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Theory and Modelling
in Chemical Sciences

A Computational Investigation on the Oxyfunctionalization of Isobutane Using Methyl(trifluoromethyl)dioxirane

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Abbreviations

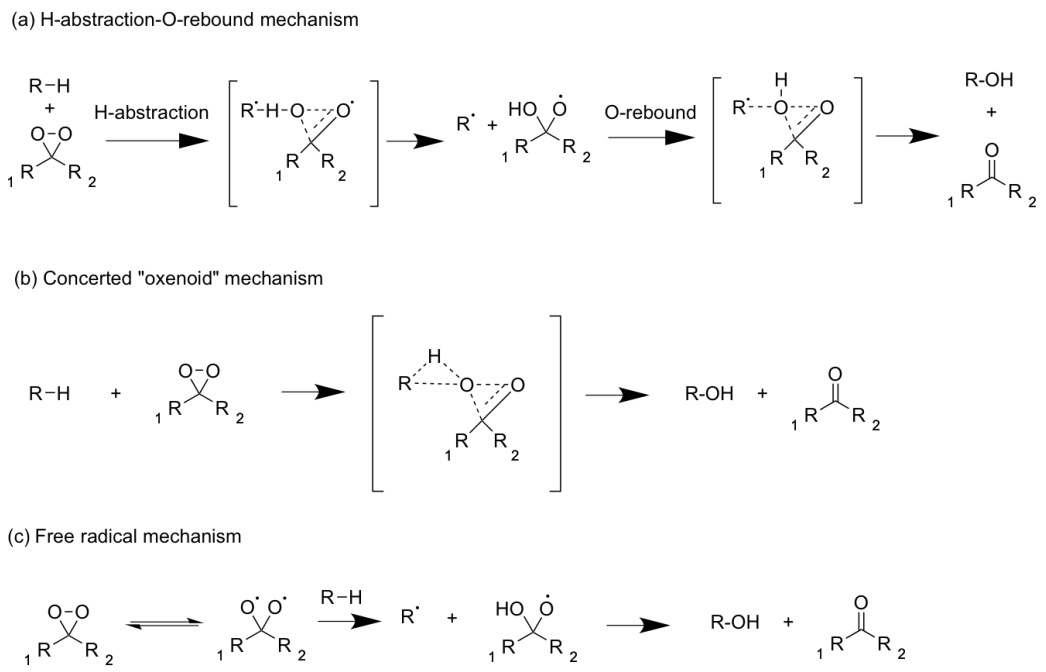
DMDO	dimethyldioxirane
TFDO	methyl(trifluoromethyl)dioxirane
CPCM	Conductor-like Polarizable Continuum Model (an implicit solvent model)
DFT	Density Functional Theory
B3LYP	Becke three-parameter Lee-Yang-Parr hybrid functional
M06-2X	Minnesota 06 density functional with 54% Hartree-Fock exchange
G4	Gaussian-4 theory for the calculation of molecular energies
TS	Transition State
IRC	Intrinsic Reaction Coordinate
GVB	General Valence Bond
CI	Configuration Interaction
PES	Potential Energy Surface

Abstract

The homolysis of methyl(trifluoromethyl)dioxirane (TFDO) and the oxyfunctionalization of isobutane by TFDO in gas phase and in PCM-modelled acetone and acetonitrile solvents have been investigated computationally using DFT and *ab initio* calculations. Homolysis of TFDO was found to be more reactive than the homolysis of DMDO at two different DFT functional levels. In addition, the activation barriers for homolysis is lower than that for oxidation of isobutane. This prompts us to propose an alternative mechanism in which TFDO homolysis occurs before the oxidation of isobutane.

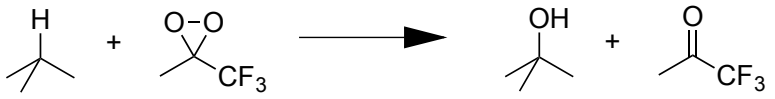
1 Introduction

The selective functionalization of C-H bonds has been actively investigated for the past 50 years.[1] The ability to directly functionalize C-H bonds at selective sites would allow synthetic chemists to circumvent the need for the prefunctionalization of the unactivated hydrocarbon substrates, thereby enhancing the overall synthetic design. Examples of C-H functionalization as a key step in the synthesis of natural products and pharmaceutical candidates to reduce the overall number of synthetic steps are abundant in the literature.[2–5] Of all C-H oxidations known to date, the selective insertion of an oxygen atom into hydrocarbon C-H bonds is particularly important. Many transition metal complexes, such as those of Fe, Cu, Ru, Cr and Pd, are known to catalyse the C-H to C-OH conversion.[6] This conversion can also be achieved without any transition metal catalysts. Since the pioneering work of Murray[7] and Curci,[8] dimethyldioxirane (DMDO) and methyl(trifluoromethyl)dioxirane (TFDO) have been widely used in the oxidation of C-H to C-OH in chemical syntheses. Three possible mechanisms for the hydroxylation of unsaturated hydrocarbons by dioxirane have been proposed (Scheme 1), based on experimental[7–11] and computational[13,20,22] studies. Previous prototypical studies on the hydroxylation of isobutane by DMDO by Cremer,[14] Rauk,[15] Bach,[16,17] Fokin,[18] Sarzi-Amade[19] and Houk[20] favoured the H-abstraction-O-rebound mechanism (Scheme 1a) in which an open-shell singlet transition state was formed by the rate-determining hydrogen abstraction, followed by an almost barrierless oxygen rebound step. Using molecular dynamics,[22] the oxygen rebound step was found to be extremely rapid, ranging from 30 to 150 fs. This short time scale for the oxygen rebound step following hydrogen abstraction allows for stereospecific oxyfunctionalization of unactivated C-H bond of alkanes. The same study also found that solvent influenced the mechanism substantially, with



Scheme 1: Proposed mechanisms of hydroxylation of unsaturated hydrocarbons by dioxirane.

a 10% oxygen-rebound trajectory in gas phase and 90% in implicit acetone solvent. It is evident that solvent effects play an important role in the oxyfunctionalization of alkane by DMDO. The alternative mechanism (Scheme 1b), proposed by Murray[7] and Curci[8] based on kinetic and isotopic effect studies, in which a concerted "oxenoid" transition state is formed without any intermediate, has largely been discredited by computational studies[20] showing that such a restricted wavefunction is unstable with respect to an open-shell unrestricted wavefunction. The free radical mechanism (Scheme 1c), favoured by Minisci,[12] in which free radicals of dioxirane are involved, is also disfavoured in the light of evidence from stereospecific and stereoselective hydroxylations of *cis*- and *trans*-1,2-dimethylcyclohexane,[7] the lack of ring opening in isopropylcyclopropane hydroxylation,[23] and ultrafast radical clock experiments.[8,24] Although the corresponding hydroxylation of isobutane by TFDO (Scheme 2) is expected to be similar to and more reactive than the DMDO counterpart, there are only scarce computational studies on this reaction. In this project, we wish to validate the mechanism of C-H to C-OH conversion of isobutane by TFDO using both Density Functional Theory (DFT) and *ab initio* methods.



Scheme 2: Conversion of isobutane to tert-butanol by TFDO.

2 Computational Methods

All DFT and *ab initio* calculations were performed using Gaussian09 program.[25] All minima and transitions structures were fully optimized separately using two unrestricted DFT methods, namely, UB3LYP[26] with 6-311G(d) basis set and UM062X[27] with 6-311+G(3df, 2p) basis set. These two functionals and their corresponding basis sets were chosen so that the TFDO calculation results can be directly compared to the DMDO results published by Houk[20] and Bach[21] at the corresponding levels of theory. Frequency analyses at the corresponding levels of theory were similarly performed on all fully optimized structures and stationary points to classify them as either minima or saddle points (transition states). In addition, all transition states (TS) were further verified by carrying out intrinsic reaction coordinate (IRC) analyses on the TS structures. Gaussian keyword *stable=opt* were used to ensure that a correct unrestricted wavefunction is obtained. Solvent corrections were modelled using the conductor-like polarizable continuum model (CPCM). The molecular energies of the previously optimized structures from UDFT calculations were also calculated using the Gaussian-4 (G4) theory.[28]

3 Results and Discussion

TFDO O-O Bond Homolysis. Goddard[29] in as early as 1978 recognized the possibility of using dioxirane for application in chemistry; he suggested that the dioxymethane diradical formed from the facile O-O bond cleavage could contribute to the chemistry of the parent dioxirane. Studies on the homolysis of the prototypical dioxirane, dimethyldioxirane (DMDO), have since been performed by various research groups.[13,20,21,31] Cremer[31] calculated an activation enthalpy of 23.1 kcal/mol for DMDO O-O bond homolysis using B3LYP with 6-31G(d,p) basis set. Bach[21] found an activation energy barrier ($\Delta E^{\ddagger}$) of 30.3 kcal/mol using UM062X with a large diffuse 6-311+G(3df,2p) basis set; this value was lowered to 28.9 kcal/mol using G4 method. Our calculations using UB3LYP/6-31G(d) in the gas phase (Fig-

ure 1 and Table 1) showed that the TFDO homolysis transition state was 20.3 kcal/mol above the TFDO ground state in terms of enthalpy and energy (both at the same value); this activation barrier is about 2.8 kcal/mol lower than the DMDO counterpart in Cremer's work.[31] On the other hand, M062X/6-311+G(3df,2p) calculations in the gas phase gave an activation barrier of $\Delta E^{\ddagger} = 26.2$ kcal/mol; this is about 4.0 kcal/mol lower than the activation barrier for DMDO homolysis performed by Bach.[21] The activation energy barriers in implicit acetone and acetonitrile solvents are not much altered as compared to the gas phase results within each functional calculation (Tables 1 and 2), suggesting that solvent effects, modelled using implicit solvent model, do not drastically affect the activation barriers of the transition states. This is likely the result of the limitations of the model, which treats dynamical species using mean field potential in an equilibrium continuum; the actual orientations of the interacting solvent molecules may affect the result more than predicted by the model. It is interesting to note that the solvent effect (within PCM model) does not affect the results quantitatively more than the choice of functionals and basis sets. In all cases, both levels of DFT calculations confirmed the experimental observation that TFDO is more reactive than DMDO when it comes to O-O bond homolysis.[8]

Reaction Phase	Molecular Structure	O-O Length[a]	C-O Length[b]	$\angle\alpha$	$\angle\beta$	Barrier A[c]	Barrier B[c]
Gas	TFDO	1.51	1.39	65.7°	116.1°	20.5 (20.3)	8.1 (7.9)
	TS	2.01	1.38	93.4°	112.6°		
	Diradical	2.32	1.35	119.3°	108.1°		
Acetone	TFDO	1.51	1.39	65.6°	116.4°	20.7 (20.5)	9.0 (8.7)
	TS	2.01	1.39	92.8°	112.9°		
	Diradical	2.32	1.34	119.5°	107.9°		
Acetonitrile	TFDO	1.51	1.39	65.6°	116.4°	20.7 (20.5)	9.0 (8.7)
	TS	2.01	1.39	92.8°	112.9°		
	Diradical	2.32	1.34	119.3°	107.9°		

Table 1: B3LYP/6-31G(d)-optimized structures for TFDO homolysis in gas phase and in acetone and acetonitrile solvents. [a,b] O-O and C-O bond lengths are labelled 1 and 2 respectively in Figure 1; both are given in Å. [c] Activation barriers for the forward and reverse reaction pathway; both ΔG and ΔE are given (the latter in brackets) in kcal/mol.

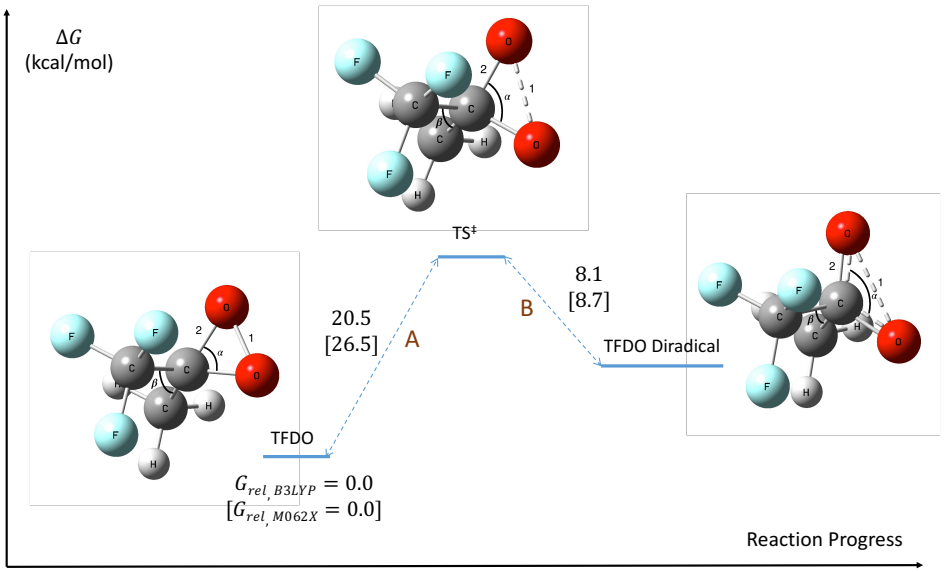


Figure 1: Reaction pathway for TFDO homolysis. The structures were optimized at two different DFT levels (UB3LYP/6-31G(d) and UM062X/6-311+G(3df,2p)) in different reaction phases. The optimized structures are similar in all phases for both functionals with varying details in the structures given in Tables 1 and 2. The free energy barriers for the reaction in gas phase calculated using the two functionals are included in the figure; the corresponding values for the solvent phase calculations are included in Tables 1 and 2.

