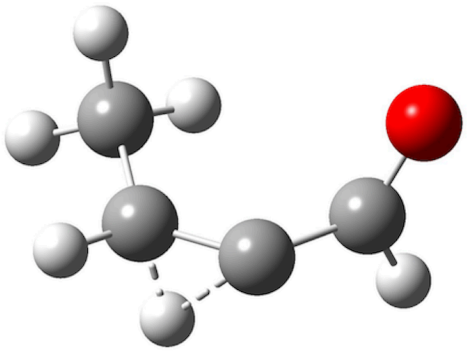
C	-1.39882	0.33099	-0.00000
O	-2.45265	-0.24958	0.00000
H	-1.35989	1.43849	-0.00001
C	-0.08666	-0.32991	0.00000
H	-0.08109	-1.41377	-0.00000
C	1.03219	0.38933	0.00000
H	0.93906	1.47321	0.00001
C	2.41636	-0.16155	-0.00000
H	2.41225	-1.24948	-0.00002
H	2.96623	0.18750	0.87591
H	2.96623	0.18752	-0.87590



TS-2s

E_{el} = -230.7211560 E_{VZP} = 0.0848514
imag freq = 439.3*i*

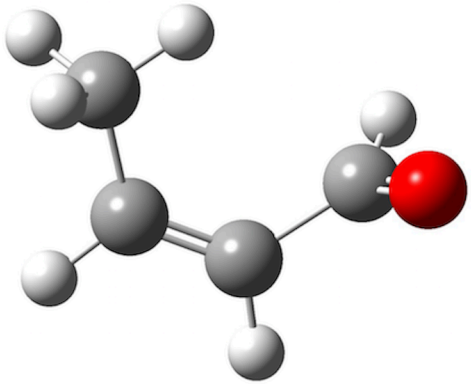
C	1.21362	0.16596	0.35798
H	-0.95006	-1.37210	0.73125
C	0.19275	1.00707	-0.20231
C	-1.15149	0.59211	-0.16252
H	-1.86322	1.23137	-0.68344
C	-1.63475	-0.82262	0.08853
H	-2.62992	-0.82629	0.52945
H	-0.95276	1.21471	0.81439
H	-1.68815	-1.34607	-0.86554
H	1.44284	0.35484	1.42903
O	1.86506	-0.61395	-0.30566



TS-4s

E_{el} = -230.8282702 E_{VZP} = 0.0893794
imag freq = 162.5*i*

C	1.18847	0.01411	0.40340
H	-0.92033	-1.48874	0.35152
C	0.09940	0.96151	0.01503
C	-1.16556	0.59781	-0.13719
H	-1.88696	1.35522	-0.42455
C	-1.69498	-0.79018	0.03924
H	-2.49787	-0.80531	0.77783
H	0.40418	1.99110	-0.13745
H	-2.11685	-1.15660	-0.89802
H	1.34035	-0.13499	1.49026
O	1.88918	-0.55752	-0.38531



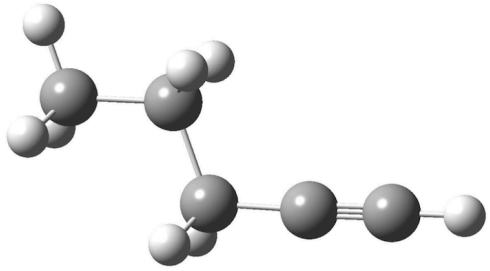
Appendix S4. Cartesian coordinates at the M06-2X/cc-pVTZ level for species in the HCO formation pathways on the triplet and singlet state surfaces in the reaction of O(^{3}P) with 1-pentyne. Electronic energies (E_{el}, hartrees) are reported at the CCSD(T)//M06-2X/cc-pVTZ level with vibrational zero-point energies (E_{VZP}, hartrees) at the M06-2X/cc-pVTZ level. For transition states, the imaginary frequency is reported in cm^{-1}. Also included are the Cartesian coordinates of the MECP near IM-1t and IM-1s, obtained at the CCSD/cc-pVTZ level.

