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Why are *sec*-Alkylperoxyl Bimolecular Self-Reactions Orders of Magnitude Faster than the Analogous Reactions of *tert*-Alkylperoxyls? The Unanticipated Role of CH Hydrogen Bond Donation.

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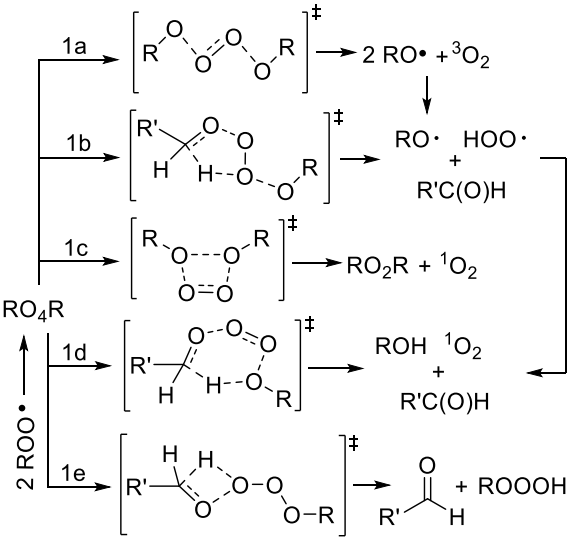
Appendix S1. Background computational studies

In pioneer accounts, Raley *et al.*[1] and Russell[2] suggested that ROO• is first involved in formation of the adduct tetraoxide RO_4R that further trifurcates into three major reaction channels (Scheme S1, reactions 1a, 1c & 1d). Various experimental works exploring MeOO• [3] and EtOO• [4] self-reaction indicated that, based on relative rate coefficients, the more dominant pathways are 1a and 1d, with 1c being minor. The kinetic branching ratio of reactions 1a and 1d vary amongst the reports but, based on the observed products the secondary oxidation reaction of EtO• by O_2 quickly consumes it and forms aldehyde and HOO•.[4a]



Scheme S1. Possible rearrangement pathways of tetraoxide.

Early computational studies investigated peroxyl self-reaction and the associated reaction pathways for tetraoxide decomposition based on reaction energetics.[5] Notably, theoretical calculations on methyl peroxyl self-reaction by Ghigo *et al* surmised that at the high temperatures associated with combustion (~900 K), most tetraoxide will dissociate to MeO• radicals and O_2.[6] More recent density functional theory studies by the separate groups of F. Wang[7] and W. Wang[8] report a high activation barrier for the classic two-step-cyclic pathway as initially proposed by Russell and Raley (Scheme 1, reaction 1c & 1d)[2]. The lowest barrier calculated by Wang and co-workers involves a cyclic rearrangement of the alpha hydrogen dissociating to $CH_3C(O)H$ + HOO• + CH_3CH_2O• (Scheme 1, 1b). In this regard, an earlier MP2 study by Feria *et al*[9] found a similar pathway for the concerted rearrangement step 1b. However, while this previous computational work has evaluated pathways 1b-1e, it has not definitively explored other possible O-O bond type fission pathways, and in particular the homolysis of $(CH_3CH_2OO)_2$ to CH_3CH_2OOO• + CH_3CH_2O• and its further dissociation of CH_3CH_2OOO• to CH_3CH_2O• + O_2 (Scheme 1, reaction 1a). It is also possible that the products of this radical reaction (1a) undergo further self-reaction to give ROH + R'C(O)H + O_2, hence providing an alternative route to the products of channels 1b and 1d.

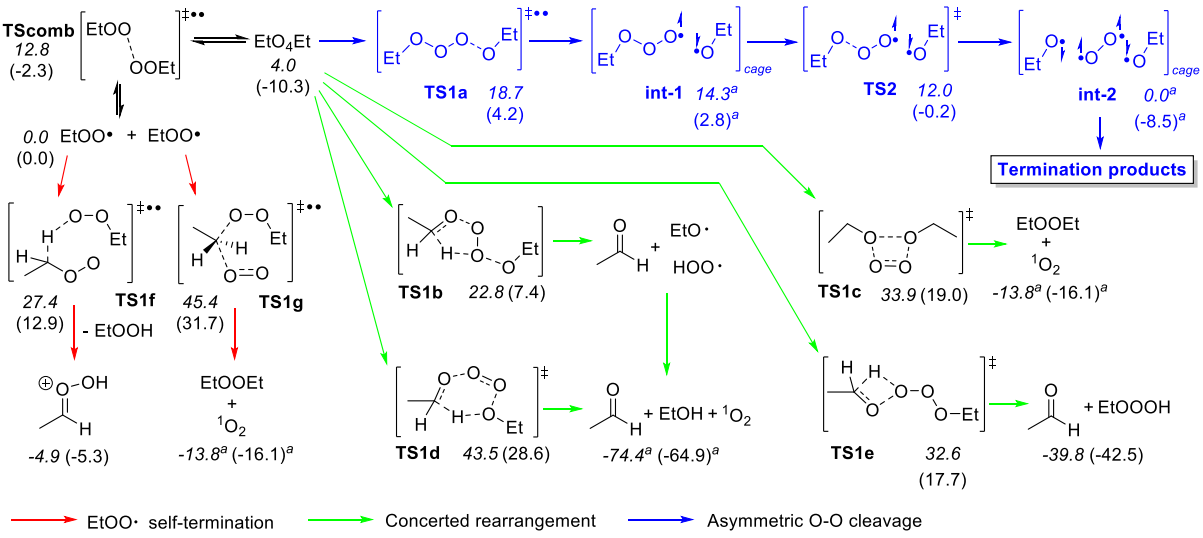


Figure S1. Reaction pathways describing the fate of EtOO• self-termination and tetroxide (EtO_4Et) decomposition. Values in italics are free energy relative and in parenthesis are enthalpies (kcal/mol) relative to 2 EtOO•. [a] Spin-projection corrected energies.

Figure S1 shows the calculated Gibbs free energy barriers and reaction energies for the possible decomposition pathways from diethyl tetraoxide EtO_4Et at room temperature. It is formed from combination of the 2 EtOO• through **TScomb** (Figure S1; $\Delta G^{\ddagger}$= 12.8 kcal/mol). In addition to the formation of the EtO_4Et via combination of two peroxyl radicals, we also considered alternative self-reaction channels.

The first is self-reaction of two peroxyl radicals via H-abstraction, **TS1f** (Figure S1), to form EtOOH and a Criegee intermediate. We find that this pathway has a free energy barrier of 27.4 kcal/mol. The second via S_H2 homolytic substitution (**TS1g**) between two peroxyl radicals but this step is highly energetically costly with calculated free barrier of 45.4 kcal/mol. Based on energetics it is more likely that the self-reaction of peroxyl radicals results in formation of the tetraoxide, which then undergoes further decomposition.

Examining Figure S1, we first note that from EtO_4Et, there is an O-O bond rupture transition state (TS) structure (Figure S1 **TS1a**, $\Delta G^{\ddagger}$= 18.7 kcal/mol). This corresponds to the single asymmetric homolytic O-O bond fragmentation experimentally observed by Brown[10] and Ingold[11] for di-*tert*-butyl tetraoxide ($^{t}BuOOOO^{t}Bu$). Nangia and Benson,[12] claimed that the corresponding intermediates $CH_3OOO\bullet$ + $CH_3O\bullet$ could not have been formed as the standard enthalpy of formation, ΔH°_f = 23.3 kcal/mol, is well above the activation enthalpy of 17.5 kcal/mol. However our calculations suggest that the radical pair **int-1** (ΔG = 14.3 kcal/mol) is more exoergic than the preceding **TS1a**. It is thus more viable for caged radical species to be present in solution phase and stabilized by non-covalent H-bond interactions with the α-hydrogen on R group in our context.

The subsequent O-O fission of **int-1** through transition state **TS2** connects to an caged radical complex **int-2** (ΔG = 0.0 kcal/mol) with overall singlet spin multiplicity, $^{3}[EtO\bullet]_2$---$^{3}O_2$. Interestingly the relative Gibbs free energy for **TS2** is lower than the preceding **int-1**, which suggests that the second O-O fragmentation is a barrierless process, which would immediately follow the first O-O fragmentation. **TS2** was fully investigated by scanning the potential energy surface (PES) for

unimolecular dissociation of O_2 at coupled cluster CCSD/6-31G(d) level of theory. Due to computational constraints, trioxyl radical was probed instead (EtOOO• ⇌ EtO• + O_2). From the PES a possible first order saddle-point structure was located just 1 kcal/mol above the minimum for which the process could be deemed diffusion controlled (Figure S2). We suspect that at a level of high correlation CCSD(T) approach to optimize the 2nd O-O fragmentation (**TS2**) would similarly yield a very low activation barrier.

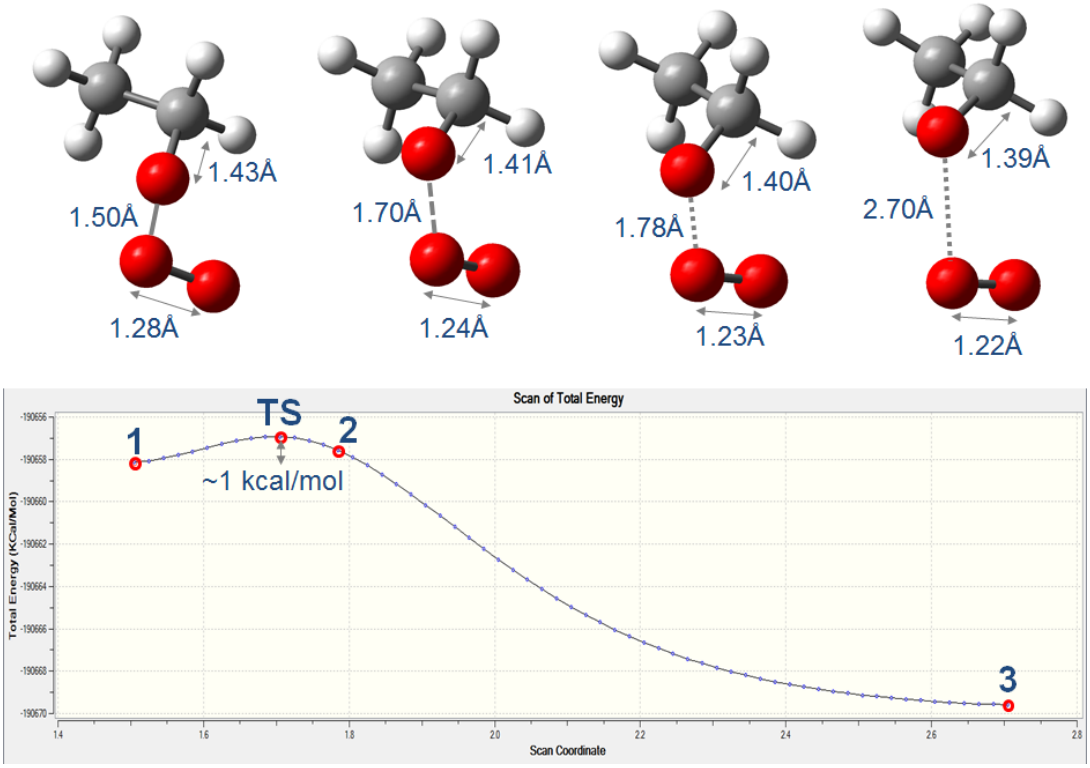


Figure S2. Potential energy scan of O_2 dissociation from EtOOO• at CCSD/6-31(d) level of theory.

The two-step O-O fragmentation process via **TS1a** is the most energetically accessible amongst the other concerted rearrangement processes that were previously studied (**TS1b-e** in Figure S1 corresponding to literature pathways 1b-1e in Scheme S1).[7-8] What is noteworthy is that the putative Russell cyclic concerted mechanism (**TS1d**, Figure S1; pathway 1d in Scheme S1) is highly unfavorable with a free energy barrier $\Delta G^{\ddagger}$ of 42.8 kcal/mol! This is presumably due to a combination of the high intrinsic barrier of C-H bond breaking, and strain in the transition state. Similarly, for pathway 1c (**TS1c**) which produces dialkyl peroxide, the high free energy barrier of 33.9 kcal/mol is due to highly strained O arrangement in the cyclic transition state. Indeed, all of the concerted mechanisms considered (**TS1b-e**), strained O-O-O-O cyclic rearrangement in the transition state resulted in higher free energy barriers than the asymmetric step-wise **TS1a**.

The 3-component radical complex **int-2** formed directly from **TS1a** can then undergo further decomposition or termination to non-radical products, or cage escape, the outcome of which depends on whether the precursor alkylperoxyl radical contains α-hydrogen – for which all of decomposition termination pathways were covered for *n*-, *s*- and *t*-butylperoxyl radicals in the main manuscript. As we show in the main manuscript, this single pathway and the subsequent decomposition of **int-2** can account for all of the different experimental products, without recourse to **TS1b-e**.

Appendix S2. Non-bonded interactions: NCI and DORI Analyses

Non-covalent interaction (NCI) analysis is used to identify weak bonding (H-bonding or Van der Waals) and non-bonding interactions (steric repulsion) between molecular fragments based on the electron density and its derivatives. The NCI topological analysis based on the reduced density gradient was computed with NCIplot programme[13, 15] to qualify isosurfaces or 3D plots of non-covalent interactions in the electronic structure of **TS1a**. Regions which are attractive have sign of the second density Hessian eigenvalue, sign(λ_2), as negative and repulsive as positive. For Van der Waals interaction, $\lambda_2 \lesssim 0$. The NCI provides a more quantitative picture of the non-covalent interactions or steric repulsions in the **TS1a** analogues (Fig. S3).