Reaction Phase	Molecular Structure	O-O Length[a]	C-O Length[b]	$\angle\alpha$	$\angle\beta$	Barrier A[c]	Barrier B[c]
Gas	TFDO	1.47	1.37	64.5°	116.2°	26.5 (26.2)	8.7 (8.5)
	TS	2.02	1.38	94.0°	112.7°		
	Diradical	2.31	1.35	117.8°	109.0°		
Acetone	TFDO	1.47	1.38	64.4°	116.5°	26.2 (26.3)	9.0 (9.0)
	TS	2.02	1.38	93.5°	113.1°		
	Diradical	2.30	1.34	117.8°	109.0°		
Acetonitrile	TFDO	1.47	1.38	64.4°	116.5°	26.2 (26.3)	9.0 (9.0)
	TS	2.02	1.38	93.5°	113.1°		
	Diradical	2.30	1.34	117.8°	109.0°		

Table 2: M062X/6-311+G(3df,2p)-optimized structures for TFDO homolysis in gas phase and in acetone and acetonitrile solvents. [a,b] O-O and C-O bond lengths are labelled 1 and 2 respectively in Figure 1; both are given in Å. [c] Activation barriers for the forward and reverse reaction pathway; both ΔG and ΔE are given (the latter in brackets) in kcal/mol.

It is perhaps unsurprising that the O-O bond length in the ground state TFDO is different when calculated using different density functionals/basis sets. Specifically, B3LYP/6-311G(d) gave an O-O bond length of 1.51Å whereas UM062X/6-311+G(3df,2p) gave a value of 1.46Å. However, it is noteworthy that the O-O bond lengths for the ground state DMDO and TFDO are the same when calculated at the same level of theory.[20,21] Interestingly, despite the different ground state TFDO O-O bond lengths calculated using UB3LYP and UM062X, both functionals located a transition state having similar O-O bond length of 2.01-2.02Å in gas phase and in acetone and acetonitrile solvents. The O-O bond length further elongates to 2.30-2.32Å as the diradical intermediate is formed (Tables 1 and 2). It is also important to note that the transition states in both gas and solvent phases have substantial diradical character, with $\langle S^2 \rangle = 0.827$ (using B3LYP) and $\langle S^2 \rangle = 0.855$ (using M062X) in the gas phase and $\langle S^2 \rangle = 0.823$ (using B3LYP) and $\langle S^2 \rangle = 0.852$ (using M062X) in both acetone and acetonitrile solvents.

TFDO Oxidation of Isobutane. In the study of DMDO oxidation of isobutane by Houk,[20] the team identified a transition state structure in which the O-O bond of DMDO is aligned with the breaking C-H bond in the H-abstraction step. Since TFDO oxidation of isobutane is likely to follow a similar mechanism, we performed a TS search with this starting geometry as our initial guess. The keyword *stable=opt* was used to ensure that the resulting wavefunction is stable with respect to an unrestricted wavefunction, as we expect the TFDO-isobutane transition structure to possess significant diradical character. Houk[20] found that the transition state for DMDO oxidation of isobutane has a diradical character with $\langle S^2 \rangle = 0.5312$ in the gas phase using UB3LYP/6-31G(d) whereas Bach[21] found a diradicaloid TS with $\langle S^2 \rangle = 0.5285$ for the same reaction using UM062X/6-311+G(3df,2p).

The reaction mechanism for the TFDO oxidation of isobutane in the gas phase closely resembles the DMDO oxidation of isobutane studied by Houk[20] and Bach.[21] The reaction pathway in the gas phase is presented in Figure 3 (Top). Specifically, TFDO and isobutane formed a complex prior to H-abstraction step; this complex was isolated as a minimization of the structure at the end of an IRC search (Figure 2). It passes through a transition state (TS1) as the H atom is abstracted by TFDO, forming a weakly-bound radical pair intermediate. This is immediately followed by a barrierless transition state (TS2) as the O atom rebounds in the second step. It is interesting to note that, despite the different TFDO-isobutane complex structures predicted by B3LYP and M062X functionals, the transition structures are the

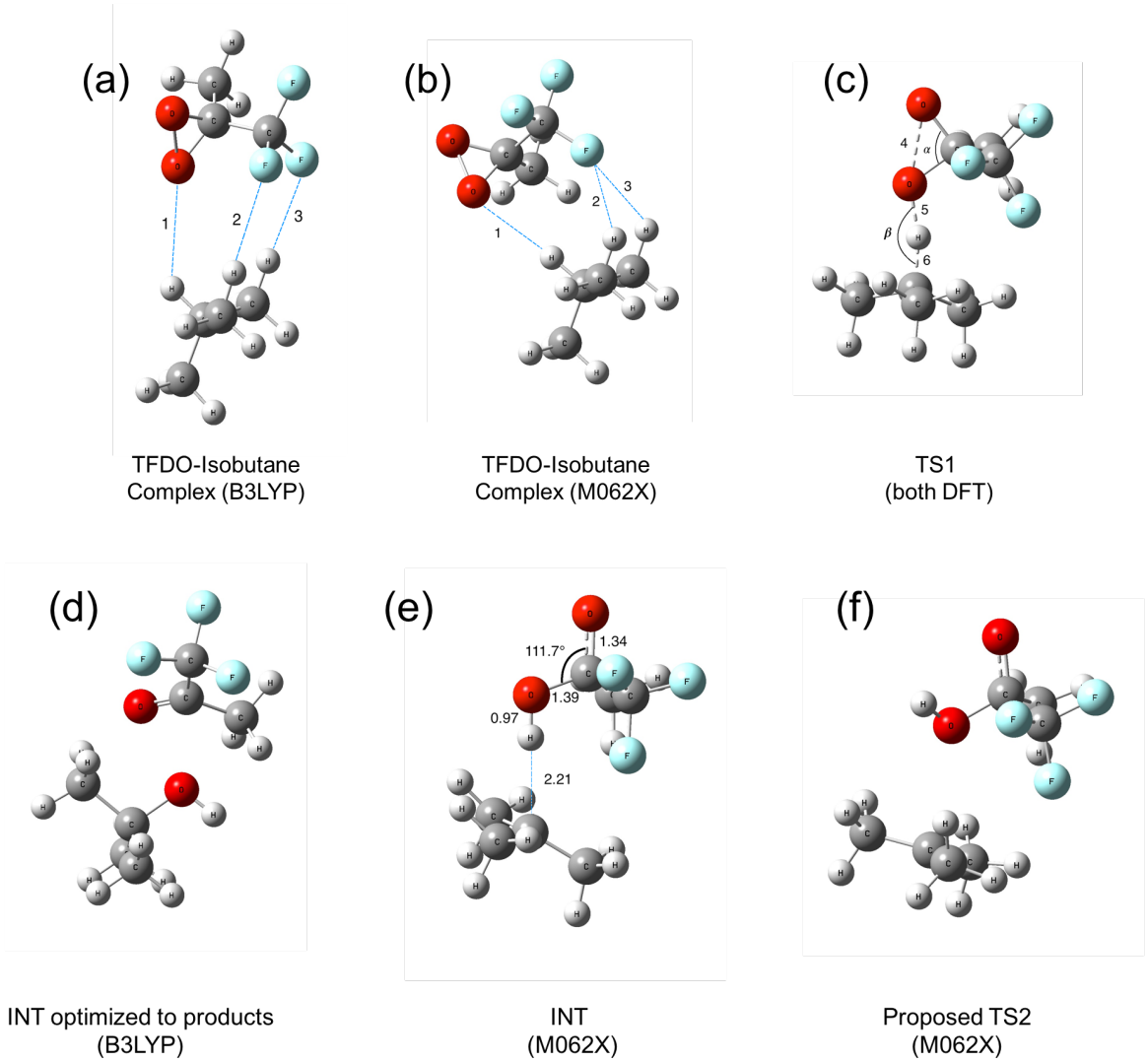


Figure 2: Optimized structures from B3LYP and M062X calculations. The optimized structures are similar for both functionals with varying details in the structures given in Table 3. Only one transition state occurs in the solvent phase.

DFT Method	Reaction Phase	Distance between atoms in Figures 2 Labelled						$\angle\alpha$	$\angle\beta$
		1	2	3	4	5	6		
B3LYP	Gas	2.91	2.65	2.61	1.93	1.29	1.25	88.2°	166.1°
	Acetone	2.92	2.63	2.62	1.87	1.34	1.23	84.9°	167.1°
	Acetonitrile	2.93	2.63	2.62	1.87	1.34	1.22	84.8°	167.1°
M062X	Gas	2.53	2.63	2.70	1.83	1.33	1.20	83.8°	167.3°
	Acetone	2.53	2.64	2.72	1.79	1.34	1.20	81.8°	168.4°
	Acetonitrile	2.53	2.64	2.72	1.79	1.34	1.20	81.7°	168.5°

Table 3: DFT-optimized structures (as in Figure 2) for the TFDO oxidation of isobutane in gas phase. All distances are given in Å.

same (Figure 2 (c)) with minute variations in the structures (Table 3). Perhaps of equal importance, the energies of the complexes are all exothermic or slightly endothermic (acetonitrile, M062X), indicating a favourable interaction between the heteroatoms and the H atoms on isobutane; the free energies are highly endergonic, indicating an entropically unfavourable contribution as the two molecules are brought together. The activation barriers (Table 4 Label B) for the TFDO oxidation of isobutane using UB3LYP/6-31G(d) gave $\Delta G^{\ddagger} = 24.8$ kcal/mol which is about 1.8 kcal/mol lower than the DMDO oxidation of isobutane ($\Delta G^{\ddagger} = 26.6$ kcal/mol) caclulated by Houk;[20] the same barrier for the TFDO oxidation using UM062X/6-311+G(3df,2p) gave $\Delta G^{\ddagger} = 33.0$ kcal/mol, which is, surprisingly, 2.8 kcal/mol higher than the DMDO oxidation at the same level of theory ($\Delta G^{\ddagger} = 30.2$ kcal/mol) in Bach's study.[21] G4 energy calculations performed on the DFT-optimized structures yielded activation barriers that are lower than those calculated using DFT methods; these activation barriers range from about 18-20 kcal/mol (Table 4). It is noteworthy that the G4 calculations gave energies that are closer to the B3LYP functional calculations than to the M062X functional calculations.

The intermediate in the gas phase TFDO oxidation of isobutane could not be found using B3LYP (the intermediate was optimized to the products) but could be obtained using M062X (Structure (e) in Figure 2). The relative energy of the intermediate above the ground state is comparable to that of the TFDO-isobutane complex. A transition structure for oxygen rebound in the gas phase using M062X could be found (imaginary frequency $= -693.3715$) but IRC search failed to connect it to the intermediate and the products, possibly due to the flat nature of the potential energy surface (PES) in the region. In the solvent phase (Figure 3, Bottom), the oxygen-rebound transition state (TS2) could not be isolated using both functionals. An IRC search of the hydrogen-abstraction transition state (TS1) leads from

the reactants, through TS1, to the product. The total energy along IRC path showed that the energy for TS2 is much lower than that for TS1, indicating that hydrogen-abstraction is the overall rate-determining step in the oxidation of isobutane by TFDO. These results indicated that oxygen-rebound is barrierless in the implicit acetone and acetonitrile solvents, possibly because the formation of diradicaloid TS2 is better stabilized by the polar solvation, rendering the activation barrier much lower.

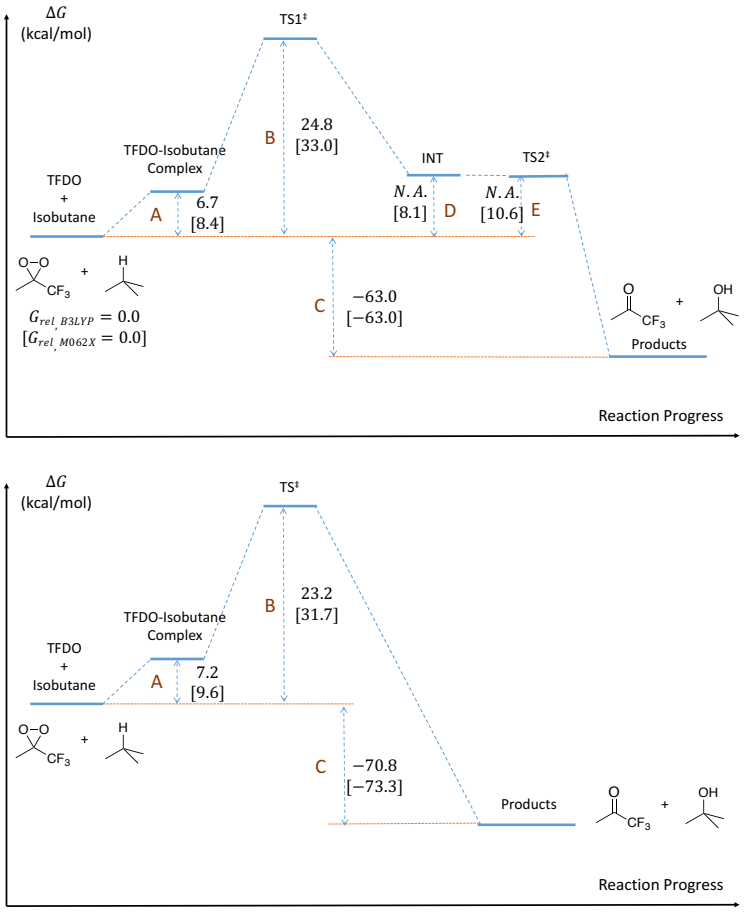


Figure 3: Reaction pathway for the TFDO oxidation of isobutane. All units are in kcal/mol. **Top**: Reaction profile in gas phase. Note that there are two transition structures for this reaction in the gas phase. The free energy barriers in the gas phase from the two functionals, B3LYP and M062X (the latter in square brackets) are included. **Bottom**: Reaction profile in both acetone and acetonitrile solvent phase. Note that there is only one transition state for this reaction in the solvent phase. The free energy barriers in the acetone solvent from the two functionals, B3LYP and M062X (the latter in square brackets), are included. All values of the barriers in gas and solvent phases calculated using the two functional methods are given in Table 4.