Species in the HCO Formation Pathways on the Triplet State Surface for O(^{3}P) + 1-Pentyne

1-pentyne

E_{el} = -194.9141125 E_{VZP} = 0.1136469

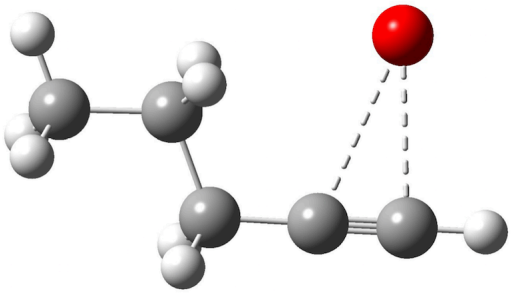
C	-2.61987	-0.24552	-0.00001
C	-1.49585	0.16724	-0.00000
C	-0.11115	0.62896	0.00001
C	0.89525	-0.52606	0.00002
C	2.32938	-0.01792	-0.00001
H	-3.61899	-0.60541	-0.00002
H	0.05652	1.26034	0.87598
H	0.71239	-1.15143	-0.87473
H	0.71241	-1.15140	0.87479
H	0.05654	1.26034	-0.87596
H	2.52669	0.59469	0.88102
H	2.52663	0.59472	-0.88103
H	3.04125	-0.84207	-0.00005



IM-0t

E_{el} = -269.8892767 E_{VZP} = 0.1148404

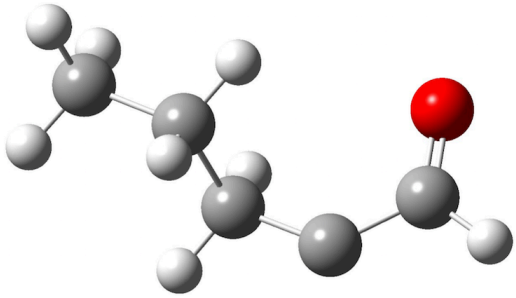
C	2.18120	-0.88297	0.09386
H	3.23867	-0.85114	0.18693
C	0.98625	-0.92718	-0.00918
C	-0.46836	-0.96687	-0.12252
H	-0.85707	-1.68871	0.60005
C	-1.12574	0.39746	0.10959
H	-0.73414	1.10680	-0.61892
H	-0.82779	0.76979	1.09071
C	-2.64133	0.30499	0.01012
H	-0.73780	-1.34039	-1.11329
O	1.92773	1.70183	-0.07330
H	-2.94629	-0.05457	-0.97387
H	-3.10707	1.27637	0.16964
H	-3.04183	-0.38539	0.75400



IM-1t

E_{el} = -269.9731778 E_{VZP} = 0.1174783

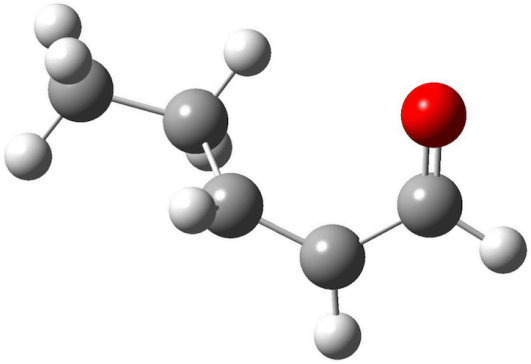
C	-2.07863	-0.10963	-0.19527
H	-3.00052	-0.48385	-0.66182
C	-0.96150	-0.98207	-0.14175
C	0.38993	-0.78345	0.38656
H	0.90685	-1.74200	0.47607
C	1.21928	0.17637	-0.48485
H	0.68402	1.12344	-0.55504
H	1.28958	-0.23134	-1.49456
C	2.60953	0.39029	0.09614
H	0.30519	-0.36334	1.39614
O	-2.01913	1.02684	0.26657
H	3.15166	-0.55349	0.17053
H	2.54886	0.82098	1.09626
H	3.19575	1.06588	-0.52519