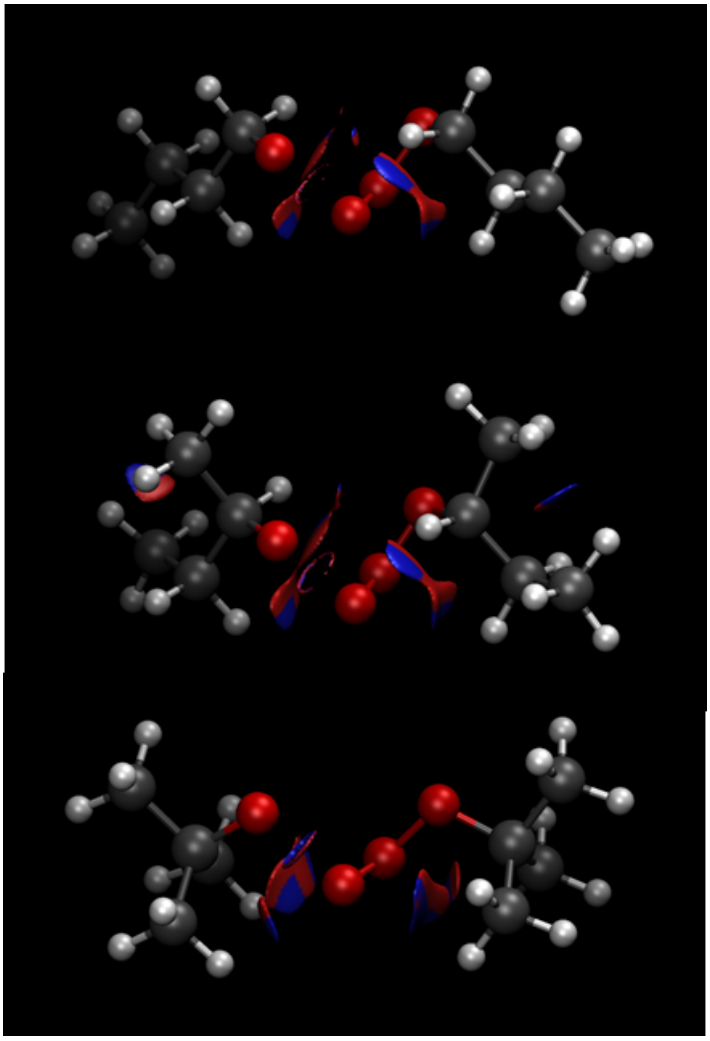


Figure S3. Non-covalent interaction (NCI) analysis is used to identify weak bonding (H-bonding and Van der Waals) and non-bonding interactions (steric repulsion) between molecular fragments based on electron density and its derivatives. Shown here are 3D plots of the interaction regions between the various fragments in **TS1a** for primary, secondary and tertiary tetroxides respectively. Blue indicates an attractive interaction, red indicates repulsion. The electron density $\rho(r)$ is set at an isovalue of 0.5 au in the sign(λ_2)$\rho(r)$ range of -0.5 to 0.5, which corresponds to blue-green-red color scale. Graphics were generated from VMD[14]. For full information on NCI see the text.

The NCI plot reveals C_α-H···O and C_β-H···O H-bonding interactions for primary and secondary **TS1a**, while tertiary exhibits only C_β-H···O interactions. To further quantify the overall strength of non-

covalent interactions for the isomers, we have employed an orbital-free density-dependent scalar field and performed the Density Overlap Regions Indicator (DORI) analyses[16] using the modified DGrid program[17] (see Figures S4 and S5). All densities were computed with ADF package[18] at the PBE0-dDsC/DZP[19] level of theory. DORI detects the regions of electron density overlap and allows discriminating between the covalent and non-covalent interactions, associated with these regions. The DORI compactness index is a dimensionless quantity that characterizes the electron compactness within a given density overlap region. It is computed as an integral of electron density over the chosen region (domain), enclosed by DORI isosurface at a chosen isovalue (in this work set to 0.95).

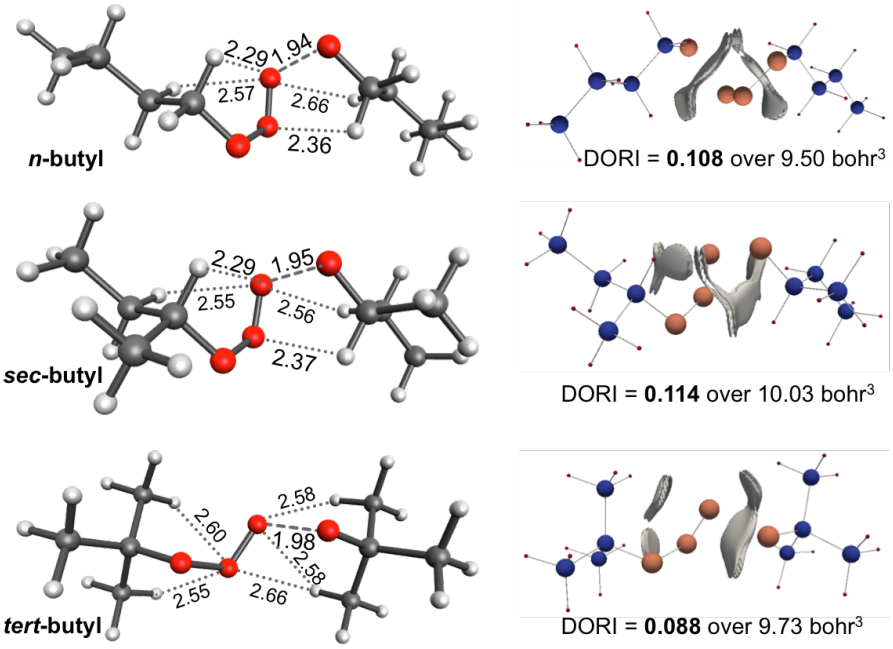


Figure S4. Optimized transition state structures **TS1a** isomers (left) showing key C_α-H···O and C_β-H···O H-bonding interactions. Cumulative Density Overlap Regions Indicator (DORI) compactness indices quantify the strength of non-covalent interactions, corresponding to the electron density overlap regions, enclosed by DORI isosurfaces at 0.95 isovalue (right) .

Appendix S3. Assessment of Hydrogen Bonding Strength in Model Systems

To assess the energetic importance of hydrogen bond formation, we calculated the energy for formation of hydrogen-bonded complexes between *s*- and *t*-dibutyl tetroxides and CH_3OCH_3 (see Figure S5). The zero-point corrected complexation energies were calculated at M11/6-311++G(d,p)//M11/6-31+G(d,p) level of theory, and the stabilization energies are 5.7 and 4.2 kcal mol^{-1} for secondary and tertiary alkyl respectively. This suggests that, provided contacts are close enough, C–H···O hydrogen bonding interactions are energetically significant. Moreover, the extra stabilization of 1.5 kcal mol^{-1} calculated in the *s*-tetroxide-ether complex could be attributed to stronger C_α-H···O bonding interactions as also indicated by the larger DORI compactness indices (Figure S5, right).

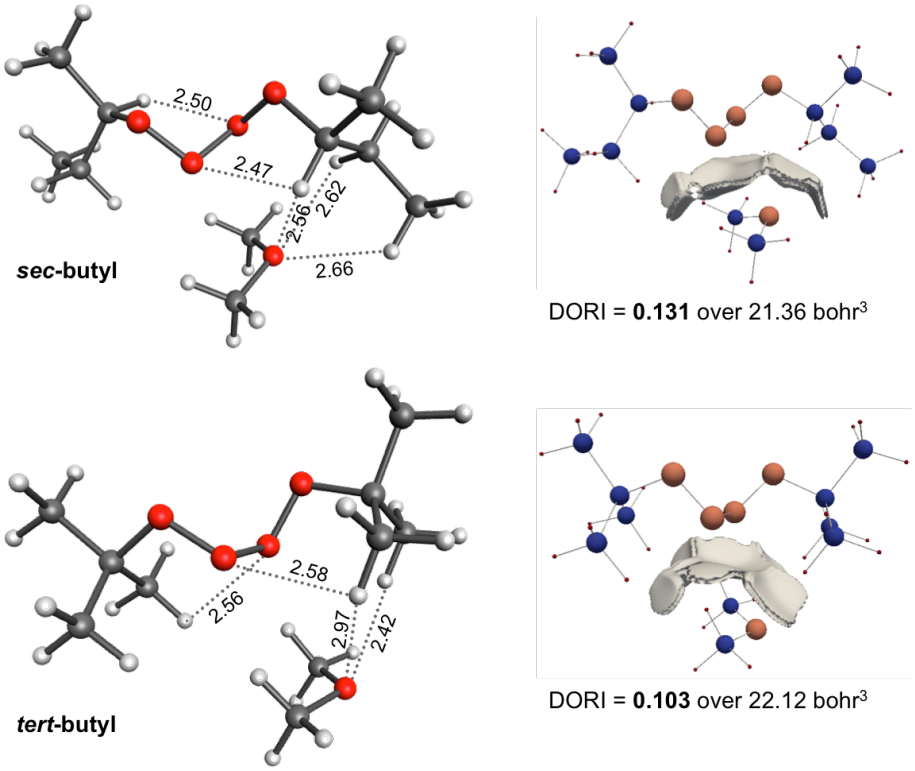


Figure S5. Geometries of the tetroxide-ether complexes, showing bond distances (Å) of key H-bonds. Cumulative DORI compactness indices quantify the strength of non-covalent interactions, corresponding to the electron density overlap regions, enclosed by DORI isosurfaces at 0.95 isovalue (right)

Appendix S4. Additional Computational details

Density functional theory (DFT) and ab initio calculations were carried out with Gaussian 09 [20] suite of programs. A survey of DFT methods was carried out to select an appropriate functional. We selected the Minnesota meta hybrid functional M11 (an improved version of the Minnesota 06 functional series) [21] with Pople's basis set 6-31+G(d,p) [22] on the basis that it provided values of the bond dissociation enthalpy (BDE) of peroxides that were close to literature values from both experiment and high-level ab initio levels of theory (Table S1).

Table S1. O-O bond dissociation enthalpies (kcal/mol) for peroxides

	Calculated	BDE from literature[a,]
HOOH	49.8	50.7 (50.5)
MeOOH	43.6	44.7 (44.6)
MeOOMe	36.3	38.5 (37.8)

[a] *Ab initio* BDE at CBSQ level of theory and in parenthesis are experimental values (see ref. [23] for related citation)

Geometries were optimized at the prescribed M11/6-31+G(d,p) and second derivative eigenvalues were inspected to ensure that the convergence corresponds correctly to a minima (all positive) or first-order saddle point (one negative). The keyword 'guess=mix' and open-shell M11 (UDFT) were implemented to optimize singlet bi- or tetra-radicaloid structures, and the spin-squared operator $\langle S^2 \rangle$ was confirmed to be approximately equal to 1 or 2 respectively (see table S2).

Improved single point calculations using open-shell coupled cluster UCCSD(T) with Dunning's correlation consistent double zeta cc-pVDZ [24] basis set was carried out on the optimized geometries. The wavefunctions from the UDFT output checkpoint files were used as initial guesses for UCCSD(T) computations by evoking 'guess=read' keyword. The T_1 diagnostic was calculated concurrently to ascertain if the single-reference UCCSD(T) wavefunction is reliable. It has been reported that values above the 'benchmark' 0.044 should be treated with multi-reference methods[25]; in the present work all species fall below this threshold (Table S2). The UCCSD(T) electronic energies were combined with M11/6-31+G(d,p) thermal and vibrational correction energies to obtain the gas phase free energy G_{gas} at ambient 298 K (table S2). The vibrational corrections were treated by means of quasiharmonic approximation in which frequencies below 100 cm^{-1} are set to 100 cm^{-1} to minimize erroneous vibrational entropies.[26]

$$k = \frac{k_B T}{h} \exp^{\frac{G}{RT}}$$

For equilibrium structures, the spin-projection method for the broken symmetry minimum structures was adapted in our computations to minimize triplet contamination in the open-shell UCCSD(T) electronic energies. It is noteworthy that we do not see significant differences in the electronic energy (within 1 kcal/mol) between the spin-projection corrected E_{AP}[UCCSD(T)] and broken symmetry E_{BS}[UCCSD(T)]; except in the case of the relative energies between the lowest state excited singlet state of O_2 and the ground state triplet. The spin-projection method however severely under-estimates the TS energies such that the first **TS1a** is negative and not meaningful. This under-estimation was also encountered in the work of Bach *et al.*[27] Previous calculations by Schegel[28] and Truhlar[29] demonstrated that UCCSD(T) calculations are less susceptible to spin contamination or unrestricted reference state and this prompts us to consider all UCCSD(T) TSs

energies as is without spin correction. The singlet spin-projected energy is estimated from equations (1) and (2) based on Yamaguchi's technique:

$$E_{AP} = E_{BS} + (1 \quad) E_{HS} \qquad (1)$$

$$= \frac{{}^{HS}\left\langle S^2 \right\rangle \quad \left\langle S^2 \right\rangle_{exact}^{LS}}{{}^{HS}\left\langle S^2 \right\rangle \quad {}^{BS}\left\langle S^2 \right\rangle} \qquad (2)$$