DFT Method	Reaction Phase	Energy Barriers in Figure 3 with the following Label				
		A	B	C	D	E[a]
B3LYP	Gas	6.7 (-0.1)	24.8 (14.5)	-63.0 (-61.3)		
	Acetone	7.2 (0.0)	23.2 (12.8)	-70.8 (-69.1)		
	Acetonitrile	7.1 (0.0)	23.1 (12.7)	-66.4 (-64.3)		
G4 using B3LYP-optimized Structures	Gas	6.5 (-0.2)		-70.0 (-68.4)		
	Acetone	6.9 (0.0)	20.0 (9.4)	-73.4 (-71.6)		
	Acetonitrile	6.9 (0.0)	20.0 (9.4)	-73.5 (-71.8)		
M062X	Gas	8.4 (-1.0)	33.0 (22.3)	-63.0 (-61.3)	8.1 (0.5)	10.6 (2.6)
	Acetone	9.6 (-0.5)	31.7 (20.6)	-73.3 (-72.5)		
	Acetonitrile	8.1 (0.1)	31.6 (20.6)	-73.5 (-72.6)		
G4 using M062X-optimized Structures	Gas		18.4 (8.0)	-70.0 (-68.4)		
	Acetone	4.9 (-2.5)	18.0 (6.9)	-75.4 (-74.1)		
	Acetonitrile	7.6 (0.0)	20.5 (9.3)	-72.8 (-71.7)		

Table 4: Energy barriers as indicated in Figure 2; both ΔG and ΔE are given (the latter in brackets) in kcal/mol. [a] Energy based on the proposed structure of TS2.

Alternative Mechanism for TFDO Oxidation of Isobutane. Figure 4 shows the energy profiles for two competing reaction pathways. The one on the right illustrates the H-abstraction-O-rebound mechanism (Scheme 1a) with an overall activation energy of the system labelled E_a, whereas the one on the left illustrates the free-radical mechanism (Scheme 1c). As the activation barrier for the homolysis of TFDO is lower than that for the direct oxidation of isobutane by TFDO calculated using both

functionals in all phases (Tables 5), it is plausible that in the oxidation of isobutane by TFDO, the oxidant TFDO undergoes homolysis before its interaction with isobutane molecule. This is in contrast to the DMDO oxidation of isobutane in which the DMDO oxidation of isobutane has a lower activation barrier ($\Delta G^{\ddagger} = 30.2$ kcal/mol) than the DMDO homolysis ($\Delta G^{\ddagger} = 30.3$ kcal/mol) as found using UM062X/6-311+G(3df, 2p) in Bach's study.[21] Evidently, the higher reactivity of TFDO is due to the increased easy of O-O bond cleavage when an additional trifluoromethyl substituent is added to the dioxirane. If the diradical obtained from TFDO homolysis is stable enough for its subsequent reaction with hydrocarbon before reverting back to ground state TFDO or undergoing other reactions (preliminary results show that TFDO can undergo a rearrangement reaction in which the methyl group on TFDO migrates to form methyl trifluoroacetate; results not shown), then the free-radical mechanism will be kinetically favoured over H-abstraction-O-rebound mechanism for TFDO oxidation. In this manner, the reaction mechanism found in this study is more consistent with the free radical mechanism as proposed by Minisci (Scheme 1c) in which the dioxirane undergoes a homolytic O-O bond cleavage to form a diradical, which then attacks hydrocarbon in a free-radical fashion. Future studies could look into the reversibility of TFDO homolysis and the oxidation of isobutane by TFDO-diradical to test the feasibility of this mechanism.

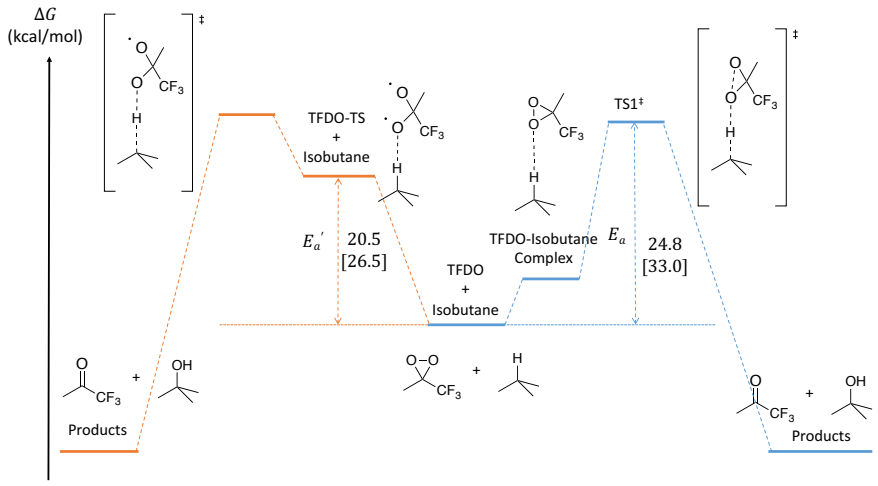


Figure 4: Alternative reaction pathways for the TFDO oxidation of isobutane as calculated by UB3LYP and UM052X DFT methods. The values in the gas phase from both functionals are given for ease of comparison. All units are in kcal/mol. All values of activation barriers in gas and solvent phases are given in Table 5.

DFT Method	Reaction Phase	Energy Barriers Labelled		$\Delta\Delta G^{\ddagger}$
		E'_a	E_a	
B3LYP	Gas	20.48	24.81	4.33
	Acetone	20.67	23.17	2.50
	Acetonitrile	20.67	23.08	2.41
M062X	Gas	26.47	32.96	6.49
	Acetone	26.23	31.67	5.44
	Acetonitrile	26.20	31.59	5.39

Table 5: Energy barriers ($\Delta G^{\ddagger}$) for TFDO homolysis and TFDO oxidation of isobutane as indicated in Figure 4. All energies are given in kcal/mol.

4 Conclusion

We have shown that TFDO is more reactive than DMDO in terms of O-O bond cleavage as the former has a much lower activation energy than the latter for homolysis using both B3LYP and M062X DFT studies. B3LYP functional showed that the oxidation of isobutane by TFDO has a lower activation barrier than the DMDO counterpart whereas M062X found a higher activation barrier at their corresponding level of theory. From experimental results, we know that TFDO oxidation of isobutane is more reactive than DMDO oxidation, suggesting that M062X calculation for this proposed mechanism is unreliable. Bach[21] has shown that M062X DFT functional provides the most accurate O-O bond energy for a series of typical peroxides and our studies of TFDO O-O bond homolysis validated its increased reactivity as compared to DMDO. As the TFDO homolysis activation barrier is much lower than TFDO oxidation of isobutane (ranging from 2-6 kcal/mol), it is plausible that the widely accepted mechanism for the oxidation of isobutane by DMDO does not apply to the case of TFDO. Future work looking into the reaction of TFDO-diradical and isobutane is needed to validate the alternatively proposed mechanism in which the homolysis of TFDO occurs before the resultant TFDO diradical reacts with isobutane in the oxidation step. Non-DFT *ab initio* calculations such as G4 and CBS-QB3 could be performed to validate these results.

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6 Supporting Information

All computational work in this project were performed using the Gaussian09 program[25] within the Dirac computational cluster located at the Department of Chemistry, University of Oxford. All energies given here are in the unit of Hartrees, as used in the Gaussian09 output files. G4 energies were calculated using the geometries previously optimized at the appropriate level of the density functional theory. Where G4 energy values are not given, it is not successfully calculated from the input and further work is needed to obtain successful calculations.

6.1 Energies and Optimized Geometries for TFDO homolysis at UB3LYP/6-311G(d) Level

6.1.1 Gas Phase

TFDO

```
SCF Done:  E(UB3LYP) =  -565.978016834
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.912351
Sum of electronic and thermal Energies=              -565.904850
Sum of electronic and thermal Enthalpies=            -565.903906
Sum of electronic and thermal Free Energies=         -565.944728

C  0.441732  0.602709  0.0
O  -0.099423  1.637888  0.75468
O  -0.099423  1.637888  -0.75468
C  1.932847  0.413777  0.0
C  -0.399055  -0.678836  0.0
H  2.41197  1.394395  0.0
H  2.241329  -0.147213  0.887272
H  2.241329  -0.147213  -0.887272
F  -0.099423  -1.415067  -1.091433
F  -1.707487  -0.428985  0.0
F  -0.099423  -1.415067  1.091433

G4(0 K)=                -565.819759 G4 Energy=                -565.812134
G4 Enthalpy=            -565.811190 G4 Free Energy=           -565.852368
```

TFDO Homolysis TS

```
SCF Done:  E(UB3LYP) =  -565.942657553
Frequencies --   -689.8773
S**2 before annihilation     0.8270,   after     0.0214
Sum of electronic and zero-point Energies=          -565.879909
Sum of electronic and thermal Energies=             -565.872448
Sum of electronic and thermal Enthalpies=           -565.871504
Sum of electronic and thermal Free Energies=        -565.912088

C  -0.742099  0.096255  -0.000119
O  -1.38253  -0.879111  0.748207
O  -1.382969  -0.878817  -0.74823
C  -1.293348  1.493012  0.000059
C  0.788353  -0.020819  -0.00006
H  -0.945355  2.032221  0.884906
H  -0.948266  2.031079  -0.886653
H  -2.38248  1.443217  0.001836
F  1.285524  0.593223  -1.083658
F  1.194144  -1.279596  -0.001025
F  1.285071  0.591509  1.084774

G4(0 K)=                -565.816726 G4 Energy=                -565.809762
G4 Enthalpy=            -565.808818 G4 Free Energy=           -565.848529
```

TFDO Diradical

```
SCF Done:  E(UB3LYP) =  -565.955824961
S**2 before annihilation     0.9099,   after     0.0297
Sum of electronic and zero-point Energies=          -565.892785
Sum of electronic and thermal Energies=             -565.884986
Sum of electronic and thermal Enthalpies=           -565.884042
Sum of electronic and thermal Free Energies=        -565.925000

C  -0.784098  -0.259918  0.000033
O  -1.138616  -0.841103  -1.161689
O  -1.138508  -0.841118  1.161779
C  0.761067  0.047028  -0.000034
C  -1.567252  1.131605  0.000079
H  -1.273822  1.669828  0.901623
H  -1.273896  1.669846  -0.901479
H  -2.635653  0.919696  0.00012
F  1.101949  0.754246  -1.087541
```

```
F  1.102067  0.75414  1.087505
F  1.456213  -1.098818  -0.000125
```

Rearrangement Product from TFDO Diradical G4 Calculation

```
C                 -0.47034300   -0.40734000    0.00011600
O                 -0.77940700   -1.56463600    0.00005900
O                 -1.28935100    0.64103100    0.00010200
C                  0.99600300    0.08977300    0.00002600
C                 -2.69411200    0.32596100   -0.00004300
H                 -3.20865200    1.28551000    0.00020500
H                 -2.95123100   -0.25179900   -0.89055300
H                 -2.95134400   -0.25227800    0.89011800
F                  1.82705600   -0.94217500    0.00079900
F                  1.23501200    0.83460900   -1.08348800
F                  1.23482200    0.83612700    1.08250600

G4(0 K)=                -565.929176 G4 Energy=                -565.921131
G4 Enthalpy=            -565.920187 G4 Free Energy=           -565.963350
```

Rearrangement Product Optimized at DFT Level

```
SCF Done:  E(UB3LYP) =  -566.090998110
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -566.023673
Sum of electronic and thermal Energies=              -566.015680
Sum of electronic and thermal Enthalpies=            -566.014736
Sum of electronic and thermal Free Energies=         -566.058196

C  -0.468825  0.403881  -0.000059
O  -0.779393  1.567718  0.000052
O  -1.294459  -0.644204  -0.00012
C  0.995088  -0.089959  -0.000018
C  -2.701355  -0.321992  0.000006
H  -3.216243  -1.281762  -0.000265
H  -2.954938  0.255689  0.891973
H  -2.954982  0.256225  -0.891599
F  1.832203  0.949266  -0.000947
F  1.23783  -0.838793  1.090772
F  1.23747  -0.840456  -1.089729
```

6.1.2 PCM Acetone

TFDO

```
SCF Done:  E(UB3LYP) =  -565.981599527
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.916200
Sum of electronic and thermal Energies=              -565.908675
Sum of electronic and thermal Enthalpies=            -565.907731
Sum of electronic and thermal Free Energies=         -565.948678

C  0.449529  0.601342  0.0
O  -0.104033  1.633936  0.754656
O  -0.104033  1.633936  -0.754656
C  1.938573  0.418765  0.0
C  -0.393287  -0.679928  0.0
H  2.416747  1.399677  0.0
H  2.247455  -0.140861  0.887552
H  2.247455  -0.140861  -0.887552
F  -0.104033  -1.417414  -1.09085
F  -1.704827  -0.420948  0.0
F  -0.104033  -1.417414  1.09085

G4(0 K)=                 -565.823798 G4 Energy=                  -565.816151
G4 Enthalpy=             -565.815207 G4 Free Energy=             -565.856525
```