IM-2t

E_{el} = -269.9805360 E_{VZP} = 0.1153033

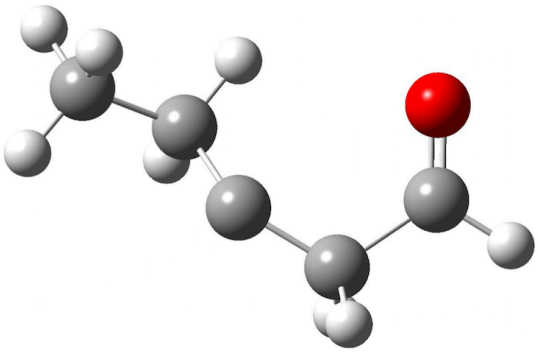
C	-2.04342	0.05492	-0.12621
H	-3.01078	0.43436	-0.49384
C	-0.97082	1.00834	-0.04625
C	0.35437	0.63003	0.41580
H	0.55135	0.64409	1.48262
C	1.26723	-0.15909	-0.46463
H	1.28579	0.28509	-1.46446
H	0.83589	-1.16046	-0.59317
C	2.67935	-0.26466	0.09720
H	-1.17749	2.02411	-0.37139
O	-1.91452	-1.12110	0.18152
H	3.31742	-0.86102	-0.55304
H	2.66476	-0.73698	1.07991
H	3.12892	0.72236	0.20571



IM-5t

E_{el} = -269.9595783 E_{VZP} = 0.1163025

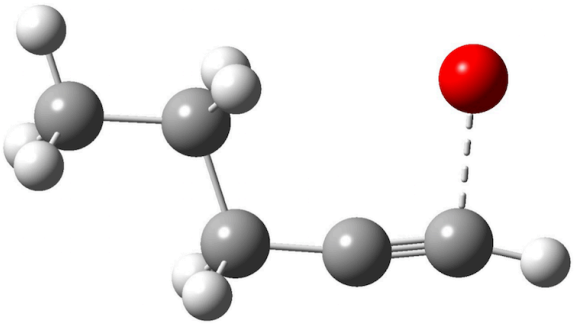
C	-0.36491	0.70227	-0.26195
C	1.02927	1.07768	-0.01660
C	-1.31868	-0.14463	0.46764
H	1.15797	1.60097	0.94558
H	1.39395	1.78496	-0.76965
C	2.01011	-0.08138	0.00765
O	1.71015	-1.23371	-0.11624
H	3.06617	0.21437	0.16529
C	-2.67397	-0.23198	-0.23522
H	-1.45965	0.24639	1.48499
H	-0.89239	-1.14883	0.57784
H	-2.55841	-0.65751	-1.23125
H	-3.11797	0.75734	-0.34100
H	-3.36187	-0.85984	0.32896



TS-1t

E_{el} = -269.8826988 E_{VZP} = 0.1141224
imag freq = 466.6*i*

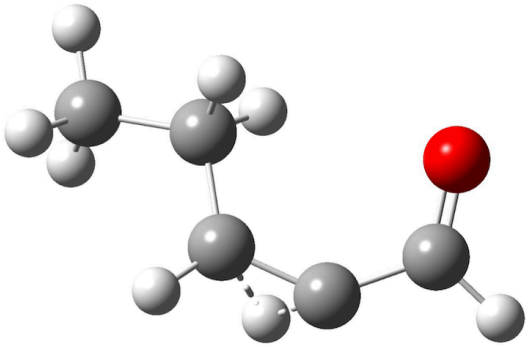
C	2.14673	-0.61191	-0.00092
H	3.20483	-0.71871	-0.00193
C	0.95767	-0.87158	-0.00006
C	-0.49446	-0.95074	0.00107
H	-0.82043	-1.51286	0.87974
C	-1.15256	0.43704	-0.00115
H	-0.80427	0.98848	-0.87425
H	-0.80308	0.99183	0.86933
C	-2.66987	0.32472	0.00005
H	-0.82167	-1.51623	-0.87499
H	-3.02352	-0.21423	-0.88028
H	-3.13528	1.30923	-0.00135
H	-3.02231	-0.21110	0.88278
O	2.06259	1.36480	0.00088