Appendix S4. Raw Computational Data

Molecules	E_{HS}[CCSD(T)] [a]	E_{BS}[CCSD(T)] [b]	E_{AP}[CCSD(T)] [c]	<S^2> [d]	G_{corr}(298K) [e]	H_{corr}(298K) [e]	ZPE 298K [e]	G(298K)	H(298K)	E + ZPE (298K)	T1 [f]
O2s	-149.9852842	-149.969762	-149.9531284*	1.03673	-0.01559322	0.00826876	0.004228	-149.968722	-149.9448597	-149.948901	0.01216174
O2t	-	-	-149.9852842	2.004191	-0.01661311	0.00828487	0.004244	-150.001897	-149.9769993	-149.98104	0.01282452
EtOH	-	-	-154.6233245	-	0.05464737	0.08523404	0.080013	-154.568677	-154.5380905	-154.543311	0.00788209
aldehyde	-	-	-153.4269649	-	0.0309025	0.05947527	0.055262	-153.396062	-153.3674896	-153.371703	0.01487743
EtOOEt	-	-	-307.9768611	-	0.10883818	0.14910337	0.140167	-307.868023	-307.8277577	-307.836694	0.01013461
EtOOOH	-	-	-304.5400048	-	0.05783919	0.09285821	0.08652	-304.482166	-304.4471466	-304.453485	0.01086824
criegee	-	-	-228.3266967	-	0.0329059	0.06530965	0.059638	-228.293791	-228.2613871	-228.267058	0.04074263
EtOOH	-	-	-229.5840992	-	0.05525718	0.09009452	0.083458	-229.528842	-229.4940047	-229.500642	0.00978235
EtOO*	-	-	-228.9512033	0.751286	0.04378758	0.07771484	0.071799	-228.907416	-228.8734885	-228.879404	0.02334087
EtO*	-	-	-153.9579136	0.7515	0.03913212	0.07019087	0.06504	-153.918781	-153.8877227	-153.892874	0.0144107
TScomb	-	-	-457.9064424	0.812751	0.11200814	0.15584157	0.145983	-457.794434	-457.7506008	-457.76046	0.03420275
EtO4Et	-	-	-457.9215784	-	0.1131511	0.15816099	0.147544	-457.808427	-457.7634174	-457.774034	0.01496069
TS1a	-	-	-457.8942969	2.01389	0.10938282	0.15409014	0.14395	-457.784914	-457.7402068	-457.750347	0.03218104
int-1	-457.8948822	-457.896032	-457.8972271*	2.052365	0.10523103	0.15476472	0.142483	-457.791996	-457.7424624	-457.754745	0.02887123
TS2	-	-	-457.8990063	6.08679	0.10335258	0.15171943	0.140135	-457.795654	-457.7472869	-457.758872	0.03373498
int-2	-457.9105204	-457.9118459	-457.9295369*	6.008892	0.09764839	0.15192381	0.137832	-457.831889	-457.7605843	-457.791704	0.0160777
TS1b	-	-	-457.8862262	-	0.1076565	0.15110171	0.141358	-457.77857	-457.7351245	-457.744868	0.0238621
TS1c	-	-	-457.8702398	-	0.10940065	0.15351723	0.143515	-457.760839	-457.7167226	-457.726725	0.02774917
TS1d	-	-	-457.851446	-	0.10589383	0.15004366	0.140015	-457.745552	-457.7014023	-457.711431	0.02470454
TS1e	-	-	-457.8695338	-	0.10672919	0.15083549	0.140985	-457.762805	-457.7186983	-457.728549	0.02063866
TS1f	-	-	-457.876745	0.981751	0.1055955	0.15028901	0.139995	-457.77115	-457.726456	-457.73675	0.03194881
TS1g	-	-	-457.8500133	1.374228	0.10613305	0.15357244	0.14238174	-457.743880	-457.6964409	-457.7076316	0.03860916
n-Butyl											
ROH	-	-	-233.0200342	-	0.106475	0.14460859	0.136727	-232.914	-232.875426	-232.883307	0.00761948
aldehyde	-	-	-231.8250713	-	0.083162	0.12013457	0.112871	-231.742	-231.704937	-231.7122	0.01230833
aldehyde* (^{3}T)	-	-	-231.7038231	2.00135	0.078831	0.1172781	0.109744	-231.625	-231.586545	-231.59408	0.01789196
ROOR	-	-	-464.7704588	-	0.213838	0.2681104	0.253841	-464.557	-464.502348	-464.516618	0.00914624
RO*	-	-	-232.354807	0.751508	0.091378	0.12969523	0.122021	-232.263	-232.225112	-232.232786	0.01225714
ROO*	-	-	-307.349157	0.751472	0.096563	0.13731207	0.128932	-307.253	-307.211845	-307.220225	0.01996798
TScomb	-	-	-614.7013189	0.814481	0.217673	0.27482076	0.259632	-614.484	-614.426498	-614.441687	0.02821251
RO4R	-	-	-614.7157274	-	0.218768	0.27717956	0.26136	-614.497	-614.438548	-614.454368	0.01303821
TS1a	-	-	-614.6890655	0.870138	0.215355	0.27302884	0.257673	-614.474	-614.416037	-614.431393	0.02705711
int-1	-614.689587	-614.6908211	-614.6914447	1.049123	0.212377	0.27379928	0.25653	-614.479	-614.417645	-614.434915	0.02441950
TS2	-	-	-614.6972258	1.953559	0.209565	0.27047194	0.253735	-614.488	-614.426754	-614.443491	0.01626112
int-2	-614.7046466	-614.7060834	-614.7068019	2.003205	0.204594	0.2708279	0.251694	-614.502	-614.435974	-614.455108	0.01379387
int-2* (^{3}T)	-614.7046466	-614.7065344	-614.7084195	3.002293	0.203686	0.27057688	0.251612	-614.505	-614.437843	-614.456808	0.01479401
^{3}[RO•]$_2$	-	-	-464.7187116	2.003197	0.203208	0.2616284	0.246014	-464.516	-464.457083	-464.472697	0.01304605
TS-H	-	-	-464.706201	2.008062	0.202765	0.25731423	0.24352	-464.503	-464.448887	-464.462681	0.01818879
***sec*-Butyl**											
ROH	-	-	-233.0258754	-	0.106595	0.14399517	0.136274	-232.919	-232.88188	-232.889602	0.00807350
ketone	-	-	-231.8344048	-	0.083256	0.11993284	0.11267	-231.751	-231.714472	-231.721735	0.01253412
ketone* (^{3}T)	-	-	-231.7093322	2.001635	0.079366	0.11759853	0.110044	-231.63	-231.591734	-231.599288	0.01829034
ROOR	-	-	-464.7855312	-	0.214289	0.26656634	0.252643	-464.571	-464.518965	-464.532888	0.00982059
RO*	-	-	-232.3588035	0.751553	0.092267	0.12983953	0.122413	-232.267	-232.228964	-232.23639	0.01306742
ROO*	-	-	-307.3546254	0.751499	0.096292	0.13667463	0.128254	-307.258	-307.217951	-307.226371	0.02013205
TScomb	-	-	-614.7142074	0.811448	0.217406	0.2736271	0.258363	-614.497	-614.44058	-614.455845	0.02883909
RO4R	-	-	-614.7265746	-	0.218145	0.27604963	0.260051	-614.508	-614.450525	-614.466524	0.01317509
TS1a	-	-	-614.6981565	0.871145	0.215397	0.27225395	0.25674	-614.483	-614.425903	-614.441416	0.02669736
int-1	-614.7004308	-614.7007149	-614.7007992	1.030846	0.212089	0.2735262	0.255999	-614.489	-614.427273	-614.4448	0.02309531
TS2	-	-	-614.7142074	1.757505	0.209845	0.27013325	0.253284	-614.504	-614.444074	-614.460924	0.02848704
int-2	-614.7144209	-614.7164387	-614.717446	2.000908	0.205187	0.27131403	0.251999	-614.512	-614.446132	-614.465447	0.01434901
int-2* (^{3}T)	-614.7144209	-614.7163571	-614.7182941	3.00513	0.204177	0.27147981	0.252189	-614.514	-614.446814	-614.466105	0.01457738
^{3}[RO•]$_2$	-	-	-464.7267998	2.003216	0.204593	0.26269438	0.247128	-464.522	-464.464105	-464.479672	0.01384900
TS-H	-	-	-464.717116	2.007529	0.202836	0.25701827	0.24299	-464.514	-464.460098	-464.474126	0.01868998
***tert*-Butyl**											
RO*	-	-	-232.3650909	0.751435	0.09242	0.12945504	0.121967	-232.273	-232.235636	-232.243124	0.01311434
ROO*	-	-	-307.3617964	0.751538	0.095939	0.13553544	0.127123	-307.266	-307.226261	-307.234674	0.02036880
ROOR	-	-	-464.7955732	-	0.212664	0.264524	0.250436	-464.583	-464.531049	-464.545137	0.00997469
TScomb	-	-	-614.7254592	0.807522	0.217305	0.27132298	0.25627	-614.508	-614.454136	-614.469189	0.02883463
RO4R	-	-	-614.7376266	-	0.218401	0.27372895	0.257861	-614.519	-614.463898	-614.479765	0.01328268
TS1a	-	-	-614.7064225	0.886257	0.2139	0.27001909	0.254395	-614.493	-614.436403	-614.452027	0.02338280
int-1	-614.7047458	-614.7057247	-614.7067161	1.006697	0.210647	0.27134801	0.253803	-614.496	-614.435368	-614.452913	0.02044604
TS2	-	-	-614.7114693	1.76101	0.209002	0.26876451	0.251695	-614.502	-614.442705	-614.459774	0.02762742
int-2	-614.7241714	-614.7246844	-614.7249412	2.004076	0.204597	0.26997119	0.250668	-614.52	-614.45497	-614.474273	0.01406218
int-2* (^{3}T)	-614.7241714	-614.724989	-614.7258065	3.004036	0.204597	0.26997119	0.250668	-614.521	-614.455835	-614.475138	0.01431414

All energies in hartrees. Single-point CCSD(T)/cc-pVDZ gas-phase electronic energy: [a] high spin UCCSD(T) electronic energies; [b] broken symmetry UCCSD(T) electronic energies & [c] spin-projected or closed shell CCSD(T) electronic energies. [d] Spin-squared operator of the CCSD(T) calculation. [e] T_1 diagnostic. [f] at M11 level of theory

Appendix S5. Gaussian archive entries

$^1O_2$

1\1\GINC-R43\FOpt\UM11\6-31+G(d,p)\O2\ROOT\03-Sep-2015\0\\# um11/6-31+G** opt scf=maxcyc=200 guess=mix # int=ultrafine freq\\O2 (singlet; delta symm)\\0,1\O,0.,0.,0.5986248719\O,0.,0.,-0.5986248719\\Version=ES64L-G09RevD.01\HF=-150.2495406\S2=1.003144\S2-1=0.\S2A=0.025158\RMSD=8.358e-09\RMSF=6.713e-05\Dipole=0.,0.,0.\Quadrupole=0.1372345,0.1372345,-0.274469,0.,0.,0.\PG=D*H [C*(O1.O1)]\\@

$^3O_2$

1\1\GINC-R39\FOpt\UM11\6-31+G(d,p)\O2(3)\ROOT\03-Sep-2015\0\\# um11/6-31+G** opt scf=maxcyc=200 # int=ultrafine freq\\O2 (triplet; sigma symm)\\0,3\O,-0.9915000146,-0.5791204217,0.0024636059\O,-0.8727889854,0.6114364217,0.0011943941\\Version=ES64L-G09RevD.01\State=3-SGG\HF=-150.2668532\S2=2.005862\S2-1=0.\S2A=2.000017\RMSD=9.689e-09\RMSF=1.588e-04\Dipole=0.,0.,0.\Quadrupole=0.1352511,-0.2746176,0.1393665,-0.0412786,0.000044,0.0004413\PG=D*H [C*(O1.O1)]\\@

EtOO•

1\1\GINC-R2587\FOpt\UM11\6-31+G(d,p)\C2H5O2(2)\ROOT\28-Aug-2015\0\\# um11/6-31+g(d,p) opt=maxcyc=200 int=ultrafine scf=maxcyc=200 # freq=noraman\\EtOO* radical\\0,2\C,-1.1957328715,0.172548364,0.0079868741\H,-0.8507191036,-0.8684410921,-0.0273754231\H,-0.8370186814,0.6878019264,-0.8916191606\H,-2.2927112774,0.1750964187,-0.0012214347\C,-0.6674781867,0.8435883665,1.2581233052\H,0.4292501213,0.8935845992,1.2877212672\H,-1.0341167879,0.3781108438,2.1828271296\O,-1.154134052,2.2118754347,1.2504903111\O,-0.7462769108,2.8673541987,2.297242881\\Version=ES64L-G09RevD.01\State=2-A\HF=-229.4327509\S2=0.752909\S2-1=0.\S2A=0.750005\RMSD=5.373e-09\RMSF=1.171e-04\Dipole=0.140594,-1.1869825,-0.4545345\Quadrupole=0.9588507,-0.8492543,-0.1095965,0.0875405,-0.4633459,-1.0799122\PG=C01 [X(C2H5O2)]\\@

EtO•

1\1\GINC-R436\FOpt\UM11\6-31+G(d,p)\C2H5O1(2)\ROOT\28-Aug-2015\0\\# um11/6-31+g(d,p) opt=maxcyc=200 int=ultrafine scf=maxcyc=200 # freq=noraman\\EtO* radical\\0,2\C,-2.3691308772,0.0228493915,-0.007383942\H,-2.0039935754,-1.013214067,-0.009263671\H,-2.0146436386,0.5192664097,-0.9197174698\H,-3.4662239504,0.0060767873,-0.0308145339\C,-1.8780295144,0.7703296931,1.2261277933\H,-0.7698121421,0.7797913387,1.2933015936\H,-2.1970623563,0.2752033442,2.1673055294\O,-2.2892995408,2.0790128262,1.3100639878\\Version=ES64L-G09RevD.01\State=2-A"\HF=-154.2900465\S2=0.752842\S2-1=0.\S2A=0.750006\RMSD=7.776e-09\RMSF=1.311e-04\Dipole=0.2736292,-0.8592328,-0.0492232\Quadrupole=1.1156688,-1.7040887,0.5884199,0.4259406,-0.0729632,-1.0450998\PG=CS [SG(C2H1O1),X(H4)]\\@

TScomb

1\1\GINC-R538\FTS\UM11\6-31+G(d,p)\C4H10O4\ROOT\28-Aug-2015\0\\# um11/6-31+G** opt=(TS,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 # int=ultrafine guess=mix freq=noraman nosymm\\TS for 2 ROO* addition to ROOOOR\\0,1\H,2.8929547482,-0.431805946,-0.1143510265\C,1.9546045463,0.0406940384,0.208054766\H,1.6161627903,-0.4145017753,1.1487445801\O,0.9452495672,-0.2714870068,-0.7848827139\O,0.6134076672,-1.5441104249,-0.709995236\H,-1.6161892954,-0.4144995308,-1.1487130967\C,-1.9546204489,0.0407331784,-0.2080373203\H,-2.892982204,-0.4317343082,0.1143824962\O,-0.9452733591,-0.2714419947,0.7849100504\O,-0.6134608389,-1.5440752583,0.7100603078\C,-2.0452832161,1.5496760142,-0.2894797259\H,-2.8330235468,1.8380254041,-0.9967980155\H,-2.2849248923,1.9821792059,0.6904186367\H,-1.0926332189,1.9660527282,-0.6413215256\C,2.0453039842,1.5496371602,0.2894510036\H,1.0926643306,1.9660479908,0.6412803634\H,2.8330516057,1.8379890212,0.9967601657\H,2.2849558305,1.9821045038,-0.6904607095\\Version=ES64L-G09RevD.01\HF=-458.8649417\S2=0.381125\S2-1=0.\S2A=0.00399\RMSD=6.226e-09\RMSF=6.589e-07\Dipole=0.0000139,1.1589267,-0.0000176\Quadrupole=6.1715756,-3.6193232,-2.5522524,-0.0001023,1.9686688,0.0000139\PG=C01 [X(C4H10O4)]\\@

EtO$_4$Et

1\1\GINC-R730\FOpt\RM11\6-31+G(d,p)\C4H10O4\ROOT\27-Apr-2015\0\\# freq m11/6-31+g(d,p) opt=maxcyc=200 int=ultrafine scf=maxcyc=200\\EtOOOOEt\\0,1\H,0.1809789359,2.374738783,-0.0746462833\C,1.2042106064,2.0923091482,-0.3641218765\O,1.1928743731,0.7179162912,-0.7813040382\O,0.6995118351,-0.0613210412,0.2753153995\O,-0.6995118351,0.0613210412,0.2753153995\O,-1.1928743731,-0.7179162912,-0.7813040382\C,-1.2042106064,-2.0923091482,-0.3641218765\H,-0.1809789359,-2.374738783,-0.0746462833\C,-2

.2114755699,-2.345497773,0.7442983163\H,-3.2196285269,-2.0565307736,0.
4213140298\H,-2.2198406271,-3.410846501,1.0103731517\H,-1.9509918259,-
1.7686015703,1.6401380138\C,2.2114755699,2.345497773,0.7442983163\H,2.
2198406271,3.410846501,1.0103731517\H,1.9509918259,1.7686015703,1.6401
380138\H,3.2196285269,2.0565307736,0.4213140298\H,1.4643112781,2.62439
97535,-1.2886477131\H,-1.4643112781,-2.6243997535,-1.2886477131\\Versi
on=ES64L-G09RevD.01\State=1-A\HF=-458.8826516\RMSD=6.018e-09\RMSF=4.60
3e-06\Dipole=0.,0.,0.3184689\Quadrupole=-1.985996,5.6066023,-3.6206062
,4.3377551,0.,0.\PG=C02 [X(C4H10O4)]\\@