TFDO Homolysis TS

```
SCF Done:  E(UB3LYP) =  -565.945981534
Frequencies --   -716.4793
S**2 before annihilation     0.8231,   after     0.0213
Sum of electronic and zero-point Energies=           -565.883517
Sum of electronic and thermal Energies=              -565.876029
Sum of electronic and thermal Enthalpies=            -565.875085
Sum of electronic and thermal Free Energies=         -565.915745

C  -0.781619  -0.054769  0.014022
O  -1.225968  -0.953641  0.9751
O  -1.24774  -0.833274  -1.027869
C  -1.449899  1.317148  0.043602
C  0.764088  0.028059  -0.000884
H  -1.136868  1.83354  0.956326
```

```
H  -1.151132  1.910601  -0.823709
H  -2.531895  1.178223  0.05102
F  1.186381  0.752165  -1.055112
F  1.31654  -1.191327  -0.081135
F  1.209762  0.62031  1.124922

G4(0 K)=                -565.819696 G4 Energy=                -565.812118
G4 Enthalpy=            -565.811174 G4 Free Energy=           -565.852086
```

TFDO Diradical

```
SCF Done:  E(UB3LYP) =  -565.960360588
S**2 before annihilation     0.8849,   after     0.0277
Sum of electronic and zero-point Energies=           -565.897755
Sum of electronic and thermal Energies=              -565.889877
Sum of electronic and thermal Enthalpies=            -565.888932
Sum of electronic and thermal Free Energies=         -565.930071

C  -0.779995  -0.269751  0.000041
O  -1.13798  -0.842603  -1.158885
O  -1.137854  -0.842546  1.159033
C  0.761788  0.050795  -0.000038
C  -1.57884  1.132444  0.00005
H  -1.280931  1.664906  0.902896
H  -1.280983  1.664888  -0.902826
H  -2.644513  0.912255  0.000081
F  1.101173  0.75598  -1.088041
F  1.101346  0.755724  1.088077
F  1.463635  -1.094125  -0.000218

G4(0 K)=                -565.934543 G4 Energy=                -565.926476
G4 Enthalpy=            -565.925532 G4 Free Energy=           -565.968728
```

Rearrangement Product from TFDO Diradical G4 Calculation

```
C  -0.470353  -0.407321  0.000038
O  -0.779362  -1.564631  0.000033
O  -1.289376  0.641024  0.000103
C  0.996003  0.08976  -0.000011
C  -2.694131  0.325932  -0.000057
H  -3.208652  1.285492  0.000682
H  -2.951391  -0.251351  -0.89083
```

```
H  -2.951339  -0.252692  0.889866
F  1.827056  -0.94217  0.000742
F  1.235099  0.834728  -1.083394
F  1.234754  0.836017  1.082582

G4(0 K)=                -565.929176 G4 Energy=                -565.921131
G4 Enthalpy=            -565.920187 G4 Free Energy=           -565.963353
```

Rearrangement Product Optimized at DFT Level

```
SCF Done:  E(UB3LYP) =  -566.090998110
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -566.023673
Sum of electronic and thermal Energies=              -566.015680
Sum of electronic and thermal Enthalpies=            -566.014736
Sum of electronic and thermal Free Energies=         -566.058199

C  -0.468834  0.403894  -0.000013
O  -0.779406  1.567725  0.000135
O  -1.294458  -0.644201  -0.000092
C  0.995091  -0.089958  -0.000035
C  -2.701345  -0.322007  0.000029
H  -3.216229  -1.281781  -0.000446
H  -2.954981  0.255496  0.892098
H  -2.954947  0.256382  -0.891472
F  1.832204  0.949263  -0.00065
F  1.237799  -0.839093  1.090547
F  1.237509  -0.840154  -1.089943
```

6.1.3 PCM Acetonitrile

TFDO

```
SCF Done:  E(UB3LYP) =  -565.981733566
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.916346
Sum of electronic and thermal Energies=              -565.908819
Sum of electronic and thermal Enthalpies=            -565.907875
Sum of electronic and thermal Free Energies=         -565.948829

C  0.449811  0.601286  0.0
```

```
O  -0.104212  1.633776  0.754662
O  -0.104212  1.633776  -0.754662
C  1.93878  0.419015  0.0
C  -0.393033  -0.680004  0.0
H  2.416861  1.399968  0.0
H  2.247677  -0.140553  0.887565
H  2.247677  -0.140553  -0.887565
F  -0.104212  -1.41753  -1.090824
F  -1.704706  -0.420612  0.0
F  -0.104212  -1.41753  1.090824

G4(0 K)=                -565.823954 G4 Energy=                -565.816306
G4 Enthalpy=            -565.815362 G4 Free Energy=           -565.856686
```

TFDO Homolysis TS

```
SCF Done:  E(UB3LYP) =  -565.946103866
Frequencies --   -717.4473
S**2 before annihilation     0.8230,   after     0.0213
Sum of electronic and zero-point Energies=           -565.883649
Sum of electronic and thermal Energies=              -565.876160
Sum of electronic and thermal Enthalpies=            -565.875216
Sum of electronic and thermal Free Energies=         -565.915880

C  -0.781697  -0.054564  0.013962
O  -1.225709  -0.95373  0.975038
O  -1.247388  -0.833587  -1.027756
C  -1.450411  1.317076  0.0435
C  0.764013  0.02839  -0.000871
H  -1.137804  1.833387  0.956412
H  -1.15152  1.910661  -0.823655
H  -2.532363  1.177842  0.050517
F  1.186591  0.752425  -1.054927
F  1.316344  -1.191267  -0.081364
F  1.209847  0.620089  1.125061

G4(0 K)=                -565.819696 G4 Energy=                -565.812118
G4 Enthalpy=            -565.811174 G4 Free Energy=           -565.852087
```

TFDO Diradical

```
SCF Done:  E(UB3LYP) =  -565.960522392
```

```
S**2 before annihilation     0.8837,   after     0.0276
Sum of electronic and zero-point Energies=          -565.897932
Sum of electronic and thermal Energies=             -565.890052
Sum of electronic and thermal Enthalpies=           -565.889107
Sum of electronic and thermal Free Energies=        -565.930244

C  -0.779801  -0.270227  0.000044
O  -1.137977  -0.842658  -1.15877
O  -1.137846  -0.842576  1.158938
C  0.761829  0.050955  -0.00004
C  -1.579287  1.132505  0.000039
H  -1.281122  1.66468  0.90294
H  -1.281167  1.664649  -0.902896
H  -2.644849  0.911973  0.000068
F  1.101103  0.756073  -1.088052
F  1.101296  0.755763  1.088113
F  1.463964  -1.093928  -0.000251

G4(0 K)=                -565.933965 G4 Energy=                -565.926822
G4 Enthalpy=            -565.925878 G4 Free Energy=           -565.966018
```

Rearrangement Product from TFDO Diradical G4 Calculation

```
C  -0.470347  -0.40734  -0.000008
O  -0.779384  -1.564647  -0.000004
O  -1.289367  0.64103  -0.000028
C  0.996003  0.089772  0.000018
C  -2.694128  0.325958  0.000014
H  -3.208688  1.285493  0.000063
H  -2.951333  -0.25202  -0.890328
H  -2.95127  -0.252056  0.890354
F  1.234934  0.835335  -1.083016
F  1.234908  0.835405  1.082975
F  1.82706  -0.942164  0.000043

G4(0 K)=                -565.929176 G4 Energy=                -565.921132
G4 Enthalpy=            -565.920187 G4 Free Energy=           -565.963349
```

Rearrangement Product Optimized at DFT Level

```
SCF Done:  E(UB3LYP) =  -566.090998101
S**2 before annihilation     0.0000,   after     0.0000
```

```
Sum of electronic and zero-point Energies=          -566.023674
Sum of electronic and thermal Energies=             -566.015680
Sum of electronic and thermal Enthalpies=           -566.014736
Sum of electronic and thermal Free Energies=        -566.058227

C  -0.4688  0.403803  -0.000041
O  -0.779354  1.567648  0.000007
O  -1.294475  -0.64421  -0.000034
C  0.995091  -0.08995  0.000003
C  -2.701446  -0.321922  -0.000009
H  -3.216324  -1.28169  -0.000042
H  -2.954958  0.255997  0.891804
H  -2.954974  0.256069  -0.891771
F  1.237647  -0.839554  1.090295
F  1.23769  -0.839649  -1.090212
F  1.832198  0.949263  -0.000026
```

6.2 Energies and Optimized Geometries for TFDO homolysis at UM062X/6-311+G(3df,2p) Level

6.2.1 Gas Phase

TFDO

```
SCF Done:  E(UM062X) =  -566.005952310
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -565.939489
Sum of electronic and thermal Energies=             -565.932104
Sum of electronic and thermal Enthalpies=           -565.931160
Sum of electronic and thermal Free Energies=        -565.971758

C  -0.78001  -0.055329  0.003646
O  -1.212611  -0.91026  1.002003
O  -1.228475  -0.868035  -1.018676
C  -1.435958  1.306494  0.017016
C  0.757231  0.024612  -0.001496
H  -1.122431  1.85159  0.906335
H  -1.141642  1.870205  -0.866873
H  -2.512663  1.162595  0.028636
F  1.178569  0.70652  -1.066404
```

```
F  1.308432  -1.175613  -0.031084
F  1.186092  0.656571  1.091964

G4(0 K)=                -565.819763 G4 Energy=                -565.812144
G4 Enthalpy=            -565.811200 G4 Free Energy=           -565.852340
```

TFDO Homolysis TS

```
SCF Done:  E(UM062X) =  -565.961045228
Frequencies --   -727.3390
S**2 before annihilation     0.8547,   after     0.0243
Sum of electronic and zero-point Energies=          -565.897612
Sum of electronic and thermal Energies=             -565.890284
Sum of electronic and thermal Enthalpies=           -565.889340
Sum of electronic and thermal Free Energies=        -565.929576

C  -0.78001  -0.055329  0.003646
O  -1.212611  -0.91026  1.002003
O  -1.228475  -0.868035  -1.018676
C  -1.435958  1.306494  0.017016
C  0.757231  0.024612  -0.001496
H  -1.122431  1.85159  0.906335
H  -1.141642  1.870205  -0.866873
H  -2.512663  1.162595  0.028636
F  1.178569  0.70652  -1.066404
F  1.308432  -1.175613  -0.031084
F  1.186092  0.656571  1.091964

G4(0 K)=                -565.819692 G4 Energy=                -565.812115
G4 Enthalpy=            -565.811171 G4 Free Energy=           -565.852082
```

TFDO Diradical

```
SCF Done:  E(UM062X) =  -565.975198585
S**2 before annihilation     0.9624,   after     0.0461
Sum of electronic and zero-point Energies=          -565.911384
Sum of electronic and thermal Energies=             -565.903754
Sum of electronic and thermal Enthalpies=           -565.902810
Sum of electronic and thermal Free Energies=        -565.943432

C  -0.78858  -0.231912  -0.000295
O  -1.161827  -0.820402  -1.153246
```

```
O  -1.161597  -0.824033  1.150801
C  0.7722  0.040726  -0.000018
C  -1.591845  1.121378  0.00179
H  -1.317067  1.669964  0.897373
H  -1.317162  1.672692  -0.892139
H  -2.649915  0.880431  0.001459
F  1.341008  -0.48453  -1.073563
F  1.042323  1.345123  0.002125
F  1.341211  -0.488232  1.071883
```

Rearrangement Product from TFDO Diradical G4 Calculation

```
C  0.470334  -0.407254  -0.000308
O  1.289384  0.641107  -0.000338
O  0.779458  -1.564552  -0.000109
C  -0.996052  0.089751  -0.00006
C  2.694094  0.325901  0.000172
H  2.951715  -0.250643  -0.89099
H  3.208672  1.285426  0.002059
H  2.950656  -0.253668  0.889657
F  -1.827004  -0.942233  -0.001384
F  -1.23506  0.833984  1.083919
F  -1.234829  0.8367  -1.082088

G4(0 K)=                -565.929175 G4 Energy=                -565.921131
G4 Enthalpy=            -565.920187 G4 Free Energy=           -565.963343
```

6.2.2 PCM Acetone

TFDO

```
SCF Done:  E(UM062X) =  -566.010029712
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.943816
Sum of electronic and thermal Energies=              -565.936428
Sum of electronic and thermal Enthalpies=            -565.935484
Sum of electronic and thermal Free Energies=         -565.976122

C  0.453441  0.599487  0.0
O  -0.109103  1.618511  0.732531
O  -0.109103  1.618511  -0.732531
C  1.933227  0.418468  0.0
```

```
C  -0.388094  -0.676508  0.0
H  2.401045  1.399039  0.0
H  2.2368  -0.1373  0.885664
H  2.2368  -0.1373  -0.885664
F  -0.109103  -1.407824  -1.077576
F  -1.684065  -0.414274  0.0
F  -0.109103  -1.407824  1.077576

G4(0 K)=                -565.819763 G4 Energy=                -565.812144
G4 Enthalpy=            -565.811200 G4 Free Energy=           -565.852340
```