TS-2t

E_{el} = -269.9007251 E_{VZP} = 0.1113563
imag freq = 1798.6*i*

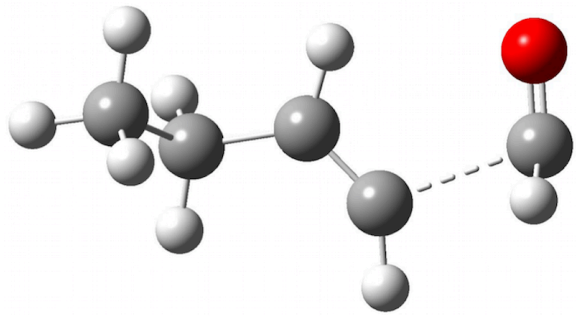
C	-2.07071	0.12375	-0.12418
H	-3.02630	0.55957	-0.44390
C	-0.96499	1.01602	-0.00360
C	0.44007	0.87503	0.23980
H	0.94821	1.71526	0.69980
C	1.14969	-0.44417	0.11152
H	0.66473	-1.03820	-0.66290
H	0.98992	-1.00005	1.04174
C	2.63756	-0.27874	-0.16660
H	-0.18430	1.38156	-0.89618
O	-1.94927	-1.08277	0.07876
H	3.11846	0.30559	0.61884
H	2.80083	0.23439	-1.11444
H	3.13292	-1.24731	-0.21471



TS-4t

E_{el} = -269.9156283 E_{VZP} = 0.1117831
imag freq = 299.2*i*

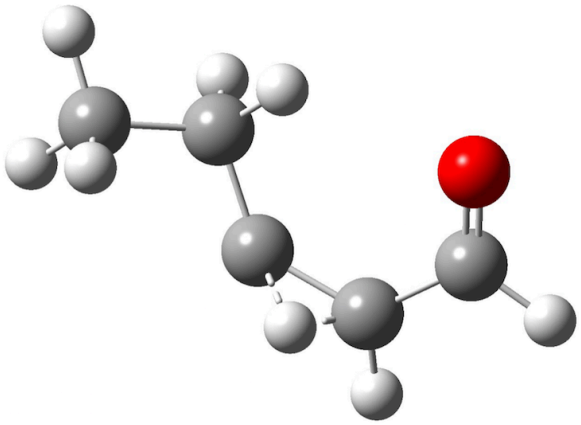
C	0.34892	0.04973	-0.24851
C	1.81552	0.30868	-0.48426
H	0.00062	-0.97213	-0.38843
C	-0.51323	0.95383	0.12110
H	-0.52337	2.01103	0.33226
C	-2.56030	0.26053	0.18202
H	-2.49639	0.56995	1.25576
O	-2.55322	-0.87224	-0.17815
H	2.03039	1.36807	-0.34423
H	2.04419	0.06784	-1.52510
C	2.68553	-0.53945	0.44103
H	3.74298	-0.36660	0.24520
H	2.48335	-1.60096	0.29679
H	2.48532	-0.29920	1.48470



TS-10t

E_{el} = -269.9021628 E_{VZP} = 0.1118352
imag freq = 1585.5*i*

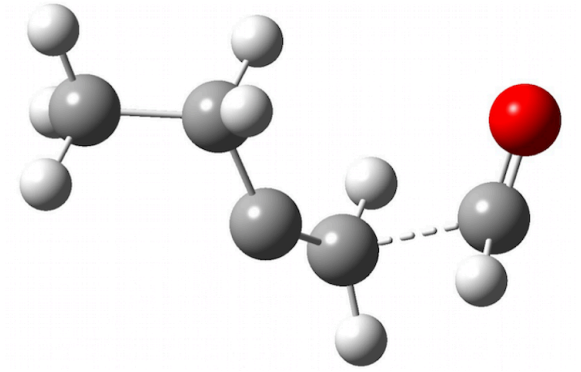
C	-0.37983	0.88007	0.15254
C	1.04850	1.05919	-0.01265
C	-1.26961	-0.25338	0.45598
H	1.44283	2.06342	0.07788
H	0.31444	0.99445	-1.01737
C	1.98753	-0.04951	-0.05518
O	1.67272	-1.22710	-0.08019
H	3.04558	0.25942	-0.08369
C	-2.59215	-0.21290	-0.30798
H	-1.46395	-0.26056	1.53489
H	-0.71432	-1.17113	0.23647
H	-3.13313	0.70936	-0.09964
H	-3.22363	-1.05215	-0.02148
H	-2.41619	-0.26686	-1.38184