TS1a

1\1\GINC-R170\FTS\UM11\6-31+G(d,p)\C4H10O4\ROOT\28-Apr-2015\0\\# freq
um11/6-31+g(d,p) opt=(TS,calcfc,noeigen,maxcyc=200) # int=ultrafine sc
f=maxcyc=200 guess=mix\\TS for single O-O break: EtO4Et\\0,1\H,1.53786
30619,0.5151130758,1.2285992476\C,2.1155030545,0.620150363,0.291288306
4\O,1.2656477267,0.8964860694,-0.7732115166\O,0.0121143462,-0.58542131
01,-0.73532778\O,-0.2522341413,-0.8302908757,0.4789834912\O,-1.1372648
044,0.1715140425,1.0724357021\C,-2.0235438468,0.7193474166,0.091612078
6\H,-1.4357538351,1.1909430291,-0.7076185637\C,-3.0189080723,-0.305011
1114,-0.4289420881\H,-3.5686658143,-0.7638650199,0.4023409735\H,-3.737
7927127,0.182185357,-1.1005571324\H,-2.5102900964,-1.0953183361,-0.995
3266089\C,3.0342909994,-0.5698298341,0.0468014868\H,3.7342088415,-0.70
03258651,0.8829936627\H,2.4401075389,-1.4876331092,-0.054673932\H,3.60
6228948,-0.4260729029,-0.8784261633\H,2.6918738511,1.5605999673,0.3969
837163\H,-2.513931045,1.5111190437,0.6742671199\\Version=ES64L-G09RevD
.01\State=1-A\HF=-458.8466454\S2=0.606464\S2-1=0.\S2A=0.011833\RMSD=8.
426e-09\RMSF=2.391e-06\Dipole=-0.291536,0.1828046,0.2438403\Quadrupole
=5.5962349,-1.4090682,-4.1871667,-0.7855279,2.5875772,0.9715278\PG=C01
[X(C4H10O4)]\\@

int-1

1\1\GINC-R813\FOpt\UM11\6-31+G(d,p)\C4H10O4\ROOT\28-Apr-2015\0\\# freq
um11/6-31+g(d,p) opt=maxcyc=200 int=ultrafine scf=maxcyc=200 guess=mi
x\\EtOOO*--*OEt radical dimer\\0,1\H,1.5367239237,0.4087104165,1.24203
22564\C,2.1414739344,0.6361198556,0.3436196827\O,1.3318234235,1.128784
6692,-0.6540712365\O,-0.2438857942,-1.1265171076,-0.7272810455\O,-0.42
70802001,-1.1173479906,0.5097324114\O,-1.0337599449,0.1289037156,1.014
6282705\C,-1.7681627077,0.8008638331,-0.0112296579\H,-1.111190763,0.98
82683738,-0.8704660933\C,-3.045536346,0.0630080529,-0.3808288666\H,-3.
6639714126,-0.1073931853,0.5092623913\H,-3.6227548183,0.655975499,-1.1
023712817\H,-2.8196181641,-0.9054994407,-0.8447763424\C,3.0214733256,-
0.5315451022,-0.0900866984\H,3.6806553556,-0.8459837978,0.7300917471\H
,2.3938529489,-1.3846098973,-0.3789893398\H,3.6363587461,-0.2471653811
,-0.9530578508\H,2.763568811,1.5135869492,0.6295428507\H,-1.9705693177
,1.7653355378,0.4746008027\\Version=ES64L-G09RevD.01\State=1-A\HF=-458
.8513721\S2=0.992423\S2-1=0.\S2A=0.048931\RMSD=5.113e-09\RMSF=8.798e-0
6\Dipole=-0.0813983,0.2910507,0.2966398\Quadrupole=5.3644561,-1.679550
6,-3.6849055,-1.0189239,2.7401485,0.7579387\PG=C01 [X(C4H10O4)]\\@

TS2

1\1\GINC-R576\FTS\UM11\6-31+G(d,p)\C4H10O4\ROOT\24-Jul-2015\0\\# um11/
6-31+G** opt=(TS,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 freq=norama
n # guess=read geom=allcheck int=ultrafine\\TS for second O-O single s
cission: dimerEt\\0,1\H,-1.51497156,-0.6699235231,1.1529061016\C,-2.16
85704032,-0.8029725244,0.261600799\O,-1.2654938844,-1.0729950619,-0.73
81689705\O,0.384066435,1.4882541667,-0.6551214719\O,0.2898916979,1.249
9084361,0.5221789265\O,0.958884687,-0.3340477096,0.9608500796\C,1.6799
350007,-0.758942879,-0.1471014895\H,1.1335748767,-0.4631739853,-1.0667
199861\C,3.116744817,-0.2533919857,-0.1578603906\H,3.6425212698,-0.569
0736244,0.7518908816\H,3.6591584003,-0.6372996194,-1.0321865787\H,3.13
11228402,0.8445339187,-0.1999001847\C,-3.0125769068,0.4453952494,0.017
4017442\H,-3.6591154681,0.6498608978,0.8811422741\H,-2.3669337251,1.31
58182865,-0.1549551759\H,-3.649311218,0.3095015188,-0.8660997266\H,-2.
7832760505,-1.697656378,0.4769922277\H,1.6032451917,-1.8607091831,-0.1
273730598\\Version=ES64L-G09RevD.01\State=1-A\HF=-458.8442162\S2=1.299
452\S2-1=0.\S2A=1.880435\RMSD=4.333e-09\RMSF=2.201e-06\Dipole=-0.14030
22,-0.0375898,0.0674525\Quadrupole=4.3837794,-1.1764125,-3.207367,-0.7
112359,-2.6217839,-0.3987174\PG=C01 [X(C4H10O4)]\\@

int-2

1\1\GINC-R2830\SP\UM11\6-31+G(d,p)\C4H10O4(5)\ROOT\23-Jul-2015\0\\# 6-
31+g(d,p) um11 nosymm scf=maxcyc=200\\EtO*--O2--*OEt trimer intm\\0,5\
H,0,1.201398,-0.984083,-0.745728\C,0,1.986949,-0.917453,0.044284\O,0,1
.275329,-0.536729,1.15303\O,0,-0.391616,1.923107,0.476917\O,0,-0.03728
4,1.533338,-0.598109\O,0,-1.095857,-0.900207,-1.041499\C,0,-1.751906,-
0.918878,0.16618\H,0,-1.041471,-0.552045,0.938888\C,0,-3.07552,-0.1649
57,0.175373\H,0,-3.766108,-0.594036,-0.561598\H,0,-3.544684,-0.211407,

1.16722\H,0,-2.912442,0.889989,-0.081362\C,0,3.088547,0.057061,-0.3609
53\H,0,3.572449,-0.270892,-1.290534\H,0,2.66953,1.059213,-0.516516\H,0
,3.853156,0.119486,0.424014\H,0,2.352893,-1.955935,0.164114\H,0,-1.877
719,-1.990994,0.429491\\Version=ES64L-G09RevD.01\HF=-458.8556441\S2=6.
011524\S2-1=0.\S2A=6.000051\RMSD=5.780e-09\Dipole=-0.0271128,-0.270620
8,0.0187057\Quadrupole=4.0195896,0.392171,-4.4117606,-0.1278641,-2.953
7032,-0.7295823\PG=C01 [X(C4H10O4)]\\@

TS1b

1\1\GINC-R193\FTS\RM11\6-31+G(d,p)\C4H10O4\ROOT\28-Aug-2015\0\\# freq
m11/6-31+g(d,p) opt=(TS,calcfc,noeigen,maxcyc=200) # int=ultrafine scf
=maxcyc=200\\TS for concerted O-O cleavage and H transfer ROOOOR -> R'
CHO + HOO* + EtO*\\0,1\H,-2.3638496536,0.5879213536,-1.2225593421\C,-1
.9166615517,0.5313930001,-0.2182030378\H,-1.5650076462,-0.502269444,-0
.0730650641\C,-2.8740851582,0.9829071103,0.8729268548\H,-3.1953395889,
2.0175712931,0.6992277179\H,-2.3883924905,0.9239513398,1.8554592103\H,
-3.761003514,0.3358539681,0.8919024829\O,-0.8006643404,1.3907973242,-0
.3588142435\H,3.9532546589,-0.6698684093,-0.4827212573\C,3.3199744585,
0.1345712586,-0.0849474446\H,3.3962798352,0.1196882439,1.0094492064\H,
3.6933754219,1.0937586319,-0.4651389091\C,1.8731554794,-0.1066397149,-
0.5036405441\H,1.6049966803,0.0951761451,-1.563010966\H,1.2368127634,0
.9014688844,-0.0401019663\O,1.2055879154,-1.0366145967,0.0731295461\O,
0.1840158491,1.1307423679,0.825562789\O,0.0376848812,-0.0036187558,1.3
339539677\\Version=ES64L-G09RevD.01\State=1-A\HF=-458.8285521\RMSD=4.9
97e-09\RMSF=1.211e-06\Dipole=-0.1068921,0.4973917,-0.5053094\Quadrupol
e=6.4127485,-5.2153338,-1.1974147,1.5843536,-0.6670211,1.1046843\PG=C0
1 [X(C4H10O4)]\\@

TS1c

1\1\GINC-R41\FTS\RM11\6-31+G(d,p)\C4H10O4\ROOT\28-Aug-2015\0\\# m11/6-
31+G** opt=(calcfc,ts,noeigen,maxcyc=200) freq=noraman # scf=maxcyc=20
0\\Concerted TS ROOOR -> ROOR + O2\\0,1\H,0.9451584527,-2.1080778696,0
.06676753\C,1.9390513718,-1.6646289376,0.2020565704\H,2.1899955762,-1.
6448167236,1.269650283\H,2.6791651613,-2.2829311128,-0.3209469674\C,1.
9455424537,-0.2694400408,-0.3867662931\H,1.6529683418,-0.263205512,-1.
4443664704\H,2.8952186907,0.2630921374,-0.2364187745\O,0.9138029528,0.
45829584,0.3306681095\O,0.8785445448,1.7469508773,-0.1521142928\O,-0.3
034959549,2.16541597,-0.0166774094\O,-0.7967979463,-0.1412250004,-0.79
56136957\C,-1.8697295168,-0.0634200969,0.0381160736\H,-2.6093746792,0.
6737892418,-0.3465817445\H,-1.5252956928,0.3972846321,1.0016935684\C,-
2.4867457502,-1.4311209961,0.3434905532\H,-1.7363472785,-2.0913429002,
0.7994845516\H,-2.8453799179,-1.9032225669,-0.5800867612\H,-3.33302580
91,-1.3287539418,1.0368991691\\Version=ES64L-G09RevD.01\State=1-A\HF=-
458.7750789\RMSD=6.349e-09\RMSF=4.423e-06\Dipole=1.0449291,-0.8256403,
0.3320153\Quadrupole=5.3890266,-3.3464006,-2.042626,-0.5534086,-1.5860
498,-0.095272\PG=C01 [X(C4H10O4)]\\@

TS1d

1\1\GINC-R209\FTS\RM11\6-31+G(d,p)\C4H10O4\ROOT\28-Aug-2015\0\\# freq
m11/6-31+g(d,p) opt=(TS,calcfc,noeigen,maxcyc=200) # int=ultrafine scf
=maxcyc=200\\TS for Russell's concerted O-O cleavage and H transfer\\0
,1\O,-0.035173315,0.2497955077,-0.1075020217\O,-0.6854367723,0.5258976
129,1.954785221\O,0.3520159233,0.0699439208,2.4719739782\O,1.509396850
6,0.8165983904,2.1908395046\C,1.3097062505,1.8304834759,1.2642919445\H
,0.9082741022,1.2208103071,0.2667522516\H,0.4150583935,2.4239406096,1.
5164818013\C,-0.1539883144,-0.5747178568,-1.2301115096\H,-0.634679445,
-0.0451648138,-2.0725588838\H,0.8492069391,-0.9102774539,-1.5554843361
\C,2.6034288101,2.6038836877,1.1376623025\H,3.4323098185,1.9374899508,
0.8705954006\H,2.8555829341,3.1246629154,2.0711990077\H,2.4895397404,3
.3509570048,0.3431527566\C,-0.9818967435,-1.8080522715,-0.8442414576\H
,-0.490573356,-2.3479458219,-0.0248195469\H,-1.0923907605,-2.482792521
2,-1.7041194532\H,-1.9773810555,-1.495512644,-0.5048969594\\Version=ES
64L-G09RevD.01\State=1-A\HF=-458.7829203\RMSD=7.153e-09\RMSF=1.185e-06
\Dipole=0.6711371,0.5149167,-0.2111265\Quadrupole=-1.3938096,2.2734061
,-0.8795965,2.3121644,0.0740672,1.7378735\PG=C01 [X(C4H10O4)]\\@

TS1e

1\1\GINC-R217\FTS\RM11\6-31+G(d,p)\C4H10O4\ROOT\28-Aug-2015\0\\# freq
m11/6-31+g(d,p) opt=(TS,calcfc,noeigen,maxcyc=200) # int=ultrafine scf
=maxcyc=200\\TS for concerted O-O cleavage and H transfer ROOOOR -> R'
CHO + ROOOH\\0,1\H,0.6457153397,-0.8474295228,0.7997076047\C,0.3401335
94,-1.5992577071,1.5377949491\H,1.1001177624,-2.3897525172,1.569037283
3\H,0.2922424092,-1.1212343116,2.5243284349\C,-1.0181261299,-2.1779666
887,1.1874566358\H,-1.7960117659,-1.4018565045,1.1306684678\H,-1.32991
57983,-2.9614012629,1.8954511702\O,-0.8677827991,-2.7736349806,-0.1148
385773\O,-2.1164277141,-3.374155669,-0.4521562114\O,-2.2528846192,-4.4
798121576,0.2337859433\O,-2.8495236267,-5.1811931622,1.9269566271\C,-2

.337504,-6.3169456514,1.537118764\H,-3.0821785564,-7.1018566806,1.2978
529984\C,-1.040553111,-6.7696889473,2.2019245237\H,-0.3234799349,-5.93
87750953,2.2077629244\H,-0.6003072567,-7.6229860559,1.671134526\H,-1.2
395126996,-7.0653327203,3.2405214386\H,-1.9970010933,-5.9747203648,0.3
854924976\\Version=ES64L-G09RevD.01\State=1-A\HF=-458.8077803\RMSD=6.5
71e-09\RMSF=4.578e-07\Dipole=0.6212026,-0.3110208,0.4988163\Quadrupole
=-3.2704958,6.7314595,-3.4609637,0.9193429,1.9763696,1.646791\PG=C01 [
X(C4H10O4)]\\@