TFDO Homolysis TS

```
SCF Done:  E(UM062X) =  -565.964838103
Frequencies --   -493.8761
S**2 before annihilation     0.8521,   after     0.0246
Sum of electronic and zero-point Energies=          -565.902076
Sum of electronic and thermal Energies=             -565.894533
Sum of electronic and thermal Enthalpies=           -565.893588
Sum of electronic and thermal Free Energies=        -565.934327

C  -0.783273  -0.04975  0.000477
O  -1.211608  -0.898179  1.006835
O  -1.214327  -0.89097  -1.009779
C  -1.448196  1.30505  0.002837
C  0.754309  0.032563  -0.000262
H  -1.147384  1.857936  0.891418
H  -1.148138  1.862933  -0.882775
H  -2.524132  1.156413  0.003077
F  1.185992  0.687555  -1.07637
F  1.303769  -1.1748  -0.006329
F  1.186916  0.677103  1.081978

G4(0 K)=                -565.819699 G4 Energy=                -565.812122
G4 Enthalpy=            -565.811177 G4 Free Energy=           -565.852089
```

TFDO Diradical

```
SCF Done:  E(UM062X) =  -565.979947964
S**2 before annihilation     0.9526,   after     0.0456
Sum of electronic and zero-point Energies=          -565.916599
Sum of electronic and thermal Energies=             -565.908910
```

```
Sum of electronic and thermal Enthalpies=           -565.907966
Sum of electronic and thermal Free Energies=        -565.948723

C  -0.78631  -0.238039  0.000121
O  -1.164729  -0.822651  -1.148059
O  -1.164469  -0.820859  1.149349
C  0.771795  0.04303  -0.000054
C  -1.597968  1.124323  -0.000755
H  -1.31713  1.66961  0.894698
H  -1.31847  1.667694  -0.897808
H  -2.654741  0.881474  0.000235
F  1.044639  1.344082  0.000567
F  1.344517  -0.486279  1.072582
F  1.344047  -0.485202  -1.073519

G4(0 K)=                -565.790788 G4 Energy=                -565.782710
G4 Enthalpy=            -565.781766 G4 Free Energy=           -565.823313
```

Rearrangement Product from TFDO Diradical G4 Calculation not Found

6.2.3 PCM Acetonitrile

TFDO

```
SCF Done:  E(UM062X) =  -566.010182580
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -565.943980
Sum of electronic and thermal Energies=             -565.936592
Sum of electronic and thermal Enthalpies=           -565.935648
Sum of electronic and thermal Free Energies=        -565.976288

C  0.453728  0.599458  0.0
O  -0.109282  1.618361  0.732541
O  -0.109282  1.618361  -0.732541
C  1.933432  0.4187  0.0
C  -0.387825  -0.676578  0.0
H  2.401232  1.399274  0.0
H  2.236981  -0.137048  0.885673
H  2.236981  -0.137048  -0.885673
```

```
F  -0.109282  -1.407925  -1.077557
F  -1.683957  -0.413977  0.0
F  -0.109282  -1.407925  1.077557

G4(0 K)=                -565.823958 G4 Energy=                -565.816316
G4 Enthalpy=            -565.815372 G4 Free Energy=           -565.856648
```

TFDO Homolysis TS

```
SCF Done:  E(UM062X) =  -565.964980070
Frequencies --   -489.8594
S**2 before annihilation     0.8520,   after     0.0246
Sum of electronic and zero-point Energies=          -565.902246
Sum of electronic and thermal Energies=             -565.894690
Sum of electronic and thermal Enthalpies=           -565.893746
Sum of electronic and thermal Free Energies=        -565.934528

C  -0.783387  -0.049556  0.000392
O  -1.211435  -0.897943  1.006945
O  -1.213859  -0.891655  -1.009515
C  -1.448685  1.304984  0.00248
C  0.754202  0.032917  -0.00024
H  -1.148032  1.858195  0.890904
H  -1.14874  1.862597  -0.883341
H  -2.524583  1.156108  0.002705
F  1.186203  0.687083  -1.076632
F  1.303601  -1.17474  -0.0057
F  1.186966  0.677637  1.08172

G4(0 K)=                -565.819699 G4 Energy=                -565.812122
G4 Enthalpy=            -565.811177 G4 Free Energy=           -565.852089
```

TFDO Diradical

```
SCF Done:  E(UM062X) =  -565.980118107
S**2 before annihilation     0.9521,   after     0.0456
Sum of electronic and zero-point Energies=          -565.916785
Sum of electronic and thermal Energies=             -565.909095
Sum of electronic and thermal Enthalpies=           -565.908151
Sum of electronic and thermal Free Energies=        -565.948903

C  -0.495062  -0.003082  -0.008377
```

```
O  -1.052138  -1.108505  0.004948
O  -1.04956  1.107414  -0.003789
C  1.052608  -0.002395  -0.005542
C  -3.046632  -0.004216  -0.013051
H  -3.261527  1.051543  -0.053831
H  -3.214729  -0.600903  -0.900709
H  -3.128811  -0.489589  0.952613
F  1.560519  -1.143962  -0.486872
F  1.536792  0.999083  -0.747107
F  1.497486  0.156637  1.251143
```

Rearrangement Product from TFDO Diradical G4 Calculation

```
C  0.47034  0.407368  0.000021
O  0.779374  1.564672  0.000018
O  1.289366  -0.641011  0.00002
C  -0.996006  -0.089782  -0.000001
C  2.694137  -0.325971  -0.000011
H  3.208657  -1.285529  -0.000179
H  2.9513  0.252114  -0.890294
H  2.951394  0.251881  0.890395
F  -1.827076  0.942143  0.000134
F  -1.23493  -0.83524  -1.083082
F  -1.234893  -0.835509  1.082917
```

```
G4(0 K)=                -565.929176 G4 Energy=                -565.921131
G4 Enthalpy=            -565.920187 G4 Free Energy=           -565.963350
```

6.3 Energies and Optimized Geometries for Oxyfunctionalization at UB3LYP/6-311G(d) Level

6.3.1 Gas Phase

TFDO

```
SCF Done:  E(UB3LYP) =  -565.978016481
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -565.912353
Sum of electronic and thermal Energies=             -565.904853
Sum of electronic and thermal Enthalpies=           -565.903909
Sum of electronic and thermal Free Energies=        -565.944728
```

```
O  -0.099528  -1.637848  0.754689
O  -0.099528  -1.637848  -0.754689
C  0.442023  -0.602818  0.0
C  1.933055  -0.413833  0.0
H  2.241587  0.147281  -0.887223
H  2.241587  0.147281  0.887223
H  2.412711  -1.394219  0.0
C  -0.398871  0.678896  0.0
F  -0.099528  1.415178  1.091194
F  -1.707686  0.428727  0.0
F  -0.099528  1.415178  -1.091194

G4(0 K)=                -565.819759 G4 Energy=                -565.812135
G4 Enthalpy=            -565.811190 G4 Free Energy=           -565.852368
```

Isobutane

```
SCF Done:  E(UB3LYP) =  -158.458807534
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -158.326495
Sum of electronic and thermal Energies=             -158.320790
Sum of electronic and thermal Enthalpies=           -158.319846
Sum of electronic and thermal Free Energies=        -158.353101

C  0.0  0.0  0.372386
H  0.0  0.0  1.472997
C  0.0  1.462262  -0.095783
H  0.0  1.521411  -1.192303
H  -0.886301  1.997679  0.265614
H  0.886301  1.997679  0.265614
C  -1.266356  -0.731131  -0.095783
H  -1.28689  -1.766399  0.265614
H  -2.173191  -0.23128  0.265614
H  -1.317581  -0.760706  -1.192303
C  1.266356  -0.731131  -0.095783
H  2.173191  -0.23128  0.265614
H  1.28689  -1.766399  0.265614
H  1.317581  -0.760706  -1.192303

G4(0 K)=                -158.297092 G4 Energy=                -158.291277
G4 Enthalpy=            -158.290333 G4 Free Energy=           -158.323785
```

TFDO-Isobutane Complex (optimized from IRC search)

```
SCF Done:  E(UB3LYP) =  -724.440156614
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -724.241190
Sum of electronic and thermal Energies=              -724.225841
Sum of electronic and thermal Enthalpies=            -724.224897
Sum of electronic and thermal Free Energies=         -724.287231

C  2.950179  0.224408  0.022988
H  2.382148  1.148541  -0.160773
O  -0.498189  1.340492  -0.516296
O  -1.78142  1.33102  -1.310336
C  -1.68148  0.795314  -0.030753
C  -2.38512  1.490351  1.100775
H  -3.439425  1.198788  1.124417
H  -1.928729  1.21225  2.055491
H  -2.304906  2.569015  0.955327
C  -1.698074  -0.736931  0.007303
C  2.64125  -0.745393  -1.126337
H  3.170046  -1.698094  -0.987926
H  1.568936  -0.96003  -1.186575
H  2.953876  -0.329234  -2.091685
C  2.489053  -0.349765  1.37047
H  2.672462  0.356347  2.189882
H  1.418733  -0.585  1.360127
H  3.028732  -1.276917  1.605673
C  4.441447  0.586564  0.059404
H  4.767068  1.032548  -0.888111
H  4.660437  1.303321  0.860355
H  5.056738  -0.306021  0.235198
F  -1.115209  -1.167545  1.148754
F  -1.057492  -1.280874  -1.028195
F  -2.973163  -1.176571  0.003726

G4(0 K)=                -724.119331 G4 Energy=                -724.103766
G4 Enthalpy=            -724.102822 G4 Free Energy=           -724.165719
```

TFDO-Isobutane TS1

```
SCF Done:  E(UB3LYP) =  -724.409773747
Frequencies --   -679.6713
```

```
S**2 before annihilation     0.4106,   after     0.0064
Sum of electronic and zero-point Energies=          -724.216908
Sum of electronic and thermal Energies=             -724.202467
Sum of electronic and thermal Enthalpies=           -724.201523
Sum of electronic and thermal Free Energies=        -724.258297

C  -2.250354  -0.094033  -0.02098
H  -1.141228  0.402914  0.250062
O  -0.115106  0.949623  0.816459
O  1.70354  1.490148  1.159326
C  1.106669  0.859695  0.114855
C  1.156304  1.601332  -1.213619
H  2.185689  1.63269  -1.583716
H  0.532219  1.117492  -1.971023
H  0.806282  2.621839  -1.043764
C  1.557344  -0.613456  -0.014128
C  -2.188652  -1.460999  0.638641
H  -3.144036  -1.98509  0.486
H  -1.393165  -2.076675  0.210545
H  -2.021046  -1.374809  1.716539
C  -2.312525  -0.122381  -1.538529
H  -2.248832  0.883842  -1.9663
H  -1.514742  -0.739483  -1.961487
H  -3.273554  -0.555244  -1.854687
C  -3.211871  0.881729  0.635199
H  -3.026699  0.961944  1.710746
H  -3.136204  1.880622  0.193964
H  -4.245105  0.529988  0.496404
F  0.790942  -1.273892  -0.932076
F  1.46015  -1.280342  1.139884
F  2.834626  -0.68238  -0.440941
```

TFDO-Isobutane Intermediate (end of IRC search; optimized to products)

```
Intermediate (Input)
C  -2.73037100   -0.22454200   -0.19100200
H  -0.85801600    0.62563100    0.30116600
O  -0.17403400    1.04546600    0.86776500
```

```
O   2.03371400    1.53322200    1.01864600
C   1.08838700    0.96468100    0.26005100
C   1.13126800    1.73517300   -1.10141100
H   2.11553500    1.65276800   -1.56385500
H   0.37359500    1.30286500   -1.76140800
H   0.89277100    2.78096400   -0.90232000
C   1.44885200   -0.53681600    0.01497400
C  -2.49932500   -1.52040700    0.52987000
H  -3.41120300   -2.14549700    0.52510400
H  -1.70504600   -2.11139300    0.06170500
H  -2.23314700   -1.35697700    1.58063500
C  -2.71167600   -0.23147600   -1.69113800
H  -2.64187100    0.78200000   -2.10534400
H  -1.87993600   -0.82850000   -2.08361800
H  -3.63785700   -0.67416000   -2.10225800
C  -3.50492900    0.85010500    0.51399500
H  -3.19390300    0.95449500    1.55987300
H  -3.39579700    1.82448200    0.02345400
H  -4.58628000    0.61946700    0.52481700
F   0.54429700   -1.10001000   -0.83318800
F   1.42346400   -1.23733400    1.15488000
F   2.66135700   -0.67012000   -0.54309200

Products
SCF Done:  E(UB3LYP) =  -724.545076783
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -724.345764
Sum of electronic and thermal Energies=              -724.330353
Sum of electronic and thermal Enthalpies=            -724.329409
Sum of electronic and thermal Free Energies=         -724.389504

C  2.950179  0.224408  0.022988
H  2.382148  1.148541  -0.160773
O  -0.498189  1.340492  -0.516296
O  -1.78142  1.33102  -1.310336
C  -1.68148  0.795314  -0.030753
C  -2.38512  1.490351  1.100775
H  -3.439425  1.198788  1.124417
H  -1.928729  1.21225  2.055491
H  -2.304906  2.569015  0.955327
C  -1.698074  -0.736931  0.007303
```

```
C  2.64125  -0.745393  -1.126337
H  3.170046  -1.698094  -0.987926
H  1.568936  -0.96003  -1.186575
H  2.953876  -0.329234  -2.091685
C  2.489053  -0.349765  1.37047
H  2.672462  0.356347  2.189882
H  1.418733  -0.585  1.360127
H  3.028732  -1.276917  1.605673
C  4.441447  0.586564  0.059404
H  4.767068  1.032548  -0.888111
H  4.660437  1.303321  0.860355
H  5.056738  -0.306021  0.235198
F  -1.115209  -1.167545  1.148754
F  -1.057492  -1.280874  -1.028195
F  -2.973163  -1.176571  0.003726
```

tert-Butanol

```
SCF Done:  E(UB3LYP) =  -233.670971084
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -233.534690
Sum of electronic and thermal Energies=              -233.528005
Sum of electronic and thermal Enthalpies=            -233.527061
Sum of electronic and thermal Free Energies=         -233.563636

C  0.48647  -0.707172  1.265665
H  0.095948  -1.729971  1.322503
H  0.16537  -0.162187  2.159499
H  1.582846  -0.770339  1.280564
C  -0.00063  0.014483  0.0
C  -1.525162  0.148661  0.0
H  -1.856679  0.699299  0.886472
H  -1.856679  0.699299  -0.886472
H  -2.005954  -0.835526  0.0
C  0.48647  -0.707172  -1.265665
H  0.16537  -0.162187  -2.159499
H  1.582846  -0.770339  -1.280564
H  0.095948  -1.729971  -1.322503
O  0.48647  1.367974  0.0
H  1.456339  1.32533  0.0
```

```
G4(0 K)=                -233.504424 G4 Energy=                -233.497536
G4 Enthalpy=            -233.496592 G4 Free Energy=           -233.533561
```