TS-14t

E_{el} = -269.9164746 E_{VZP} = 0.1117987
imag freq = 391.5*i*

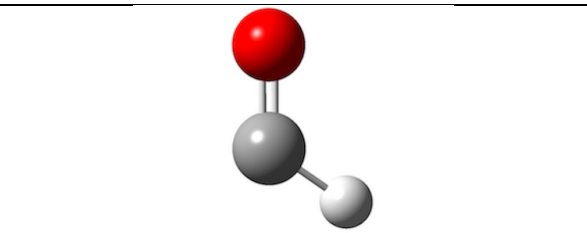
C	-0.43900	0.68231	-0.30666
C	0.54545	1.36750	0.27539
C	-1.22134	-0.52500	-0.00220
H	0.78588	1.20181	1.32454
H	0.94140	2.27288	-0.16820
C	2.09212	-0.03192	-0.36518
O	2.24707	-0.99445	0.29746
H	2.01155	-0.01991	-1.47535
C	-2.73010	-0.27113	0.00987
H	-0.89073	-0.91009	0.97047
H	-0.98478	-1.30271	-0.73449
H	-2.98741	0.47384	0.76128
H	-3.27143	-1.18900	0.23349
H	-3.06386	0.09819	-0.95877



^{2}HCO

E_{el} = -113.6837609 E_{VZP} = 0.0132749

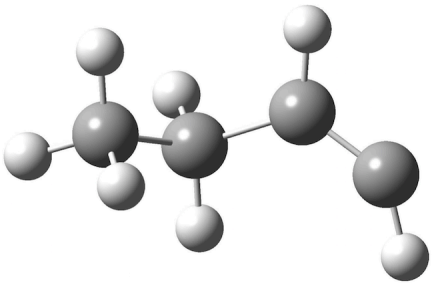
H	-0.86747	1.20854	0.00000
C	0.06196	0.58132	0.00000
O	0.06196	-0.58706	0.00000



$^2CH_3CH_2CHCH$

E_{el} = -156.2340474 E_{VZP} = 0.0952780

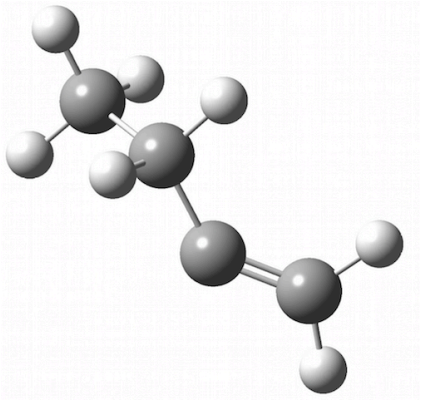
C	-1.90735	0.06360	-0.29879
C	-0.79548	0.33469	0.32708
H	-0.72008	1.26046	0.89647
C	0.44538	-0.52689	0.31169
H	0.24402	-1.44231	-0.24508
H	0.68118	-0.81897	1.33797
C	1.63474	0.21496	-0.29384
H	-2.27360	-0.73667	-0.92325
H	1.84208	1.13212	0.25864
H	1.42941	0.48820	-1.32854
H	2.53319	-0.40102	-0.27303



$^2CH_3CH_2CCH_2$

E_{el} = -156.5120562 E_{VZP} = 0.0948598

C	-0.72374	-0.03486	-0.38003
C	-1.91727	-0.17977	0.12733
C	0.55513	0.60544	-0.03389
C	1.70034	-0.40116	0.08918
H	-2.17963	0.26965	1.08575
H	-2.69506	-0.74242	-0.37550
H	0.42922	1.14944	0.91114
H	0.80117	1.35097	-0.79365
H	1.48391	-1.13471	0.86455
H	2.63132	0.10427	0.34166
H	1.84237	-0.93509	-0.84947