TS1f

1\1\GINC-R1751\FTS\UM11\6-31+G(d,p)\C4H10O4\ROOT\28-Aug-2015\0\\# um11
/6-31+G** opt=(TS,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 # int=ultr
afine guess=mix freq=noraman nosymm\\TS for ROO* H abstraction from RO
O*\\0,1\H,2.5876583642,0.9363111187,-0.8652608539\C,1.8717871706,0.273
8398009,-0.357217969\H,1.3892951344,-0.3777131202,-1.1024909576\O,0.85
0832151,1.09514173,0.2399925117\O,0.0545031843,1.6160871966,-0.7289837
806\H,-0.8947870221,0.8122658988,-0.7397179712\C,-1.7034049496,-0.1238
483049,-0.3329283868\H,-2.1950132279,-0.4910940676,-1.241242621\O,-0.8
374335476,-1.0701828527,0.1782321981\O,-0.3354198665,-1.8839031642,-0.
7036326229\C,-2.5089246514,0.5146533628,0.7644693376\H,-3.0813827749,1
.3558125235,0.3569185271\H,-3.2065827077,-0.2034658186,1.2174304922\H,
-1.832946356,0.896644082,1.5407738372\C,2.498822229,-0.5281592218,0.76
47511928\H,1.7484292445,-1.1891412261,1.217081171\H,3.3143438979,-1.14
58261146,0.3680574227\H,2.907139728,0.1339791773,1.5387974723\\Version
=ES64L-G09RevD.01\HF=-458.8433367\S2=0.737441\S2-1=0.\S2A=0.037984\RMS
D=6.215e-09\RMSF=2.423e-06\Dipole=-0.4930083,0.0232038,0.1008113\Quadr
upole=8.0651314,-6.8602437,-1.2048876,-1.1004772,-0.2228871,-0.2299015
\PG=C01 [X(C4H10O4)]\\@

TS1g

1\1\GINC-R37\FTS\UM11\6-31+G(d,p)\C4H10O4\ROOT\16-Jan-2016\0\\# um11/6
-31+G** opt=(calcfc,ts,noeigen,maxcyc=200) freq int=ultrafine scf=maxc
yc=200 guess=read geom=allcheck\\EtOO* + EtOO* -> EtOOEt + 1O2\\0,1\C,
-1.0962774595,-0.3430985285,-0.191556439\C,-1.083533563,-1.5822002046,
0.6539471051\H,-1.8801446783,-1.5372658161,1.4098385398\H,-0.119912784
7,-1.6726619422,1.170134258\H,-1.2335045309,-2.4741388497,0.0360932502
\O,-2.8126109474,0.3610677138,0.4231675819\O,-3.1083692192,1.434832100
8,-0.1160172764\H,-0.655946396,0.5831280442,0.1715761474\H,-1.50361186
28,-0.3411465451,-1.1989144665\O,0.6405716961,-0.6974112548,-1.0968047
311\O,1.6206411622,-0.5888062602,-0.1876102346\C,2.2286270985,0.712847
6707,-0.2690192315\H,1.4538024195,1.4644411032,-0.0454437901\H,2.57168
71682,0.8589900358,-1.3026811093\C,3.363706585,0.7424142977,0.73479734
49\H,4.105623637,-0.0308785983,0.5007652793\H,2.9890548154,0.571457436
6,1.7516546832\H,3.8593468598,1.7208585966,0.7068620888\\Version=ES64L
-G09RevD.01\State=1-A\HF=-458.803962\S2=1.107353\S2-1=0.\S2A=0.785588\
RMSD=8.067e-09\RMSF=1.808e-06\Dipole=1.0763414,0.1812552,0.3134706\Qua
drupole=-0.6790025,0.1989615,0.480041,6.3252431,1.0591637,-0.4817154\P
G=C01 [X(C4H10O4)]\\@

EtOH

1\1\GINC-CA012\FOpt\RM11\6-31+G(d,p)\C2H6O1\ROOT\04-Sep-2015\0\\# m11/
6-31+G** int=ultrafine freq=noraman opt=maxcyc=200 scf=maxcyc=200\\Eth
anol\\0,1\C,-2.3600503965,0.0401545124,0.0174087217\H,-2.0107922827,-1
.0006114469,-0.0136207398\H,-2.0054936805,0.559366255,-0.8822008866\H,
-3.4575236542,0.0455909999,0.0068427887\C,-1.8477158335,0.7433969206,1
.2605801433\H,-0.743908675,0.7386517723,1.2742222359\H,-2.2021983947,0
.2226616162,2.1670986059\O,-2.3382660816,2.0808622962,1.2323058864\H,-
2.0324047925,2.5603713528,2.0089602473\\Version=AS64L-G09RevD.01\State
=1-A'\HF=-154.9657945\RMSD=2.245e-09\RMSF=8.080e-05\Dipole=0.4232014,-
0.3100647,0.5120081\Quadrupole=-0.7483599,-0.391188,1.1395479,0.996277
7,0.4843126,1.8012263\PG=CS [SG(C2H2O1),X(H4)]\\@

aldehyde

1\1\GINC-R1983\FOpt\RM11\6-31+G(d,p)\C2H4O1\ROOT\09-Jul-2014\0\\# m11/
6-31+G** opt freq=noraman\\Acetaldehyde\\0,1\C,-2.3527369222,0.0191123
064,0.0171933131\H,-2.0058861727,-1.0195231036,-0.0165850337\H,-2.0060
655968,0.5539146911,-0.8769705985\H,-3.4504932805,0.0427820943,0.00742
91437\C,-1.8569478725,0.7443985292,1.2461073794\O,-2.1222913095,1.9010
288246,1.4810248986\H,-1.2186464458,0.1679682681,1.9556224674\\Version
=ES64L-G09RevD.01\State=1-A\HF=-153.753906\RMSD=3.004e-09\RMSF=2.694e-
05\Dipole=0.1348858,-1.1052252,-0.4182938\Quadrupole=0.9868641,-1.5311
037,0.5442396,0.0932921,0.2350672,-1.2384991\PG=C01 [X(C2H4O1)]\\@

EtOOEt

1\1\GINC-CA012\FOpt\RM11\6-31+G(d,p)\C4H10O2\ROOT\04-Sep-2015\0\\# m11
/6-31+G** int=ultrafine freq=noraman opt=maxcyc=200 scf=maxcyc=200\\Et

OOEt\\0,1\C,-2.7331047584,-0.5384614132,0.0342937689\H,-2.3767314672,-1.5762333069,0.0173472631\H,-2.3744747888,-0.0316779904,-0.8709108137\H,-3.8303485024,-0.5460224918,0.018212406\C,-2.2208767293,0.1832512314,1.2678484258\H,-1.1196824685,0.188986703,1.3117100155\H,-2.5802592958,1.2241301138,1.3125793189\O,-2.7239071456,-0.5274637662,2.3921571808\O,-2.2267165341,0.1731060876,3.5359896308\C,-2.7297490469,-0.5376074241,4.660298387\H,-2.3703683177,-1.5784869771,4.6155682832\H,-3.8309432843,-0.5433409396,4.6164360091\C,-2.217520577,0.1841049081,5.8938530436\H,-2.5738919819,1.2218774639,5.910798782\H,-2.5761521084,-0.3226774078,6.7990576272\H,-1.1202768322,0.1916639871,5.9099351728\\Version=AS64L-G09RevD.01\State=1-A\HF=-308.6449007\RMSD=1.714e-09\RMSF=1.426e-04\Dipole=-0.000001,0.0000007,0.\Quadrupole=-1.8373823,-2.1166643,3.9540466,-0.3998323,-0.8444099,-1.1960726\PG=C02 [X(C4H10O2)]\\@

EtOOOH

1\1\GINC-CA012\FOpt\RM11\6-31+G(d,p)\C2H6O3\ROOT\04-Sep-2015\0\\# m11/6-31+G** int=ultrafine freq=noraman opt=maxcyc=200 scf=maxcyc=200\\Ethyltrioxide\\0,1\C,-3.0032352379,-0.1527775097,0.0123803419\H,-2.6516359001,-1.1917895116,-0.0138161106\H,-2.6448687075,0.3619805516,-0.8873457953\H,-4.0999706413,-0.1528803718,0.0033808995\C,-2.4810287336,0.5333340243,1.2620516933\H,-1.3798957984,0.5625677611,1.2821179795\H,-2.8455727341,0.0439658325,2.1793179718\O,-2.9827879725,1.8679954857,1.2138364924\O,-2.4753830873,2.4751690319,2.3936980533\O,-3.008258937,3.7870512154,2.2814996853\H,-2.6499126505,4.1791516405,3.0936251889\\Version=AS64L-G09RevD.01\State=1-A\HF=-305.1758145\RMSD=8.236e-09\RMSF=4.665e-05\Dipole=0.4278852,-0.5124362,0.4028631\Quadrupole=-2.6177414,1.9261485,0.6915929,1.0420699,0.4577334,4.2779886\PG=C01 [X(C2H6O3)]\\@

criegee

1\1\GINC-R927\FOpt\RM11\6-31+G(d,p)\C2H4O2\ROOT\07-Sep-2015\0\\# m11/6-31+G** opt freq int=ultrafine\\Criegee intm\\0,1\C,-0.9232989348,0.0802490449,0.0710909704\H,-0.7395601733,0.7680324422,-0.7621794032\C,-0.7387877484,-1.3911174352,0.014862439\H,-0.9902974572,-1.8439928135,0.9793396966\H,-1.3771007553,-1.8176694549,-0.7714928562\H,0.3028379433,-1.6271739783,-0.2439815239\O,-1.3168264221,0.6040403254,1.1348775191\O,-1.4794244523,1.9448672594,1.1683018581\\Version=ES64L-G09RevD.01\State=1-A\HF=-228.8070731\RMSD=9.701e-09\RMSF=1.691e-05\Dipole=0.5922946,-1.9403707,-1.1850726\Quadrupole=0.9215911,-2.0907432,1.1691521,0.8279531,0.1350363,-1.4988255\PG=C01 [X(C2H4O2)]\\@

EtOOH

1\1\GINC-CA012\FOpt\RM11\6-31+G(d,p)\C2H6O2\ROOT\04-Sep-2015\0\\# m11/6-31+G** int=ultrafine freq=noraman opt=maxcyc=200 scf=maxcyc=200\\Ethylperoxide\\0,1\C,-3.0022846619,-0.1591323915,0.0102558197\H,-2.6455940886,-1.1969320124,-0.0069287802\H,-2.6443837483,0.3472446549,-0.8950752112\H,-4.0994854705,-0.1676214125,-0.0043517178\C,-2.4881611473,0.5411083061,1.2548981568\H,-1.3869973329,0.5768940158,1.2823992683\H,-2.8497372903,0.0593245749,2.1777989113\O,-2.9892107192,1.8708336506,1.2049985922\O,-2.487294462,2.500431447,2.3888631885\H,-2.862348939,3.3867606771,2.2885064225\\Version=AS64L-G09RevD.01\State=1-A\HF=-230.0728593\RMSD=9.521e-09\RMSF=1.471e-04\Dipole=-0.057421,-0.1235994,-0.1652393\Quadrupole=-1.515246,3.3750098,-1.8597638,-0.8922767,-0.7550575,1.2844599\PG=C01 [X(C2H6O2)]\\@

===*n*-Butyl===

***n*BuOH**

1\1\GINC-R233\FOpt\UM11\6-31+G(d,p)\C4H10O1\ROOT\10-Jan-2016\0\\# um11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafine\\ROH R = n-butyl\\0,1\H,-1.6312030428,0.7879105911,0.893540971\C,-1.4607286717,0.1603929607,0.\C,-0.0313543937,-0.3560455056,0.\H,0.1083790786,-0.9982335642,0.8834169086\H,0.1083790786,-0.9982335642,-0.8834169086\C,0.998615618,0.7756684626,0.\H,0.8392657466,1.4170976636,-0.881963668\H,0.8392657466,1.4170976636,0.881963668\C,2.4353117859,0.2505030294,0.\H,3.1667839034,1.069530458,0.\H,2.6245541611,-0.3710642882,0.8869531147\H,2.6245541611,-0.3710642882,-0.8869531147\H,-1.6312030428,0.7879105911,-0.893540971\O,-2.3377216839,-0.9606171455,0.\H,-3.2533422156,-0.6638836336,0.\\Version=ES64L-G09RevD.01\State=1-A'\HF=-233.5416819\S2=0.\S2-1=0.\S2A=0.\RMSD=3.586e-09\RMSF=1.858e-05\Dipole=-0.1526295,0.6932483,0.\Quadrupole=3.1305003,-2.730262,-0.4002384,-2.4299568,0.,0.\PG=CS [SG(C4H2O1),X(H8)]\\@

aldehyde

1\1\GINC-R328\FOpt\RM11\6-31+G(d,p)\C4H8O1\ROOT\17-Dec-2015\0\\# m11/6-31+g(d,p) freq opt=maxcyc=200 scf=maxcyc=300 int=ultrafine\\Butanal (singlet)\\0,1\O,-0.6950898665,0.2094174114,0.5210707193\C,-1.7493963085,0.7761823168,0.3457464047\C,-3.0279600017,0.0985155468,-0.0780212293

\H,-3.7236914051,0.1446594365,0.7777645277\H,-2.8144698174,-0.95873976
78,-0.2841816864\H,-1.8184215777,1.8822354121,0.4927882707\C,-3.670152
0654,0.7990232832,-1.2842262428\H,-3.8059335556,1.8682176039,-1.056386
5943\H,-2.9845020184,0.7462871921,-2.1431719999\C,-5.0160733947,0.1748
338624,-1.6551608132\H,-5.4646594459,0.6768414036,-2.522136644\H,-4.89
94593508,-0.8891898849,-1.9044405088\H,-5.7256530723,0.2461013738,-0.8
184032538\\Version=ES64L-G09RevD.01\State=1-A\HF=-232.3308584\RMSD=7.5
19e-09\RMSF=4.624e-06\Dipole=-1.208268,0.3910312,-0.3104446\Quadrupole
=-4.4192578,2.4787275,1.9405303,1.3087702,-2.463999,0.8367613\PG=C01 [
X(C4H8O1)]\\@

aldehyde* (triplet)

1\1\GINC-R512\FOpt\UM11\6-31+G(d,p)\C4H8O1(3)\ROOT\17-Dec-2015\0\\# um
11/6-31+g(d,p) freq opt=maxcyc=200 scf=maxcyc=300 int=ultrafine\\Butan
al (triplet)\\0,3\O,-0.9146395161,0.1752278678,1.0641950336\C,-1.64417
82438,0.7788844347,0.1565524088\C,-2.9778360374,0.109860476,-0.1589753
285\H,-3.6118945253,0.0993651539,0.7458454623\H,-2.7876321677,-0.93954
31452,-0.4286106119\H,-1.6659741855,1.874054706,0.3030642241\C,-3.6978
812567,0.8271432868,-1.3038957243\H,-3.8587308933,1.8811376663,-1.0280
774822\H,-3.048848387,0.8292442312,-2.1914143889\C,-5.0374596947,0.164
895081,-1.6296159211\H,-5.5493849988,0.6826400177,-2.4512364896\H,-4.8
95025878,-0.8830778505,-1.9297097063\H,-5.7059760958,0.1745532642,-0.7
568805161\\Version=ES64L-G09RevD.01\State=3-A\HF=-232.2095959\S2=2.004
94\S2-1=0.\S2A=2.000013\RMSD=6.649e-09\RMSF=1.803e-05\Dipole=-0.761167
6,0.2874852,-0.3147332\Quadrupole=-2.2559394,2.496353,-0.2404136,1.015
8809,-1.4003748,1.038386\PG=C01 [X(C4H8O1)]\\@