1,1,1-Trifluoroacetone

```
SCF Done:  E(UB3LYP) =  -490.863846686
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -490.802298
Sum of electronic and thermal Energies=              -490.795260
Sum of electronic and thermal Enthalpies=            -490.794315
Sum of electronic and thermal Free Energies=         -490.834510

O  -1.244532  1.465101  0.000001
C  -0.9009  0.307555  0.000005
C  -1.828903  -0.880763  0.000006
H  -1.639348  -1.504424  -0.881171
H  -1.639455  -1.504317  0.881287
H  -2.86406  -0.536294  -0.000069
C  0.611798  -0.038063  0.000008
F  0.913234  -0.777296  1.091286
F  1.374342  1.053618  0.000036
F  0.913218  -0.777228  -1.091341

G4(0 K)=                -490.722002 G4 Energy=                -490.714917
G4 Enthalpy=            -490.713973 G4 Free Energy=           -490.754160
```

6.3.2 PCM Acetone

TFDO

```
SCF Done:  E(UB3LYP) =  -565.981599527
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.916200
Sum of electronic and thermal Energies=              -565.908675
Sum of electronic and thermal Enthalpies=            -565.907731
Sum of electronic and thermal Free Energies=         -565.948678

C  0.449529  0.601342  0.0
O  -0.104033  1.633936  0.754656
O  -0.104033  1.633936  -0.754656
C  1.938573  0.418765  0.0
```

```
C  -0.393287  -0.679928  0.0
H  2.416747  1.399677  0.0
H  2.247455  -0.140861  0.887552
H  2.247455  -0.140861  -0.887552
F  -0.104033  -1.417414  -1.09085
F  -1.704827  -0.420948  0.0
F  -0.104033  -1.417414  1.09085

G4(0 K)=                -565.823798 G4 Energy=                -565.816151
G4 Enthalpy=            -565.815207 G4 Free Energy=           -565.856525
```

Isobutane

```
SCF Done:  E(UB3LYP) =  -158.459053982
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -158.327040
Sum of electronic and thermal Energies=             -158.321332
Sum of electronic and thermal Enthalpies=           -158.320387
Sum of electronic and thermal Free Energies=        -158.353646

C  0.0  0.0  0.372484
H  0.0  0.0  1.473023
C  0.0  1.462264  -0.095884
H  0.0  1.520434  -1.192589
H  -0.886642  1.997052  0.265958
H  0.886642  1.997052  0.265958
C  -1.266358  -0.731132  -0.095884
H  -1.286177  -1.766381  0.265958
H  -2.172819  -0.230671  0.265958
H  -1.316735  -0.760217  -1.192589
C  1.266358  -0.731132  -0.095884
H  2.172819  -0.230671  0.265958
H  1.286177  -1.766381  0.265958
H  1.316735  -0.760217  -1.192589

G4(0 K)=                -158.297712 G4 Energy=                -158.291892
G4 Enthalpy=            -158.290948 G4 Free Energy=           -158.324406
```

TFDO-Isobutane Complex (optimized from IRC search)

```
SCF Done:  E(UB3LYP) =  -724.443884035
S**2 before annihilation     0.0000,   after     0.0000
```

```
Sum of electronic and zero-point Energies=          -724.245369
Sum of electronic and thermal Energies=             -724.230066
Sum of electronic and thermal Enthalpies=           -724.229122
Sum of electronic and thermal Free Energies=        -724.290895

C  2.949423  0.224666  0.021183
H  2.361203  1.135132  -0.167972
O  -0.528013  1.350827  -0.536029
O  -1.823115  1.320056  -1.309823
C  -1.699202  0.795636  -0.024644
C  -2.393267  1.484049  1.113363
H  -3.441115  1.173497  1.156866
H  -1.913841  1.219176  2.060169
H  -2.336307  2.563345  0.96285
C  -1.691013  -0.737665  0.0123
C  2.524013  -0.331894  1.38765
H  3.083221  -1.246328  1.627558
H  2.712631  0.392594  2.18945
H  1.456915  -0.580991  1.402077
C  4.434288  0.614099  0.020539
H  4.733032  1.045833  -0.942483
H  4.654372  1.351242  0.802411
H  5.068156  -0.264154  0.202883
C  2.636582  -0.772569  -1.103662
H  1.567359  -1.008979  -1.137093
H  2.923127  -0.369619  -2.082904
H  3.185897  -1.712308  -0.956822
F  -1.085334  -1.166207  1.140628
F  -1.050044  -1.26685  -1.036519
F  -2.954685  -1.202881  0.016942

G4(0 K)=                -724.123614 G4 Energy=                -724.108035
G4 Enthalpy=            -724.107090 G4 Free Energy=           -724.169936
```

TFDO-Isobutane TS1

```
CF Done:  E(UB3LYP) =  -724.417352481
Frequencies --   -702.7386
S**2 before annihilation     0.2195,   after     0.0016
Sum of electronic and zero-point Energies=          -724.224068
Sum of electronic and thermal Energies=             -724.209675
```

```
Sum of electronic and thermal Enthalpies=           -724.208731
Sum of electronic and thermal Free Energies=        -724.265406

C  -2.270482  -0.101332  -0.020518
H  -1.183293  0.39144  0.253637
O  -0.104071  0.926843  0.833334
O  1.646122  1.490918  1.177542
C  1.106509  0.859923  0.105616
C  1.133789  1.608744  -1.214471
H  2.162056  1.671522  -1.583234
H  0.52439  1.110204  -1.973505
H  0.752163  2.617843  -1.0446
C  1.588078  -0.602259  -0.021683
C  -2.315952  -0.124033  -1.539446
H  -3.274121  -0.558745  -1.859634
H  -2.251494  0.883311  -1.963149
H  -1.515219  -0.740443  -1.958111
C  -3.251318  0.863152  0.625043
H  -3.094748  0.931705  1.706096
H  -3.175687  1.865417  0.191874
H  -4.275984  0.501136  0.457128
C  -2.215973  -1.473555  0.630419
H  -1.410067  -2.083811  0.213331
H  -2.078765  -1.397506  1.713482
H  -3.16548  -1.996975  0.447598
F  0.833472  -1.288618  -0.920386
F  1.523044  -1.259923  1.14445
F  2.865921  -0.642684  -0.454916

G4(0 K)=                -724.107626 G4 Energy=                -724.093075
G4 Enthalpy=            -724.092131 G4 Free Energy=           -724.149085
```

tert-Butanol

```
SCF Done:  E(UB3LYP) =  -233.675286508
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -233.539188
Sum of electronic and thermal Energies=             -233.532510
Sum of electronic and thermal Enthalpies=           -233.531566
Sum of electronic and thermal Free Energies=        -233.568125
```

```
C  0.487554  -0.705718  1.265121
H  0.101802  -1.730383  1.315751
H  0.158739  -0.167411  2.160747
H  1.583653  -0.760238  1.281519
C  -0.001654  0.013992  0.0
C  -1.526544  0.143655  0.0
H  -1.863464  0.689876  0.887898
H  -1.863464  0.689876  -0.887898
H  -2.001347  -0.843068  0.0
C  0.487554  -0.705718  -1.265121
H  0.158739  -0.167411  -2.160747
H  1.583653  -0.760238  -1.281519
H  0.101802  -1.730383  -1.315751
O  0.487554  1.37205  0.0
H  1.45799  1.325715  0.0

G4(0 K)=                -233.509245 G4 Energy=                -233.502369
G4 Enthalpy=            -233.501425 G4 Free Energy=           -233.538367
```

1,1,1-Trifluoroacetone

```
SCF Done:  E(UB3LYP) =  -490.868313968
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -490.807102
Sum of electronic and thermal Energies=              -490.799997
Sum of electronic and thermal Enthalpies=            -490.799053
Sum of electronic and thermal Free Energies=         -490.839982

O  -1.236869  1.465615  -0.003276
C  -0.905199  0.301665  -0.004193
C  -1.835804  -0.877826  -0.001031
H  -1.695208  -1.462634  -0.917548
H  -1.603042  -1.53926  0.841006
H  -2.86864  -0.533477  0.065195
C  0.608784  -0.043421  -0.001961
F  0.930553  -0.692283  1.13822
F  1.367547  1.05276  -0.092762
F  0.908028  -0.857372  -1.036495

G4(0 K)=                -490.726969 G4 Energy=                -490.719835
G4 Enthalpy=            -490.718891 G4 Free Energy=           -490.759570
```

6.3.3 PCM Acetonitrile

TFDO

```
SCF Done:  E(UB3LYP) =  -565.981733566
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.916346
Sum of electronic and thermal Energies=              -565.908819
Sum of electronic and thermal Enthalpies=            -565.907875
Sum of electronic and thermal Free Energies=         -565.948829

C  0.449811  0.601286  0.0
O  -0.104212  1.633776  0.754662
O  -0.104212  1.633776  -0.754662
C  1.93878  0.419015  0.0
C  -0.393033  -0.680004  0.0
H  2.416861  1.399968  0.0
H  2.247677  -0.140553  0.887565
H  2.247677  -0.140553  -0.887565
F  -0.104212  -1.41753  -1.090824
F  -1.704706  -0.420612  0.0
F  -0.104212  -1.41753  1.090824

G4(0 K)=                 -565.823954 G4 Energy=                  -565.816306
G4 Enthalpy=             -565.815362 G4 Free Energy=             -565.856686
```

Isobutane

```
SCF Done:  E(UB3LYP) =  -158.459063973
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -158.327061
Sum of electronic and thermal Energies=              -158.321353
Sum of electronic and thermal Enthalpies=            -158.320409
Sum of electronic and thermal Free Energies=         -158.353666

C  0.0  0.0  0.372508
H  0.0  0.0  1.473041
C  0.0  1.46226  -0.095892
H  0.0  1.520358  -1.192605
H  -0.886655  1.997026  0.265964
H  0.886655  1.997026  0.265964
C  -1.266355  -0.73113  -0.095892
```

```
H  -1.286148  -1.766378  0.265964
H  -2.172802  -0.230647  0.265964
H  -1.316669  -0.760179  -1.192605
C  1.266355  -0.73113  -0.095892
H  2.172802  -0.230647  0.265964
H  1.286148  -1.766378  0.265964
H  1.316669  -0.760179  -1.192605

G4(0 K)=                -158.297737 G4 Energy=                -158.291917
G4 Enthalpy=            -158.290973 G4 Free Energy=           -158.324430
```

TFDO-Isobutane Complex (optimized from IRC search)

```
SCF Done:  E(UB3LYP) =  -724.444032133
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -724.245559
Sum of electronic and thermal Energies=              -724.230242
Sum of electronic and thermal Enthalpies=            -724.229298
Sum of electronic and thermal Free Energies=         -724.291182

C  2.951049  0.225436  0.019854
H  2.36279  1.134903  -0.174059
O  -0.532238  1.351824  -0.539363
O  -1.827817  1.316541  -1.312214
C  -1.701924  0.795122  -0.025881
C  -2.396705  1.484209  1.11113
H  -3.44388  1.171605  1.155726
H  -1.916158  1.222041  2.058106
H  -2.342018  2.56334  0.958619
C  -1.690139  -0.738129  0.013787
C  4.435895  0.614925  0.017155
H  5.069789  -0.262297  0.204303
H  4.73466  1.041437  -0.948197
H  4.655842  1.356336  0.795015
C  2.638354  -0.777795  -1.09971
H  1.569192  -1.014788  -1.131625
H  2.924686  -0.379987  -2.081132
H  3.187966  -1.716574  -0.947937
C  2.525563  -0.323866  1.389217
H  2.714537  0.404768  2.187151
H  1.45835  -0.57233  1.405032
```

```
H  3.084534  -1.23723  1.633742
F  -1.082726  -1.163535  1.142263
F  -1.048347  -1.267439  -1.03475
F  -2.952529  -1.206531  0.01966

G4(0 K)=                -724.123803 G4 Energy=                -724.108219
G4 Enthalpy=            -724.107275 G4 Free Energy=           -724.170167
```