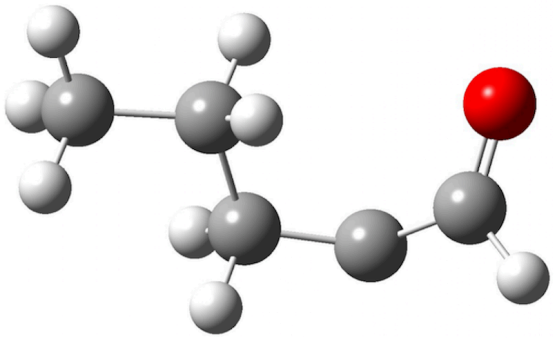


MECP in the Vicinity of IM-1t and IM-1s in the O(^{3}P) + 1-Pentyne Reaction (M06-2x/cc-pVTZ level)

MECP for *O(^{3}P) + 1-pentyne*

E_{el} = -270.398355 E_{VZP} (est.) = 0.115707

C	-1.92248	0.05720	0.38791
C	-0.96845	0.97886	-0.11632
C	0.48873	0.94229	-0.07534
C	1.11393	-0.46227	-0.00922
C	2.63296	-0.37546	0.05208
H	-2.55324	0.40609	1.22701
H	0.91800	1.52290	-0.89730
H	0.76421	1.49371	0.83955
H	0.79005	-1.03425	-0.87873
H	0.72368	-0.98645	0.86401
H	2.95584	0.17636	0.93656
H	3.03316	0.13885	-0.82242
H	3.08541	-1.36473	0.09421
O	-2.10571	-1.02757	-0.14377



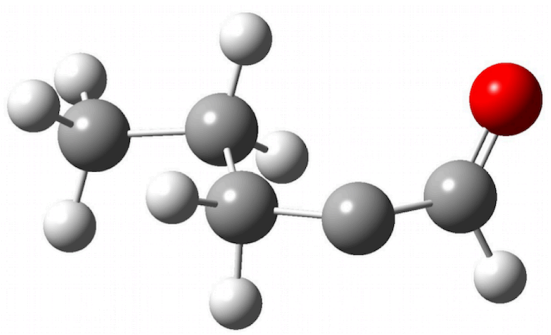
Species in the HCO Formation Pathways on the Singlet State Surface for O(^{3}P) + 1-Pentyne

Note that ^{2}HCO and $^2CH_3CH_2CHCH$ are listed in the triplet section but also appear as products on the singlet surface.

IM-1s

E_{el} = -269.9632421 E_{VZP} = 0.1149591

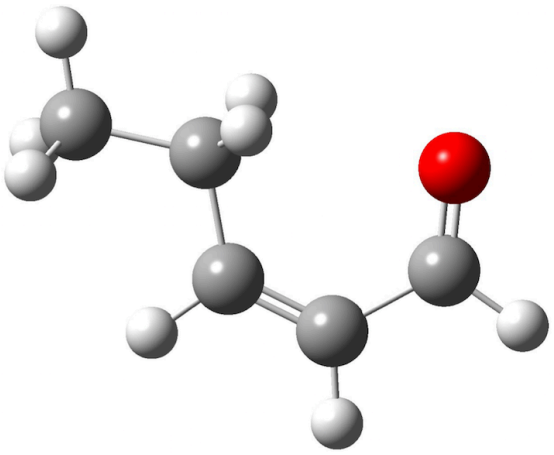
C	1.81855	0.04422	0.37194
H	-0.68448	-0.96742	0.86800
C	0.99236	1.05211	-0.19796
C	-0.44703	0.91312	-0.15135
H	-0.95563	1.54823	-0.88029
C	-1.09237	-0.46763	-0.01196
C	-2.60850	-0.37194	0.07820
H	-0.55229	1.48605	0.80362
H	-0.79853	-1.07361	-0.86951
H	2.13857	0.24090	1.41855
O	2.23377	-0.90225	-0.27183
H	-3.02199	0.10551	-0.81100
H	-2.91338	0.21746	0.94444
H	-3.06055	-1.35835	0.16762