^{n}BuOO^{n}Bu

1\1\GINC-R39\FOpt\RM11\6-31+G(d,p)\C8H18O2\ROOT\07-Jan-2016\0\\# m11/6
-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafine\\n
BuOOnBu\\0,1\C,0.2882104421,2.9579778727,-0.0000382393\H,-0.3522711729
,3.0961574725,-0.8846924478\H,-0.352342568,3.0961067834,0.8845723273\C
,0.8361379285,1.5392724657,-0.000052555\H,1.4500261616,1.3454199205,-0
.895751835\H,1.4500063863,1.3453934996,0.8956548288\O,-0.2788822432,0.
6593517332,-0.0000778252\O,0.2788822417,-0.6593517335,-0.0000857341\C,
-0.8361379292,-1.5392724662,-0.0000431796\H,-1.450042789,-1.3454165036
,-0.8957303211\H,-1.4499897601,-1.3453969175,0.895676342\C,-0.28821044
28,-2.9579778733,-0.0000444815\H,0.3523603563,-3.0961094947,0.88455278
49\H,0.3522533818,-3.0961547627,-0.8847119885\C,1.4117073296,3.9988035
673,0.000037298\H,2.0537950292,3.8444705567,-0.8817923681\H,2.05370745
1,3.844428445,0.88192205\C,0.8710207863,5.4295784505,0.0000473584\H,0.
2479222829,5.6129348454,0.8872217938\H,1.682946369,6.1688308165,0.0001
044204\H,0.2480067279,5.6129774818,-0.8871767652\C,-1.4117073284,-3.99
88035685,0.0000504996\H,-2.0536893372,-3.8444312415,0.8819488839\H,-2.
0538131393,-3.8444677636,-0.8817655322\C,-0.8710207838,-5.4295784505,0
.0000450828\H,-1.6829463637,-6.1688308187,0.0001167662\H,-0.2480251165
,-5.6129748161,-0.8871924802\H,-0.24790389,-5.6129375106,0.8872060767\
\Version=ES64L-G09RevD.01\State=1-A\HF=-465.7961474\RMSD=4.911e-09\RMS
F=2.661e-05\Dipole=0.,0.,0.0000406\Quadrupole=-1.9216159,3.31268,-1.39
10641,3.1457697,0.0000118,-0.0000208\PG=C01 [X(C8H18O2)]\\@

^{n}BuO•

1\1\GINC-CA037\FOpt\UM11\6-31+G(d,p)\C4H9O1(2)\ROOT\11-Sep-2015\0\\# u
m11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafi
ne\\RO* R = n-butyl\\0,2\H,-2.0181003583,-0.6835087497,1.2570296745\C,
-2.3657632063,-0.9518540652,0.2356703344\O,-1.2533156179,-1.3139368185
,-0.4832642314\C,-3.2092369938,0.1610230575,-0.3789334164\H,-2.5757572
098,1.0515720319,-0.5135749528\H,-3.5305056673,-0.1529156831,-1.384284
7791\C,-4.4272555887,0.5048670712,0.4809919706\H,-5.0451017862,-0.3977
57175,0.6187819756\H,-4.0922643907,0.80431959,1.4877489549\C,-5.275703
1248,1.620027541,-0.1313166238\H,-6.1459358159,1.8572471871,0.49475322
58\H,-4.6857585972,2.5400213929,-0.2514313086\H,-5.6445148307,1.330477
564,-1.1257961394\H,-2.9631934698,-1.8758155122,0.3951253137\\Version=
AS64L-G09RevD.01\State=2-A"\HF=-232.8661577\S2=0.752851\S2-1=0.\S2A=0.
750006\RMSD=4.430e-09\RMSF=1.045e-04\Dipole=-0.7731046,0.2733732,0.469
5545\Quadrupole=-2.6217226,1.0239681,1.5977545,2.8306567,1.9630085,-0.
73058\PG=CS [SG(C4H1O1),X(H8)]\\@

^{n}BuOO•

1\1\GINC-CA116\FOpt\UM11\6-31+G(d,p)\C4H9O2(2)\ROOT\11-Sep-2015\0\\# u
m11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafi
ne\\ROO* R = n-butyl\\0,2\H,-1.9977452139,-0.646646918,1.2348620605\C,
-2.391463238,-0.9385048158,0.2512959668\O,-1.250335797,-1.2568495664,-
0.5866103862\O,-0.3655253026,-0.302346171,-0.5578945263\C,-3.230389573
6,0.161921205,-0.3766008763\H,-2.5921742505,1.0471694184,-0.5164621322
\H,-3.5632198125,-0.1633276614,-1.374316808\C,-4.4404000048,0.51326505
28,0.4939396114\H,-5.0574564175,-0.3862797661,0.6490258577\H,-4.094058

605,0.8292071209,1.4907502128\C,-5.2918810168,1.6200383266,-0.13034959
16\H,-6.1551584895,1.8679161732,0.5007162462\H,-4.701168476,2.53636379
84,-0.2699042113\H,-5.6708695122,1.3144477443,-1.1158992598\H,-2.93910
032,-1.886475951,0.3323338462\\Version=AS64L-G09RevD.01\State=2-A\HF=-
308.0092353\S2=0.752951\S2-1=0.\S2A=0.750005\RMSD=5.840e-09\RMSF=3.561
e-05\Dipole=-1.1799634,0.0294294,0.5035732\Quadrupole=-3.7174892,1.917
7154,1.7997738,1.1747575,1.7872287,-0.8970353\PG=C01 [X(C4H9O2)]\\@

TScomb (*n*Bu)

1\1\GINC-R123\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\10-Dec-2015\0\\# um11/
6-31+g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=300 # freq=n
oraman guess=read geom=allcheck nosymm iop(1/8=1) int=ultrafine\\TS fo
r ROO-OOR symmetric O-O bond cleavage (R = n-Bu)\\0,1\H,1.696274817,0.
9506834805,-0.5312236007\C,2.0048717075,-0.0962204213,-0.67099719\O,0.
8959977431,-0.9184787451,-0.2352382758\O,0.5432088923,-0.5870042125,0.
9918053941\O,-0.5495023407,0.9112101607,0.7234890883\O,-0.9006373932,0
.7973317906,-0.5429200671\C,-2.0090157538,-0.1253472746,-0.6685565979\
H,-1.7007489079,-1.0589941727,-0.174546781\C,3.2769110742,-0.425256105
9,0.0923326168\H,3.0885582523,-0.2766582412,1.1658945744\H,3.522603719
9,-1.488798529,-0.0534957149\C,-3.2819787042,0.4469470894,-0.067715855
3\H,-3.0940976701,0.6806460241,0.9906549413\H,-3.5287806573,1.39330153
09,-0.5739131862\C,4.4466856272,0.4517985732,-0.3632949654\H,4.6101125
118,0.3168603945,-1.444815025\H,4.1853587345,1.5120374718,-0.218339361
4\C,-4.4505156594,-0.5352365976,-0.1904757703\H,-4.6137105806,-0.78439
16787,-1.2515470458\H,-4.1878506999,-1.4788076375,0.313585509\C,5.7353
841818,0.1301009097,0.3953499333\H,6.5678675455,0.7644338675,0.0636577
678\H,5.6019963017,0.2850546395,1.4754268167\H,6.0286620835,-0.9185256
609,0.2432570072\C,-5.739889314,0.0282049768,0.4093434001\H,-6.5713873
111,-0.6830286045,0.3189115316\H,-5.606654224,0.2583483292,1.475941372
3\H,-6.0345481671,0.9582402504,-0.0975813979\H,-2.0951209373,-0.291308
6246,-1.7507214218\H,2.0925041281,-0.3151889828,-1.7435716962\\Version
=ES64L-G09RevD.01\HF=-616.0160412\S2=0.39613\S2-1=0.\S2A=0.004405\RMSD
=9.963e-09\RMSF=3.156e-06\Dipole=0.0008065,-0.1389154,-0.7764745\Quadr
upole=7.2791092,-4.5741311,-2.7049781,1.1448094,-0.1946137,0.3318099\P
G=C01 [X(C8H18O4)]\\@

^{n}BuO$_4$^{n}Bu

1\1\GINC-R2648\FOpt\RM11\6-31+G(d,p)\C8H18O4\ROOT\29-Aug-2015\0\\# m11
/6-31+G** opt=maxcyc=200 scf=maxcyc=200 # int=ultrafine freq=noraman\\
RO4R R = n-butyl\\0,1\H,1.9763174323,-0.4753494767,1.3688126546\C,2.43
80483583,-0.081888124,0.4492179699\O,1.3958123989,0.3638825816,-0.4302
994485\O,0.5235071272,-0.710133293,-0.6631849499\O,-0.3222712691,-0.81
86348814,0.4516407937\O,-1.267960507,0.2144979605,0.3681611311\C,-2.28
11401957,-0.1739397213,-0.5705118885\H,-1.7977903067,-0.4009748493,-1.
5340932316\C,3.3637177691,-1.0967791382,-0.2044127127\H,2.7761402896,-
1.9771610385,-0.5056527128\H,3.7829841844,-0.6580041536,-1.1231505225\
C,-3.1311281804,-1.3324211284,-0.0709722321\H,-2.4825551324,-2.2036695
481,0.1060716301\H,-3.5752331385,-1.0575736387,0.8983662551\C,4.491997
6078,-1.521587144,0.7397479328\H,5.0661783969,-0.6334583537,1.04980345
3\H,4.0587647971,-1.9466925211,1.6593157119\C,-4.2319315545,-1.6969982
508,-1.0710874273\H,-4.8677155486,-0.8159274124,-1.2557049961\H,-3.774
8457533,-1.9572693824,-2.0392513878\C,5.4315323599,-2.5415071795,0.094
2051449\H,6.2367251328,-2.8394912731,0.7786129276\H,4.8830146897,-3.44
859182,-0.1972890204\H,5.895275612,-2.1276411186,-0.812663959\C,-5.095
4451137,-2.8602591229,-0.580315377\H,-5.8814412741,-3.1138302393,-1.30
38176776\H,-4.4840414886,-3.7592105868,-0.4168688226\H,-5.5822528393,-
2.6114083085,0.3735431403\H,-2.8751359617,0.7435001224,-0.6884696389\H
,2.9676936477,0.8486653295,0.6981898402\\Version=ES64L-G09RevD.01\Stat
e=1-A\HF=-616.0343344\RMSD=4.471e-09\RMSF=5.818e-06\Dipole=0.0135084,-
0.3878381,-0.0275023\Quadrupole=7.4173507,-4.2394015,-3.1779492,0.1678
481,3.3597023,0.0415354\PG=C01 [X(C8H18O4)]\\@

TS1a (*n*Bu)

1\1\GINC-R2666\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\29-Aug-2015\0\\# um11
/6-31+G** opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 # int=ultr
afine freq=noraman guess=mix nosymm\\TS for single RO--O bond cleavage
 (R = n-butyl)\\0,1\H,-1.7167763377,-1.0172019141,0.8552839289\C,-2.04
46847764,-1.0809158782,-0.2008426902\O,-0.9485608961,-1.1711932189,-1.
0483966151\O,0.0948681513,0.3976064813,-0.5964078458\O,0.0365060908,0.
549234975,0.6588948874\O,0.8643136842,-0.4184895409,1.3818980063\C,1.9
970625414,-0.8098301419,0.6032034693\H,1.6575288539,-1.2509086397,-0.3
453590118\C,-3.021615975,0.0356307915,-0.5549734375\H,-2.4931794739,0.
9992496412,-0.4783229428\H,-3.3236319462,-0.0779828999,-1.6074690479\C
,2.9996509213,0.3175216963,0.3982138175\H,2.5254853671,1.132299243,-0.
1703382988\H,3.2819784172,0.7280831484,1.379883574\C,-4.2497341831,0.0
392549441,0.357930283\H,-4.7694312326,-0.9296073904,0.278313718\H,-3.9
24527216,0.130464132,1.4068802142\C,4.2430875797,-0.1714121807,-0.3504

05369\H,4.7110102535,-0.9944842209,0.2136357221\H,3.9406035869,-0.5926
430661,-1.3221385399\C,-5.2201165133,1.172313448,0.0199507555\H,-6.097
6383757,1.1650317393,0.679990728\H,-4.7288706055,2.1505644098,0.122141
4461\H,-5.5765302097,1.0865128583,-1.0166258091\C,5.2620358239,0.94822
75369,-0.5681319792\H,6.1493521482,0.5873684815,-1.1045778974\H,4.8231
507042,1.7675738555,-1.1551251288\H,5.5954205948,1.3676132753,0.391936
9412\H,2.4152736563,-1.6141192018,1.2261263681\H,-2.5261296332,-2.0750
943637,-0.3043172465\\Version=ES64L-G09RevD.01\HF=-615.9986343\S2=0.59
9913\S2-1=0.\S2A=0.011563\RMSD=3.907e-09\RMSF=1.181e-06\Dipole=0.26255
47,-0.1420298,0.2601413\Quadrupole=6.7913688,-1.6907059,-5.1006629,0.1
298485,-0.0902582,-0.9542625\PG=C01 [X(C8H18O4)]\\@

int-1 (*n*Bu)

1\1\GINC-R2462\FOpt\UM11\6-31+G(d,p)\C8H18O4\ROOT\31-Aug-2015\0\\# um1
1/6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=mix
nosymm\\ROOO* + RO* caged complex (R = n-Butyl)\\0,1\H,-1.667657,-0.80
9825,1.104875\C,-2.024209,-1.222339,0.140277\O,-0.960509,-1.608601,-0.
639722\O,0.171161,0.866993,-0.728221\O,0.058006,1.054029,0.502269\O,0.
773299,0.060985,1.328752\C,1.818857,-0.57325,0.59235\H,1.410665,-1.008
876,-0.33048\C,-3.018936,-0.293041,-0.554183\H,-2.480333,0.610861,-0.8
79525\H,-3.394243,-0.785828,-1.464079\C,3.006054,0.346365,0.337503\H,2
.690287,1.185809,-0.301137\H,3.340008,0.7741,1.295393\C,-4.178368,0.09
144,0.367639\H,-4.703815,-0.819599,0.698489\H,-3.777044,0.565165,1.278
086\C,4.157307,-0.405906,-0.336686\H,4.469374,-1.246657,0.303942\H,3.8
00292,-0.849546,-1.279545\C,-5.168795,1.039133,-0.311053\H,-5.992571,1
.312723,0.361454\H,-4.668424,1.965845,-0.626485\H,-5.604555,0.574995,-
1.207412\C,5.356214,0.50223,-0.61471\H,6.178488,-0.049746,-1.088668\H,
5.074651,1.327953,-1.283605\H,5.738802,0.943641,0.31675\H,2.082881,-1.
401491,1.266782\H,-2.521186,-2.184573,0.403722\\Version=ES64L-G09RevD.
01\HF=-616.0035318\S2=0.991131\S2-1=0.\S2A=0.049\RMSD=6.868e-09\RMSF=3
.115e-06\Dipole=0.0825206,-0.2074871,0.335339\Quadrupole=6.6896555,-2.
3402464,-4.3494092,0.367046,-0.5730417,-1.6044865\PG=C01 [X(C8H18O4)]\
\@