TFDO-Isobutane TS1

```
SCF Done:  E(UB3LYP) =  -724.417642437
Frequencies --   -706.6959
S**2 before annihilation     0.2123,   after     0.0015
Sum of electronic and zero-point Energies=          -724.224355
Sum of electronic and thermal Energies=             -724.209960
Sum of electronic and thermal Enthalpies=           -724.209016
Sum of electronic and thermal Free Energies=        -724.265712

C  -2.271188  -0.101613  -0.020625
H  -1.184597  0.391132  0.253036
O  -0.103698  0.926228  0.833568
O  1.644038  1.49101  1.17799
C  1.10658  0.859917  0.105069
C  1.133245  1.608905  -1.214731
H  2.161725  1.674178  -1.582448
H  0.52581  1.108948  -1.974376
H  0.748863  2.617035  -1.045318
C  1.589147  -0.601932  -0.021964
C  -3.252086  0.863158  0.624496
H  -4.276555  0.499943  0.458206
H  -3.094544  0.93338  1.70533
H  -3.177702  1.864761  0.1896
C  -2.217038  -1.473608  0.630882
H  -1.411907  -2.084616  0.213359
H  -2.079174  -1.397252  1.71387
H  -3.167044  -1.996337  0.448894
C  -2.316683  -0.125008  -1.539538
H  -2.252799  0.88214  -1.963709
H  -1.515748  -0.741298  -1.957994
H  -3.274704  -0.560425  -1.859169
F  0.834397  -1.289493  -0.919188
```

```
F  1.525975  -1.258841  1.144941
F  2.866716  -0.641489  -0.456117

G4(0 K)=                -724.107853 G4 Energy=                -724.093298
G4 Enthalpy=            -724.092354 G4 Free Energy=           -724.149338
```

tert-Butanol

```
SCF Done:  E(UB3LYP) =  -233.675455445
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -233.539369
Sum of electronic and thermal Energies=              -233.532691
Sum of electronic and thermal Enthalpies=            -233.531747
Sum of electronic and thermal Free Energies=         -233.568306

C  0.487581  -0.705679  1.265131
H  0.101842  -1.730347  1.31556
H  0.158489  -0.167537  2.160784
H  1.583659  -0.760028  1.281674
C  -0.001638  0.013957  0.0
C  -1.526551  0.143475  0.0
H  -1.863679  0.689535  0.887959
H  -1.863679  0.689535  -0.887959
H  -2.001149  -0.843325  0.0
C  0.487581  -0.705679  -1.265131
H  0.158489  -0.167537  -2.160784
H  1.583659  -0.760028  -1.281674
H  0.101842  -1.730347  -1.31556
O  0.487581  1.372221  0.0
H  1.458038  1.325867  0.0

G4(0 K)=                -233.509445 G4 Energy=                -233.502568
G4 Enthalpy=            -233.501624 G4 Free Energy=           -233.538568
```

1,1,1-Trifluoroacetone

```
SCF Done:  E(UB3LYP) =  -490.868313968
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -490.807102
Sum of electronic and thermal Energies=              -490.799997
Sum of electronic and thermal Enthalpies=            -490.799053
Sum of electronic and thermal Free Energies=         -490.839982
```

```
O  -1.236681  1.465611  -0.003305
C  -0.905348  0.301458  -0.004213
C  -1.836022  -0.877744  -0.001024
H  -1.696085  -1.461979  -0.918012
H  -1.602685  -1.53971  0.840417
H  -2.86879  -0.533386  0.066105
C  0.60868  -0.043621  -0.001979
F  0.930765  -0.691887  1.138377
F  1.367355  1.052828  -0.093114
F  0.90823  -0.857649  -1.036237

G4(0 K)=                -490.727146 G4 Energy=                -490.720015
G4 Enthalpy=            -490.719070 G4 Free Energy=           -490.759706
```

6.4 Energies and Optimized Geometries for Oxyfunctionalization at UM062X/6-311+G(3df,2p) Level

6.4.1 Gas Phase

TFDO

```
SCF Done:  E(UM062X) =  -566.005952310
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -565.939489
Sum of electronic and thermal Energies=             -565.932104
Sum of electronic and thermal Enthalpies=           -565.931160
Sum of electronic and thermal Free Energies=        -565.971758

C  -0.78001  -0.055329  0.003646
O  -1.212611  -0.91026  1.002003
O  -1.228475  -0.868035  -1.018676
C  -1.435958  1.306494  0.017016
C  0.757231  0.024612  -0.001496
H  -1.122431  1.85159  0.906335
H  -1.141642  1.870205  -0.866873
H  -2.512663  1.162595  0.028636
F  1.178569  0.70652  -1.066404
F  1.308432  -1.175613  -0.031084
F  1.186092  0.656571  1.091964
```

```
G4(0 K)=                -565.819763 G4 Energy=                -565.812144
G4 Enthalpy=            -565.811200 G4 Free Energy=           -565.852340
```

Isobutane

```
CF Done:  E(UM062X) =  -158.415865949
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -158.284339
Sum of electronic and thermal Energies=              -158.278565
Sum of electronic and thermal Enthalpies=            -158.277621
Sum of electronic and thermal Free Energies=         -158.311028

C  0.0  0.0  0.380811
H  0.0  0.0  1.475437
C  0.0  1.449261  -0.096323
H  0.0  1.486878  -1.188678
H  -0.88342  1.983329  0.256592
H  0.88342  1.983329  0.256592
C  -1.255097  -0.72463  -0.096323
H  -1.275903  -1.756728  0.256592
H  -2.159323  -0.2266  0.256592
H  -1.287674  -0.743439  -1.188678
C  1.255097  -0.72463  -0.096323
H  2.159323  -0.2266  0.256592
H  1.275903  -1.756728  0.256592
H  1.287674  -0.743439  -1.188678

G4(0 K)=                -158.297091 G4 Energy=                -158.291276
G4 Enthalpy=            -158.290332 G4 Free Energy=           -158.323783
```

TFDO-Isobutane Complex (optimized from IRC search)

```
SCF Done:  E(UM062X) =  -724.425562934
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -724.226396
Sum of electronic and thermal Energies=              -724.212209
Sum of electronic and thermal Enthalpies=            -724.211265
Sum of electronic and thermal Free Energies=         -724.269438

C  2.463642  0.002281  -0.076558
H  1.494923  0.481128  -0.255945
O  -0.757426  1.312399  -1.060429
```

```
O  -2.135795  1.608686  -0.661102
C  -1.31151  0.80847  0.090406
C  -0.825658  1.295571  1.416227
H  -1.601243  1.154514  2.167794
H  0.060248  0.73665  1.715315
H  -0.585731  2.351575  1.324621
C  -1.652341  -0.67762  0.005788
C  2.541801  -0.403873  1.392086
H  3.495777  -0.896635  1.595306
H  2.473755  0.464111  2.051598
H  1.74528  -1.102792  1.654611
C  3.554892  1.012917  -0.416065
H  3.492339  1.326338  -1.458808
H  3.483885  1.903152  0.210788
H  4.541008  0.569023  -0.257622
C  2.561796  -1.223029  -0.97979
H  1.777098  -1.945879  -0.755542
H  2.478847  -0.945129  -2.031187
H  3.526536  -1.716824  -0.837984
F  -0.571941  -1.403379  0.301337
F  -2.07685  -1.025721  -1.191442
F  -2.599287  -0.974922  0.89641
```

TFDO-Isobutane TS1

```
SCF Done:  E(UM062X) =  -724.383158224
Frequencies --  -1025.3457
S**2 before annihilation     0.3800,   after     0.0076
Sum of electronic and zero-point Energies=          -724.189353
Sum of electronic and thermal Energies=             -724.175149
Sum of electronic and thermal Enthalpies=           -724.174205
Sum of electronic and thermal Free Energies=        -724.230255

C  -2.196352  -0.101439  -0.012717
H  -1.129727  0.372547  0.278037
O  -0.07705  0.940911  0.862875
O  1.640766  1.510153  1.134087
C  1.082515  0.855719  0.097958
C  1.054977  1.561348  -1.235437
H  2.065763  1.630136  -1.635122
```

```
H  0.430981  1.022679  -1.947477
H  0.658791  2.560894  -1.074036
C  1.555864  -0.602284  -0.014007
C  -2.251714  -0.104259  -1.52369
H  -3.219994  -0.502861  -1.843602
H  -2.158438  0.903714  -1.929067
H  -1.473364  -0.735722  -1.950919
C  -3.178374  0.848744  0.635605
H  -3.017769  0.905171  1.711647
H  -3.095494  1.851517  0.2175
H  -4.19764  0.489851  0.461766
C  -2.178404  -1.4788  0.610327
H  -1.411497  -2.110059  0.164384
H  -2.003737  -1.420133  1.684155
H  -3.149788  -1.957996  0.450235
F  0.768339  -1.281215  -0.865738
F  1.528843  -1.232007  1.146201
F  2.798496  -0.652602  -0.492846

G4(0 K)=                -724.105304 G4 Energy=                -724.090612
G4 Enthalpy=            -724.089668 G4 Free Energy=           -724.146750
```

TFDO-Isobutane Intermediate

```
SCF Done:  E(UM062X) =  -724.421598655
S**2 before annihilation     1.0090,   after     0.0728
Sum of electronic and zero-point Energies=           -724.225520
Sum of electronic and thermal Energies=              -724.209843
Sum of electronic and thermal Enthalpies=            -724.208899
Sum of electronic and thermal Free Energies=         -724.269832

C  2.4995  -0.114763  0.009359
H  0.571359  0.519029  -0.871896
O  -0.260519  0.898869  -1.189103
O  -2.294743  1.559041  -0.456647
C  -1.201002  0.842811  -0.164488
C  -0.654305  1.415861  1.162249
H  -1.403338  1.357174  1.945886
H  0.225359  0.832682  1.436027
H  -0.368449  2.448922  0.982293
C  -1.618337  -0.636166  0.043117
```

```
C  2.555393  -0.844731  1.309338
H  3.582843  -1.171871  1.524689
H  2.247644  -0.213318  2.145064
H  1.930832  -1.738724  1.297931
C  2.983317  1.298346  -0.020009
H  2.669458  1.819037  -0.926549
H  2.629371  1.863041  0.844652
H  4.082051  1.334967  0.005254
C  2.609207  -0.92401  -1.241839
H  1.970021  -1.807645  -1.205281
H  2.350439  -0.34416  -2.129993
H  3.640282  -1.278614  -1.383469
F  -0.532423  -1.385462  0.269558
F  -2.228619  -1.117018  -1.029802
F  -2.431003  -0.776174  1.084137
```

tert-Butanol

```
SCF Done:  E(UM062X) =  -233.645800708
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -233.509547
Sum of electronic and thermal Energies=              -233.502925
Sum of electronic and thermal Enthalpies=            -233.501981
Sum of electronic and thermal Free Energies=         -233.538438

C  0.483612  -0.701684  1.255308
H  0.087091  -1.716672  1.302301
H  0.162443  -0.15746  2.143339
H  1.574343  -0.765373  1.264455
C  0.000029  0.017881  0.0
C  -1.515565  0.141013  0.0
H  -1.844692  0.686543  0.884247
H  -1.844692  0.686543  -0.884247
H  -1.981229  -0.844599  0.0
C  0.483612  -0.701684  -1.255308
H  0.162443  -0.15746  -2.143339
H  1.574343  -0.765373  -1.264455
H  0.087091  -1.716672  -1.302301
O  0.483612  1.359461  0.0
H  1.443827  1.341683  0.0
```

```
G4(0 K)=                -233.504408 G4 Energy=                -233.497530
G4 Enthalpy=            -233.496586 G4 Free Energy=           -233.533534
```

1,1,1-Trifluoroacetone

```
SCF Done:  E(UM062X) =  -490.886757799
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -490.824842
Sum of electronic and thermal Energies=             -490.817847
Sum of electronic and thermal Enthalpies=           -490.816903
Sum of electronic and thermal Free Energies=        -490.857239

O  -1.23769  1.452405  0.003774
C  -0.901514  0.308624  0.003905
C  -1.817049  -0.878662  0.000631
H  -1.543531  -1.560062  -0.805394
H  -1.702294  -1.42202  0.939606
H  -2.84242  -0.542082  -0.113629
C  0.609112  -0.036509  0.002484
F  0.88998  -0.87862  1.000971
F  1.365423  1.032944  0.130465
F  0.927538  -0.649412  -1.141759

G4(0 K)=                -490.721999 G4 Energy=                -490.714917
G4 Enthalpy=            -490.713973 G4 Free Energy=           -490.754138
```

6.4.2 PCM Acetone

TFDO

```
SCF Done:  E(UM062X) =  -566.010029712
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -565.943816
Sum of electronic and thermal Energies=             -565.936428
Sum of electronic and thermal Enthalpies=           -565.935484
Sum of electronic and thermal Free Energies=        -565.976122

C  0.453441  0.599487  0.0
O  -0.109103  1.618511  0.732531
O  -0.109103  1.618511  -0.732531
C  1.933227  0.418468  0.0
C  -0.388094  -0.676508  0.0
```

```
H  2.401045  1.399039  0.0
H  2.2368  -0.1373  0.885664
H  2.2368  -0.1373  -0.885664
F  -0.109103  -1.407824  -1.077576
F  -1.684065  -0.414274  0.0
F  -0.109103  -1.407824  1.077576

G4(0 K)=                -565.819763 G4 Energy=                -565.812144
G4 Enthalpy=            -565.811200 G4 Free Energy=           -565.852340
```