cis-IM-2s

E_{el} = -270.0757868 E_{VZP} = 0.1193254

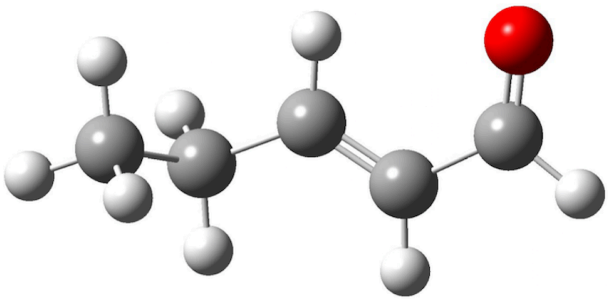
C	1.95700	-0.01517	-0.00005
H	3.01624	0.30091	-0.00025
C	0.97646	1.08220	0.00003
C	-0.34658	0.89764	0.00003
H	-0.97084	1.78808	0.00006
C	-1.07407	-0.41109	-0.00002
H	-0.74703	-0.99717	0.86169
H	-0.74705	-0.99709	-0.86179
C	-2.58699	-0.23534	-0.00002
O	1.67989	-1.19068	0.00006
H	1.38006	2.08692	0.00003
H	-3.09360	-1.19886	-0.00005
H	-2.91594	0.31662	-0.88137
H	-2.91595	0.31657	0.88137



trans-IM-2s

E_{el} = -270.0774196 E_{VZP} = 0.1195995

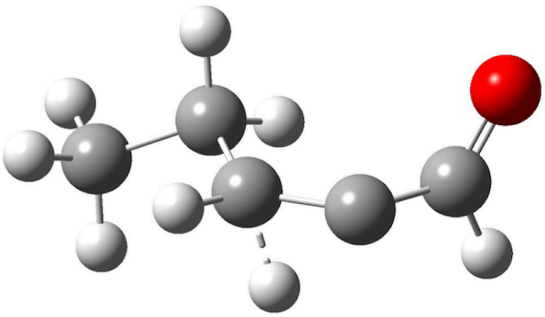
C	-1.62098	-0.40918	-0.05532
H	-1.10664	-1.33207	-0.37247
C	-0.79783	0.79979	0.09758
C	0.51405	0.87202	-0.13191
H	0.99457	1.83377	0.03120
C	1.44856	-0.21072	-0.57165
H	1.90332	0.09998	-1.51611
H	0.92548	-1.14373	-0.76656
C	2.55484	-0.43440	0.46179
O	-2.80810	-0.42149	0.15329
H	-1.34578	1.67554	0.42377
H	3.27115	-1.17408	0.10778
H	2.13638	-0.78488	1.40464
H	3.09443	0.49239	0.65854



TS-2s

E_{el} = -269.9608538 E_{VZP} = 0.1136101
imag freq = 427.8*i*

C	1.77010	-0.00209	0.43020
H	-0.63012	-1.17111	0.45645
C	0.95034	1.04524	-0.11405
C	-0.43299	0.84395	-0.25544
H	-0.98879	1.64144	-0.75108
C	-1.15982	-0.48819	-0.20829
C	-2.61826	-0.33769	0.20343
H	-0.24072	1.32510	0.80565
H	-1.09302	-0.92190	-1.20795
H	1.90575	0.03022	1.53281
O	2.37122	-0.79740	-0.26200
H	-3.14586	0.33737	-0.47139
H	-2.70131	0.06782	1.21255
H	-3.13201	-1.29705	0.18385



TS-4s

E_{el} = -270.0676705 E_{VZP} = 0.1185071
imag freq = 160.8*i*

C	1.65311	-0.18846	0.47257
H	1.59161	-0.55453	1.51608
C	0.79933	0.99230	0.13884
C	-0.45571	0.89339	-0.27487
H	-1.00137	1.80662	-0.49430
C	-1.21645	-0.38267	-0.46669
H	-0.59364	-1.23935	-0.20463
H	-1.45569	-0.48988	-1.52791
C	-2.51198	-0.39679	0.34401
O	2.38766	-0.72500	-0.31004
H	1.27115	1.96168	0.25862
H	-3.07614	-1.31039	0.16253
H	-3.14493	0.44966	0.07544
H	-2.30206	-0.33041	1.41136