TS1b (*n*Bu)

1\1\GINC-R476\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\28-Dec-2015\0\\# um11/
6-31+G** opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 # int=ultra
fine freq=noraman guess=read geom=allcheck\\TS for 2nd O-O cleavage (R
= n-Bu)\\0,1\H,1.6108368573,0.9308724927,0.988287175\C,2.0404056174,1.
3067061969,0.0305349311\O,0.9272109162,1.514577036,-0.7441765854\O,-0.
2506069969,-1.2952831958,-0.7752457552\O,0.0644650216,-1.1989027328,0.
3835152696\O,-0.7434059387,0.1478800803,1.208906802\C,-1.7381506272,0.
5787367761,0.3437015882\H,-1.3619721008,0.5215843356,-0.7006763176\C,3
.0300483659,0.2881793236,-0.5366196318\H,2.4886069493,-0.6425725291,-0
.7653041798\H,3.4245869573,0.6682544968,-1.4920374402\C,-3.0556096811,
-0.1741009284,0.497207733\H,-2.8731416672,-1.2448068297,0.3071936186\H
,-3.3958011972,-0.0918487281,1.5410233663\C,4.183259775,0.0108831323,0
.4302159642\H,4.6910050298,0.9576116674,0.6764316412\H,3.7776225919,-0
.3780305903,1.3781666292\C,-4.1324321923,0.3477637685,-0.4563967542\H,
-4.2953982213,1.421811813,-0.2704656339\H,-3.7712752142,0.2656765893,-
1.4941697414\C,5.1958417718,-0.9811885558,-0.1441038606\H,6.0164362286
,-1.1746536602,0.5592665581\H,4.7145391891,-1.9425476989,-0.3738955317
\H,5.6341807351,-0.5977296988,-1.0766731299\C,-5.4548471548,-0.4064402
132,-0.3086166557\H,-6.2191759654,-0.0224683826,-0.9970676737\H,-5.319
855943,-1.4773690801,-0.5178200352\H,-5.8459462397,-0.3147759151,0.714
8787554\H,-1.8369967231,1.6635587221,0.5359346295\H,2.5283948563,2.269
0483081,0.283545265\\Version=ES64L-G09RevD.01\State=1-A\HF=-615.996535
9\S2=1.297267\S2-1=0.\S2A=1.869774\RMSD=7.125e-09\RMSF=6.174e-07\Dipol
e=0.1392103,0.0207527,0.0442927\Quadrupole=5.8454196,-1.7809431,-4.064
4765,0.1177673,0.9306692,1.1756064\PG=C01 [X(C8H18O4)]\\@

int-2 (*n*Bu)

1\1\GINC-R47\FOpt\UM11\6-31+G(d,p)\C8H18O4\ROOT\10-Dec-2015\0\\# um11/
6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=read g
eom=allcheck nosymm int=ultrafine\\RO* + 3O2 + RO* caged complex (R =
n-Butyl)\\0,1\H,1.5004435705,0.8293717816,0.8374158664\C,1.971260073
,1.1597798079,-0.118556647\O,0.8984338418,1.2884204758,-0.9628671631\O
,-0.6600409628,-1.3219377403,-1.2551007387\O,-0.0400384734,-1.42338960
25,-0.2371033085\O,-0.809732107,0.584456004,1.4879477201\C,-1.82683878
59,0.9179812713,0.6272498728\H,-1.4037136535,1.0043430495,-0.396548729
7\C,3.0282664533,0.1540695076,-0.5734201716\H,2.5397674172,-0.81631508
49,-0.7507454391\H,3.4420343331,0.4845224992,-1.5392018858\C,-3.040426
1903,-0.0066197328,0.6771984454\H,-2.6910385146,-1.0460227739,0.572680
0154\H,-3.5135944337,0.0670841938,1.6686691878\C,4.1546421831,0.002958
6661,0.4514666739\H,4.6105964458,0.9880306439,0.6425952622\H,3.7311231
197,-0.3329991265,1.4116829849\C,-4.0517957839,0.3163222087,-0.4244256
125\H,-4.3695096844,1.3682527758,-0.3364481133\H,-3.5566120929,0.22431

80859,-1.4050610791\C,5.2310084276,-0.9804817535,-0.0107378671\H,6.032
4204309,-1.0823373298,0.7328655248\H,4.8018024117,-1.9778936804,-0.182
9809283\H,5.6866348706,-0.6473959496,-0.9543648099\C,-5.2769065534,-0.
5978221677,-0.376242931\H,-5.9905908935,-0.360908221,-1.1762802163\H,-
4.9825243775,-1.6512644035,-0.4878003474\H,-5.8021501598,-0.4996883164
,0.5846739351\H,-2.1012455633,1.9662352234,0.8803411417\H,2.4070996516
,2.1538906881,0.1079693579\\Version=ES64L-G09RevD.01\HF=-616.0102655\S
2=1.995121\S2-1=0.\S2A=4.089958\RMSD=8.837e-09\RMSF=3.873e-06\Dipole=0
.0071087,0.0774829,0.0213279\Quadrupole=5.8698314,-0.9668697,-4.902961
8,-0.5221629,0.3546037,1.3442531\PG=C01 [X(C8H18O4)]\\@

int-2* (*n*Bu; triplet)

1\1\GINC-R44\FOpt\UM11\6-31+G(d,p)\C8H18O4(3)\ROOT\10-Dec-2015\0\\# um
11/6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=rea
d geom=allcheck nosymm int=ultrafine\\RO* + 3O2 + RO* caged complex (R
= n-Butyl)\\0,3\H,1.2181129109,0.7311721064,0.6102790275\C,1.750951
9827,1.0973345947,-0.3057593812\O,0.7571852692,1.2111704996,-1.2385208
763\O,-0.8397414443,-1.3331819363,-1.3925089605\O,-0.1005164467,-1.510
1854164,-0.4683311646\O,-0.6659188078,0.5639959863,1.7015511523\C,-1.6
590975585,0.9388683467,0.8391367679\H,-1.1536619147,0.9806781589,-0.16
09540574\C,2.8827386051,0.1403522529,-0.6762061148\H,2.4492569649,-0.8
407895133,-0.9229966792\H,3.3765116,0.5103279435,-1.5885306096\C,-2.86
58712236,0.0035973734,0.788426071\H,-2.5040236437,-1.0325278504,0.7043
822856\H,-3.4116104326,0.0700769479,1.7427631824\C,3.9062112824,0.0016
006429,0.4529449621\H,4.3068861293,0.9960168219,0.7085301279\H,3.40092
2446,-0.370109117,1.3587721354\C,-3.7995621145,0.3391403306,-0.3764088
098\H,-4.1196091654,1.3910727721,-0.2998819954\H,-3.2399240221,0.25441
65852,-1.3222997985\C,5.0561759249,-0.9354812035,0.0804255239\H,5.7832
714155,-1.0280301759,0.8978788175\H,4.6807658446,-1.9422003211,-0.1525
85224\H,5.5909873522,-0.5665382987,-0.8066136942\C,-5.0274927411,-0.57
14575661,-0.4173196718\H,-5.6863287154,-0.3242558051,-1.2600808627\H,-
4.729268712,-1.6247270978,-0.5200970011\H,-5.6145626726,-0.4808481481,
0.5079455344\H,-1.9454237784,1.994909776,1.0219900957\H,2.1214106659,2
.1005623105,-0.0110607826\\Version=ES64L-G09RevD.01\HF=-616.0109199\S2
=2.98483\S2-1=0.\S2A=2.022768\RMSD=6.130e-09\RMSF=6.222e-06\Dipole=0.0
001532,0.069853,0.0227667\Quadrupole=5.9301512,-0.4979305,-5.4322207,-
0.2484846,-0.2650386,1.3440821\PG=C01 [X(C8H18O4)]\\@

^{3}[*n*BuO•]$_2$ (alkoxyl radical dimer, triplet)

1\1\GINC-R91\FOpt\UM11\6-31+G(d,p)\C8H18O2(3)\ROOT\11-Jan-2016\0\\# um
11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafin
e iop(1/8=1)\\RO*--*OR dimer caged complex (R = n-Butyl)\\0,3\H,1.7735
955548,2.1903584372,0.4008250723\C,1.707319048,1.6684528842,-0.5810036
1\O,0.4529933578,1.9756947971,-1.0481975824\O,-0.295198553,1.480359609
7,1.721401677\C,-1.5615847987,1.4499501039,1.1909111476\H,-1.580168181
7,2.2962390491,0.4669252711\C,1.9840583989,0.1787128578,-0.402466254\H
,1.2301441756,-0.2284044098,0.2882602684\H,1.8523664108,-0.3278530803,
-1.37205806\C,-1.9369463783,0.1494208609,0.487038535\H,-1.2043136847,-
0.0288208205,-0.3146626579\H,-1.8515392729,-0.6825942627,1.2043347948\
C,3.3917738467,-0.0814810429,0.1381933304\H,4.1365517772,0.3606606447,
-0.5438585548\H,3.509944475,0.4353153242,1.1043058415\C,-3.3525697866,
0.1994796855,-0.0919046748\H,-4.0736409353,0.4123780083,0.7143866374\H
,-3.4239571267,1.0390745027,-0.8021186836\C,3.678322675,-1.5734652826,
0.3148468952\H,4.6895770108,-1.7483523726,0.70537332\H,2.9625423701,-2
.0274811863,1.0148310984\H,3.5899874962,-2.1055458769,-0.6433722048\C,
-3.7376261194,-1.102964041,-0.7952638477\H,-4.7537827148,-1.0551165877
,-1.208625302\H,-3.0461676175,-1.3183138529,-1.6222818331\H,-3.6968056
763,-1.9519122039,-0.0976104281\H,-2.2927078902,1.7365469305,1.9752962
471\H,2.4666831392,2.1699503243,-1.2164324432\\Version=ES64L-G09RevD.0
1\State=3-A\HF=-465.7400609\S2=2.00579\S2-1=0.\S2A=2.00002\RMSD=3.099e
-09\RMSF=2.776e-06\Dipole=-0.0087801,-0.2423174,-0.0451389\Quadrupole=
4.9207419,-2.1226293,-2.7981126,0.1670682,-2.2021667,0.2157964\PG=C01
[X(C8H18O2)]\\@

TS-H (*n*Bu)

1\1\GINC-R53\FTS\UM11\6-31+G(d,p)\C8H18O2(3)\ROOT\05-Jan-2016\0\\# um1
1/6-31+G(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 freq=n
oraman int=ultrafine\\PES for H abstraction: nBuO*--*OnBu (diradical t
riplet)\\0,3\H,0.3755924257,-0.8988669759,0.0720780692\C,1.3592377677,
-0.2983228006,0.3906889339\O,1.0680033017,0.7643928751,1.1593891753\O,
-0.9320554343,-1.3008090356,-0.2568556536\C,-1.7285630433,-0.297081191
5,0.2985671578\H,-1.3639470263,-0.0393054038,1.3136871975\C,-1.8244813
298,0.9608066051,-0.5603001793\H,-2.2007707827,0.6840381438,-1.5577538
583\H,-0.8090768088,1.3674046192,-0.7025514538\C,2.0931425123,0.100669
7358,-0.9076370865\H,1.4770362355,0.8435668543,-1.4355642647\H,3.04642
97715,0.5838927293,-0.6451702098\H,1.985751302,-1.0007346727,0.9809275
199\H,-2.7287015899,-0.7506643517,0.4443492466\C,-2.7166706358,2.03037

69501,0.0722729109\H,-2.3231539732,2.2837827708,1.0698260653\H,-3.7260
983888,1.6172079981,0.2319749532\C,-2.8073227387,3.2953687138,-0.78277
41827\H,-3.2197485009,3.0683943376,-1.7765273866\H,-3.449200262,4.0549
958655,-0.3170697099\H,-1.8120650782,3.7393632552,-0.9291209381\C,2.31
22672184,-1.125570005,-1.7963978038\H,2.9254334954,-1.8637702017,-1.25
56918858\H,1.3397772706,-1.6022274677,-1.9914151989\C,2.9911556279,-0.
7518756589,-3.1150660885\H,3.9711732871,-0.2856497834,-2.9387895349\H,
3.1475476331,-1.6360521992,-3.7465150134\H,2.3776267638,-0.038104186,-
3.682963261\\Version=ES64L-G09RevD.01\State=3-A\HF=-465.7277101\S2=2.0
09662\S2-1=0.\S2A=2.000045\RMSD=3.114e-09\RMSF=9.533e-07\Dipole=0.4612
255,0.1350692,-0.2109832\Quadrupole=4.565578,-3.5260857,-1.0394923,-3.
4195556,-1.2689675,-1.347456\PG=C01 [X(C8H18O2)]\\@

===*sec*-Butyl===

^{s}BuOH

1\1\GINC-R356\FOpt\UM11\6-31+G(d,p)\C4H10O1\ROOT\10-Jan-2016\0\\# um11
/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafine\
\ROH R = sec-butyl\\0,1\C,-0.5149200692,-0.1544269588,0.3917524649\H,-
0.3854364406,-0.1470551725,1.4911621663\C,-0.8846102246,1.2496140258,-
0.0803814745\H,-0.1358040129,1.9872761707,0.2378223368\H,-0.9594459245
,1.2688203129,-1.1770967541\H,-1.8533200802,1.5624880571,0.3368987088\
C,0.7700120448,-0.6775789132,-0.2437079077\H,0.9036169411,-1.716653028
7,0.0897973128\H,0.6192533241,-0.7122278497,-1.3338909667\C,2.00276722
65,0.1569935548,0.1060871163\H,2.9179142702,-0.3194335375,-0.268320446
9\H,1.9524193131,1.1628193837,-0.3332680304\H,2.1089303682,0.270858894
1,1.195472322\O,-1.5361490577,-1.0906494257,0.0419378063\H,-2.38274611
85,-0.7905311928,0.3909320061\\Version=ES64L-G09RevD.01\State=1-A\HF=-
233.5474852\S2=0.\S2-1=0.\S2A=0.\RMSD=9.334e-09\RMSF=4.574e-06\Dipole=
-0.0321792,0.6091336,0.3410544\Quadrupole=2.3310044,-2.3142921,-0.0167
122,-1.6898215,-1.5834176,-0.4901306\PG=C01 [X(C4H10O1)]\\@

ketone

1\1\GINC-R3196\FOpt\RM11\6-31+G(d,p)\C4H8O1\ROOT\17-Dec-2015\0\\# m11/
6-31+g(d,p) freq opt=maxcyc=200 scf=maxcyc=200 int=ultrafine\\s-Bu ket
one (singlet)\\0,1\O,-0.6970427532,0.0132954407,0.0554959208\C,-1.6779
215345,0.7287931845,0.107632897\C,-3.0551212299,0.211337919,-0.2748149
59\H,-3.610584112,0.0546656525,0.6647689438\H,-2.9154553912,-0.7708181
247,-0.7424101117\C,-1.5763647103,2.1711262713,0.5630066868\H,-0.60659
16611,2.3355274447,1.0424899261\H,-1.6622714199,2.8341620006,-0.310452
3326\H,-2.3949781799,2.427636461,1.249893391\C,-3.8396511417,1.1656814
168,-1.1826177608\H,-4.8027854994,0.7219083931,-1.4637157071\H,-4.0474
483985,2.1222293906,-0.6842856335\H,-3.2862779584,1.3770595398,-2.1080
512509\\Version=ES64L-G09RevD.01\State=1-A\HF=-232.3430138\RMSD=2.823e
-09\RMSF=1.534e-05\Dipole=-1.0963862,0.7577464,0.0101126\Quadrupole=-2
.0677957,0.289013,1.7787827,3.047521,-0.2114939,0.540768\PG=C01 [X(C4H
8O1)]\\@

ketone* (triplet)