Isobutane

```
SCF Done:  E(UM062X) =  -158.416235130
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -158.285010
Sum of electronic and thermal Energies=             -158.279271
Sum of electronic and thermal Enthalpies=           -158.278327
Sum of electronic and thermal Free Energies=        -158.312678

C  -0.000211  0.0  0.381261
H  -0.000051  0.0  1.475816
C  -1.449477  0.000099  -0.096445
H  -1.485526  0.000102  -1.189128
H  -1.983201  -0.883775  0.256565
H  -1.98308  0.884046  0.256566
C  0.724668  -1.254842  -0.096448
H  1.756005  -1.276006  0.259236
H  0.224671  -2.159097  0.254162
H  0.745469  -1.284276  -1.189064
C  0.72484  1.254743  -0.096448
H  0.224968  2.159067  0.254164
H  1.756181  1.275764  0.259234
H  0.745643  1.284175  -1.189064

G4(0 K)=                -158.297650 G4 Energy=                -158.291848
G4 Enthalpy=            -158.290904 G4 Free Energy=           -158.325356
```

TFDO-Isobutane Complex (optimized from IRC search)

```
SCF Done:  E(UM062X) =  -724.429369327
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -724.230713
```

```
Sum of electronic and thermal Energies=             -724.216516
Sum of electronic and thermal Enthalpies=           -724.215572
Sum of electronic and thermal Free Energies=        -724.273497

C  2.475991  0.000191  -0.075414
H  1.511693  0.488826  -0.251933
O  -0.748548  1.294058  -1.064297
O  -2.123861  1.613387  -0.67153
C  -1.311719  0.812641  0.095834
C  -0.823605  1.303612  1.416597
H  -1.604338  1.180781  2.165599
H  0.050928  0.731669  1.724174
H  -0.564032  2.354416  1.320709
C  -1.665862  -0.671497  0.013474
C  3.576181  1.004389  -0.405759
H  4.557895  0.551136  -0.24545
H  3.519892  1.323372  -1.447553
H  3.507967  1.890877  0.226668
C  2.567149  -1.219429  -0.987364
H  1.775888  -1.937534  -0.769682
H  2.490584  -0.933301  -2.037411
H  3.527649  -1.721428  -0.844683
C  2.547238  -0.415987  1.39066
H  2.477998  0.448482  2.05401
H  1.745528  -1.111778  1.645768
H  3.49872  -0.914522  1.592539
F  -0.586046  -1.406905  0.277612
F  -2.115449  -1.007897  -1.183294
F  -2.599542  -0.973428  0.912981

G4(0 K)=                -724.123615 G4 Energy=                -724.108035
G4 Enthalpy=            -724.107091 G4 Free Energy=           -724.169931
```

TFDO-Isobutane TS1

```
SCF Done:  E(UM062X) =  -724.390484828
Frequencies --  -1250.8327
S**2 before annihilation     0.2479,   after     0.0029
Sum of electronic and zero-point Energies=          -724.197070
Sum of electronic and thermal Energies=             -724.182815
Sum of electronic and thermal Enthalpies=           -724.181871
```

```
Sum of electronic and thermal Free Energies=         -724.238322

C  -2.206533  -0.108301  -0.012922
H  -1.149708  0.372454  0.290265
O  -0.075088  0.922868  0.877047
O  1.600428  1.500825  1.153497
C  1.075821  0.857477  0.093742
C  1.034274  1.574601  -1.228842
H  2.043548  1.664664  -1.628012
H  0.420361  1.030933  -1.945363
H  0.618051  2.565364  -1.063933
C  1.570413  -0.59277  -0.023588
C  -3.204857  0.823505  0.636329
H  -4.215356  0.452876  0.438978
H  -3.064706  0.86246  1.716122
H  -3.128457  1.831854  0.230939
C  -2.179467  -1.493349  0.591788
H  -1.398196  -2.109063  0.148558
H  -2.030197  -1.449443  1.670247
H  -3.141913  -1.979346  0.40355
C  -2.242384  -0.089881  -1.523857
H  -2.154205  0.923973  -1.914198
H  -1.456669  -0.71116  -1.95241
H  -3.205049  -0.492878  -1.854238
F  0.808426  -1.284435  -0.879374
F  1.54447  -1.225009  1.140987
F  2.822234  -0.621658  -0.481697

G4(0 K)=                -724.107626 G4 Energy=                -724.093075
G4 Enthalpy=            -724.092130 G4 Free Energy=           -724.149086
```

tert-Butanol

```
SCF Done:  E(UM062X) =  -233.650538912
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -233.514549
Sum of electronic and thermal Energies=             -233.507930
Sum of electronic and thermal Enthalpies=           -233.506986
Sum of electronic and thermal Free Energies=        -233.543438

C  0.484981  -0.699616  1.254674
```

```
H  0.097903  -1.718383  1.292838
H  0.152095  -0.165574  2.145082
H  1.575863  -0.749866  1.266633
C  -0.001914  0.017307  0.0
C  -1.517535  0.135505  0.0
H  -1.852586  0.675622  0.88601
H  -1.852586  0.675622  -0.88601
H  -1.975887  -0.853318  0.0
C  0.484981  -0.699616  -1.254674
H  0.152095  -0.165574  -2.145082
H  1.575863  -0.749866  -1.266633
H  0.097903  -1.718383  -1.292838
O  0.484981  1.363605  0.0
H  1.44642  1.339406  0.0

G4(0 K)=                -233.509228 G4 Energy=                -233.502362
G4 Enthalpy=            -233.501417 G4 Free Energy=           -233.538337
```

1,1,1-Trifluoroacetone

```
SCF Done:  E(UM062X) =  -490.891977186
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -490.830254
Sum of electronic and thermal Energies=              -490.823313
Sum of electronic and thermal Enthalpies=            -490.822368
Sum of electronic and thermal Free Energies=         -490.862228

O  -1.229827  1.453414  -0.005315
C  -0.906856  0.302496  -0.005769
C  -1.823595  -0.876035  -0.000942
H  -1.726877  -1.402492  -0.951928
H  -1.534955  -1.571639  0.787452
H  -2.846766  -0.542784  0.137816
C  0.605517  -0.042161  -0.003401
F  0.935503  -0.619641  1.154358
F  1.358677  1.032119  -0.159871
F  0.894355  -0.903167  -0.98006

G4(0 K)=                -490.726969 G4 Energy=                -490.719835
G4 Enthalpy=            -490.718891 G4 Free Energy=           -490.759566
```

6.4.3 PCM Acetonitrile

TFDO

```
SCF Done:  E(UM062X) =  -566.010182580
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -565.943980
Sum of electronic and thermal Energies=              -565.936592
Sum of electronic and thermal Enthalpies=            -565.935648
Sum of electronic and thermal Free Energies=         -565.976288

C  0.453728  0.599458  0.0
O  -0.109282  1.618361  0.732541
O  -0.109282  1.618361  -0.732541
C  1.933432  0.4187  0.0
C  -0.387825  -0.676578  0.0
H  2.401232  1.399274  0.0
H  2.236981  -0.137048  0.885673
H  2.236981  -0.137048  -0.885673
F  -0.109282  -1.407925  -1.077557
F  -1.683957  -0.413977  0.0
F  -0.109282  -1.407925  1.077557

G4(0 K)=                 -565.823958 G4 Energy=                  -565.816316
G4 Enthalpy=             -565.815372 G4 Free Energy=             -565.856648
```

Isobutane

```
SCF Done:  E(UM062X) =  -158.416249631
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -158.285038
Sum of electronic and thermal Energies=              -158.279299
Sum of electronic and thermal Enthalpies=            -158.278354
Sum of electronic and thermal Free Energies=         -158.312706

C  -0.000209  0.0  0.381267
H  -0.000048  0.0  1.475819
C  -1.449477  0.000097  -0.096451
H  -1.485469  0.0001  -1.189145
H  -1.983171  -0.883793  0.256586
H  -1.983053  0.884058  0.256587
C  0.724669  -1.254844  -0.096455
```

```
H  1.756006  -1.27598  0.259255
H  0.224643  -2.15908  0.254184
H  0.745442  -1.284234  -1.189081
C  0.724837  1.254747  -0.096455
H  0.224934  2.15905  0.254186
H  1.756177  1.275744  0.259253
H  0.745612  1.284135  -1.189081

G4(0 K)=                -158.297681 G4 Energy=                -158.291877
G4 Enthalpy=            -158.290933 G4 Free Energy=           -158.325391
```

TFDO-Isobutane Complex (optimized from IRC search)

```
SCF Done:  E(UM062X) =  -724.429524465
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=           -724.230834
Sum of electronic and thermal Energies=              -724.215736
Sum of electronic and thermal Enthalpies=            -724.214792
Sum of electronic and thermal Free Energies=         -724.276110

C  2.476518  0.000201  -0.075257
H  1.513144  0.49092  -0.250995
O  -0.747671  1.293172  -1.064418
O  -2.122539  1.614291  -0.671506
C  -1.311264  0.812916  0.096198
C  -0.822544  1.303669  1.416713
H  -1.603818  1.182766  2.165455
H  0.050698  0.730136  1.724959
H  -0.560777  2.353889  1.320418
C  -1.666797  -0.670947  0.013877
C  3.578426  1.003405  -0.4031
H  4.559376  0.548426  -0.243004
H  3.523242  1.324399  -1.444356
H  3.510969  1.888777  0.230964
C  2.566059  -1.217537  -0.989891
H  1.773947  -1.935152  -0.77362
H  2.489773  -0.929041  -2.039329
H  3.52596  -1.721006  -0.848329
C  2.5468  -0.419219  1.389901
H  2.478287  0.443911  2.055043
H  1.744162  -1.114533  1.643356
```

```
H  3.497682  -0.919288  1.590859
F  -0.587049  -1.407312  0.275306
F  -2.118718  -1.006282  -1.182576
F  -2.59914  -0.972944  0.914529

G4(0 K)=                -724.123680 G4 Energy=                -724.108124
G4 Enthalpy=            -724.107179 G4 Free Energy=           -724.169919
```

TFDO-Isobutane TS1

```
SCF Done:  E(UM062X) =  -724.390775366
Frequencies --  -1262.4859
S**2 before annihilation     0.2432,   after     0.0028
Sum of electronic and zero-point Energies=          -724.197382
Sum of electronic and thermal Energies=             -724.183123
Sum of electronic and thermal Enthalpies=           -724.182179
Sum of electronic and thermal Free Energies=        -724.238657

C  -2.20685  -0.108555  -0.012946
H  -1.150295  0.37218  0.290535
O  -0.075044  0.922415  0.877575
O  1.599009  1.500396  1.154171
C  1.07548  0.857475  0.093552
C  1.033592  1.575076  -1.228581
H  2.042925  1.666315  -1.627328
H  0.420578  1.030979  -1.945531
H  0.616092  2.565302  -1.06366
C  1.570858  -0.592501  -0.024005
C  -3.205556  0.822393  0.636897
H  -4.215815  0.451644  0.438637
H  -3.066026  0.860113  1.716829
H  -3.129226  1.83112  0.232443
C  -2.179438  -1.494149  0.590551
H  -1.39739  -2.108979  0.147438
H  -2.031545  -1.451273  1.669262
H  -3.141371  -1.980498  0.400701
C  -2.242243  -0.088739  -1.523849
H  -2.154497  0.925528  -1.913155
H  -1.456141  -0.709255  -1.952816
H  -3.204668  -0.491936  -1.854643
F  0.810006  -1.284555  -0.880065
```

```
F  1.544737  -1.224935  1.140766
F  2.823101  -0.62048  -0.480966

G4(0 K)=                -724.107853 G4 Energy=                -724.093298
G4 Enthalpy=            -724.092354 G4 Free Energy=           -724.149338
```

tert-Butanol

```
SCF Done:  E(UM062X) =  -233.650729745
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -233.514761
Sum of electronic and thermal Energies=             -233.508139
Sum of electronic and thermal Enthalpies=           -233.507195
Sum of electronic and thermal Free Energies=        -233.543651

C  0.485028  -0.699547  1.254673
H  0.098163  -1.718394  1.292585
H  0.151753  -0.165794  2.145134
H  1.575906  -0.749421  1.266746
C  -0.001962  0.017256  0.0
C  -1.517586  0.135314  0.0
H  -1.852869  0.675217  0.886091
H  -1.852869  0.675217  -0.886091
H  -1.975691  -0.853607  0.0
C  0.485028  -0.699547  -1.254673
H  0.151753  -0.165794  -2.145134
H  1.575906  -0.749421  -1.266746
H  0.098163  -1.718394  -1.292585
O  0.485028  1.363766  0.0
H  1.446514  1.339412  0.0

G4(0 K)=                -233.509428 G4 Energy=                -233.502561
G4 Enthalpy=            -233.501617 G4 Free Energy=           -233.538538
```

1,1,1-Trifluoroacetone

```
SCF Done:  E(UM062X) =  -490.892166285
S**2 before annihilation     0.0000,   after     0.0000
Sum of electronic and zero-point Energies=          -490.830462
Sum of electronic and thermal Energies=             -490.823516
Sum of electronic and thermal Enthalpies=           -490.822571
Sum of electronic and thermal Free Energies=        -490.862471
```

```
O  -1.229564  1.45341  -0.005384
C  -0.907018  0.302244  -0.005809
C  -1.823863  -0.875933  -0.00092
H  -1.726932  -1.402444  -0.951892
H  -1.535273  -1.571503  0.787514
H  -2.847029  -0.542633  0.137601
C  0.605377  -0.04242  -0.003462
F  0.935626  -0.619409  1.154448
F  1.358422  1.032192  -0.159937
F  0.894705  -0.903233  -0.979955

G4(0 K)=                -490.726969 G4 Energy=                -490.719835
G4 Enthalpy=            -490.718890 G4 Free Energy=           -490.759567
```