1\1\GINC-R183\FOpt\UM11\6-31+G(d,p)\C4H8O1(3)\ROOT\11-Jan-2016\0\\# um
11/6-31+g(d,p) freq opt=maxcyc=200 scf=maxcyc=200 int=ultrafine\\s-Bu
ketone (triplet)\\0,3\O,-0.8309336432,-0.0571375255,0.5177390489\C,-1.
6376908664,0.8104444624,-0.0654460314\C,-3.0143972854,0.2196641968,-0.
3612779276\H,-3.5210587209,0.0021804504,0.5969354182\H,-2.872603658,-0
.7422357365,-0.8723581299\C,-1.5524720687,2.1969053412,0.545460236\H,-
0.5061351896,2.4877662751,0.6934658013\H,-2.0224308859,2.9191465795,-0
.1325310414\H,-2.0675032063,2.2321237999,1.5217603204\C,-3.8693701134,
1.1547308721,-1.2170022776\H,-4.8120000538,0.6627667154,-1.4895676744\
H,-4.1211343794,2.077786076,-0.6780589238\H,-3.344763929,1.4284634931,
-2.1421788186\\Version=ES64L-G09RevD.01\State=3-A\HF=-232.2176839\S2=2
.004741\S2-1=0.\S2A=2.000012\RMSD=2.215e-09\RMSF=8.993e-06\Dipole=-0.6
756495,0.4855923,-0.082131\Quadrupole=-0.7096326,0.6847553,0.0248773,2
.1451436,0.0800414,1.2369378\PG=C01 [X(C4H8O1)]\\@

^{s}BuOO^{s}Bu

1\1\GINC-R41\FOpt\RM11\6-31+G(d,p)\C8H18O2\ROOT\07-Jan-2016\0\\# m11/6
-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafine\\s
BuOOsBu\\0,1\C,0.3210811962,2.9072091238,-0.0802202944\H,1.0887995333,
3.5155652135,0.421685929\H,-0.6142016101,3.0461396735,0.4849692958\C,0
.7375060457,1.4434916519,0.0423021483\H,1.6243549575,1.2506113719,-0.5
865073126\O,-0.352908929,0.6994870865,-0.518062381\O,0.0884579202,-0.6
481719536,-0.657077046\C,-0.8581963139,-1.4843508715,0.0231883038\H,-0
.9501836152,-1.1089134057,1.0590866177\C,-0.228241803,-2.8747274057,0.
0241411889\H,-0.9632883948,-3.5733594446,0.4516800923\H,-0.069746246,-
3.1794440532,-1.0220997496\C,1.0060012157,1.0199359263,1.4809906609\H,
1.2473119035,-0.0498276203,1.5299973243\H,1.8544645711,1.5834399233,1.
8930436989\H,0.1208767271,1.2153368533,2.1038850245\C,0.1431070376,3.3

600134202,-1.529767299\H,-0.6303755604,2.7637419872,-2.0292565681\H,-0
.1465003465,4.4177978513,-1.5815333961\H,1.0785951694,3.2378966487,-2.
0946074892\C,-2.2098013022,-1.443347144,-0.677114949\H,-2.9398898168,-
2.0603746794,-0.1352172297\H,-2.5842900097,-0.4139243913,-0.7242753191
\H,-2.1125443041,-1.8295374951,-1.7014108232\C,1.0854424369,-2.9378875
702,0.8041600476\H,1.5004247746,-3.954300391,0.8021000056\H,1.83083949
33,-2.2628640996,0.3635547249\H,0.9328987895,-2.6396358461,1.852370914
5\\Version=ES64L-G09RevD.01\State=1-A\HF=-465.8108898\RMSD=3.087e-09\R
MSF=2.707e-06\Dipole=0.0612175,-0.0373136,0.5369287\Quadrupole=-0.4306
026,2.6171029,-2.1865003,2.0897958,-0.1425244,0.0871668\PG=C01 [X(C8H1
8O2)]\\@

^{s}BuO•

1\1\GINC-CA116\FOpt\UM11\6-31+G(d,p)\C4H9O1(2)\ROOT\11-Sep-2015\0\\# u
m11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafi
ne\\RO* R = sec-butyl\\0,2\O,-1.2399299902,0.6548679264,0.5043240277\C
,-2.4129245424,0.3163550469,-0.1356845237\H,-2.040686214,-0.0812347467
,-1.110127599\C,-3.2952855083,1.5376148737,-0.413071274\H,-4.107512059
5,1.2944046693,-1.1101859312\H,-3.7403279488,1.8997744921,0.5246765897
\H,-2.6887786323,2.343084305,-0.8440353657\C,-3.1316098013,-0.83417516
63,0.5907113761\H,-2.3999402237,-1.6398516866,0.7419969725\H,-3.423263
3881,-0.4748114699,1.5896480817\C,-4.3575961578,-1.3511191012,-0.16378
00708\H,-4.7741720768,-2.2384765475,0.3298099617\H,-5.1533592689,-0.59
55794934,-0.2114301221\H,-4.098930798,-1.6337619116,-1.1953616229\\Ver
sion=AS64L-G09RevD.01\State=2-A\HF=-232.8708187\S2=0.752955\S2-1=0.\S2
A=0.750006\RMSD=1.183e-09\RMSF=1.036e-05\Dipole=-0.7768931,-0.2757121,
-0.4042765\Quadrupole=-2.4757512,1.0840504,1.3917009,-1.2315941,-1.830
1948,-0.381845\PG=C01 [X(C4H9O1)]\\@

^{s}BuOO•

1\1\GINC-CA037\FOpt\UM11\6-31+G(d,p)\C4H9O2(2)\ROOT\11-Sep-2015\0\\# u
m11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafi
ne\\ROO* R = sec-butyl\\0,2\O,-0.3583515348,-0.2247882398,0.6181171238
\O,-1.2749997706,0.6974048916,0.595368903\C,-2.4468071216,0.277515062,
-0.1769252767\H,-2.0502126235,-0.1083176783,-1.1285516102\C,-3.2642298
724,1.539247408,-0.3836365643\H,-4.1085196363,1.3348963618,-1.05364721
76\H,-3.6583251592,1.9031945965,0.57519769\H,-2.64952723,2.3284413286,
-0.8336681906\C,-3.1632489438,-0.8291616159,0.5895853562\H,-2.43386365
12,-1.6280239387,0.782519273\H,-3.4791872861,-0.4288905389,1.565415994
5\C,-4.3653456225,-1.381270027,-0.1794572677\H,-4.7978718996,-2.242625
2518,0.3446152329\H,-5.1585853133,-0.6295274581,-0.2902610226\H,-4.072
2483452,-1.7161388802,-1.1852844237\\Version=AS64L-G09RevD.01\State=2-
A\HF=-308.0157915\S2=0.752967\S2-1=0.\S2A=0.750005\RMSD=7.142e-09\RMSF
=1.898e-05\Dipole=-1.1943668,-0.0067719,-0.4748962\Quadrupole=-3.09374
23,1.6748875,1.4188549,-0.0802618,-1.5984047,-0.7323339\PG=C01 [X(C4H9
O2)]\\@

TScomb (^{s}Bu)

1\1\GINC-R3175\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\09-Dec-2015\0\\# um11
/6-31+g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=300 # freq=
noraman guess=read geom=allcheck nosymm iop(1/8=1) int=ultrafine\\TS f
or ROO-OOR symmetric O-O bond cleavage (R = iso-Bu)\\0,1\H,-1.72684417
62,-0.2682468454,-1.0034946998\C,-1.9955537151,0.2133007935,-0.0499287
101\O,-0.8880186457,-0.0881214121,0.8553704023\O,-0.552662539,-1.35820
95091,0.7556709223\O,0.5526652939,-1.3581828488,-0.7557194188\O,0.8880
152468,-0.0880899695,-0.8553785186\C,1.9955478295,0.2133091621,0.04993
13387\H,1.7268395582,-0.2682699039,1.0034818105\C,2.0057855139,1.72416
55723,0.1841566497\H,2.8049053082,2.037722365,0.8674949615\H,2.1778958
441,2.1967131811,-0.7933209863\H,1.0482192021,2.0731337758,0.590747387
9\C,-2.0057992212,1.7241614057,-0.1841061359\H,-2.8049212511,2.0377358
421,-0.8674337331\H,-2.1779110747,2.1966771016,0.7933866607\H,-1.04823
50897,2.0731474064,-0.5906866564\C,-3.2746860478,-0.3937424272,0.51659
34589\H,-3.0741014873,-1.4544857429,0.7232078751\H,-3.4998915365,0.092
0931814,1.4789014339\C,3.274683846,-0.3937098337,-0.5166084273\H,3.074
1045713,-1.4544475114,-0.7232569227\H,3.4998885002,0.0921575355,-1.478
9005651\C,-4.4589105618,-0.260546909,-0.4433284474\H,-5.3375134294,-0.
7895364094,-0.0529324416\H,-4.7467685732,0.7888066508,-0.5949667931\H,
-4.219499419,-0.6913893368,-1.4263893698\C,4.4589062484,-0.2605393903,
0.4433195676\H,5.3375121573,-0.789512557,0.052908256\H,4.7467592577,0.
7888106604,0.5949916675\H,4.2194953901,-0.6914140271,1.4263664332\\Ver
sion=ES64L-G09RevD.01\HF=-616.0303365\S2=0.375678\S2-1=0.\S2A=0.003879
\RMSD=7.665e-09\RMSF=1.691e-06\Dipole=-0.0000031,0.9215532,0.0000155\Q
uadrupole=7.147088,-3.3065004,-3.8405876,0.0000101,0.7563738,0.0000052
\PG=C01 [X(C8H18O4)]\\@

^{s}BuO$_4$^{s}Bu

1\1\GINC-R243\FOpt\RM11\6-31+G(d,p)\C8H18O4\ROOT\29-Aug-2015\0\\# m11/

6-31+G** opt=maxcyc=200 scf=maxcyc=200 # int=ultrafine freq=noraman\\R
O4R R=sec-butyl\\0,1\H,2.0297760242,-0.312902657,1.2005335678\C,2.4479
980816,0.0990005209,0.2666277446\O,1.3317064138,0.5106691717,-0.556277
3923\O,0.4477923753,-0.5662873252,-0.6979889197\O,-0.3333477352,-0.628
5901862,0.469670313\O,-1.2800703112,0.4009016701,0.3983348049\C,-2.371
5182946,-0.0206812529,-0.4524069656\H,-1.9313843247,-0.3437444218,-1.4
108777657\C,-3.1943656432,1.2425753292,-0.6528263934\H,-4.0053050125,1
.0571510955,-1.3682025705\H,-3.6343988634,1.5663248899,0.3007516841\H,
-2.56304734,2.0504229378,-1.0419981898\C,3.194579529,1.3928140194,0.55
25009199\H,4.0166147576,1.2086692918,1.2554352872\H,3.6125616697,1.805
1217181,-0.3765024409\H,2.5170963742,2.1338520301,0.9935382515\C,3.283
4043579,-0.9548381499,-0.4561526173\H,2.6196176628,-1.7828210492,-0.74
15540293\H,3.6683469584,-0.5114083109,-1.3876417705\C,-3.1412658015,-1
.168240375,0.1968124263\H,-2.4288181144,-1.9724664879,0.4275945323\H,-
3.5499948879,-0.811653353,1.1550758961\C,4.4333849658,-1.4820371212,0.
4052684172\H,4.9489922197,-2.3115486251,-0.0951258466\H,5.1812340715,-
0.7032747819,0.6080872305\H,4.0639773812,-1.8546493859,1.3722250764\C,
-4.2596149191,-1.7042426908,-0.7000928667\H,-4.7239188701,-2.594522882
6,-0.2571963597\H,-5.05289046,-0.9595576579,-0.8518906175\H,-3.8706876
345,-1.9888154398,-1.6890629663\\Version=ES64L-G09RevD.01\State=1-A\HF
=-616.0464747\RMSD=9.863e-09\RMSF=4.392e-06\Dipole=0.0072846,-0.244470
1,-0.0081702\Quadrupole=6.6760426,-3.0351996,-3.640843,0.2104136,2.371
8752,0.0908626\PG=C01 [X(C8H18O4)]\\@

TS1a (^{s}Bu)

1\1\GINC-R43\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\31-Aug-2015\0\\# um11/6
-31+g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=300 # freq=no
raman guess=mix nosymm iop(1/8=1)\\TS for single RO--O bond cleavage (
R = iso-butyl)\\0,1\C,-2.0244983762,-0.4446857878,-0.138858103\O,-0.80
89586408,-1.0410396134,-0.635793475\O,-0.0737544831,-0.128011292,-1.49
9902655 2\O,-0.1626318973,1.0791863436,-1.1168200464\O,0.9245768512,1.2
692060913,0.4904484665\C,2.049883795,0.4806946133,0.2462107268\C,2.756
4124263,0.4117200468,1.6131562017\H,3.6064040058,-0.2792697865,1.54932
93579\H,3.1233222886,1.4064617708,1.8991444298\H,2.0650771328,0.050426
2163,2.3834055021\C,-2.5407733102,-1.4946980052,0.8377103719\H,-3.4131
373362,-1.1016124783,1.3741512766\H,-2.8347776476,-2.4086163491,0.3036
934081\H,-1.7666647857,-1.7457100146,1.5727971186\C,-2.9871531793,-0.1
409770852,-1.286111281\H,-2.490314101,0.5336717959,-1.9977407895\H,-3.
194222699,-1.0809567122,-1.8206157262\C,2.9357223817,1.0672600536,-0.8
561103469\H,2.3150512188,1.1899019555,-1.755618145\H,3.2467876834,2.07
65960567,-0.5451927181\H,1.7306450932,-0.5458493739,-0.0227156394\H,-1
.7565879773,0.4735585001,0.4059165011\C,-4.2870983807,0.5021822411,-0.
7969142532\H,-4.909777911,0.8164425403,-1.6439793517\H,-4.8822748417,-
0.1935278223,-0.1900034477\H,-4.0805376513,1.3937157528,-0.1866858353\
C,4.1508198204,0.1937098637,-1.1736352324\H,4.6858607219,0.5690945499,
-2.0554084426\H,4.8664853972,0.1699479329,-0.3401800346\H,3.8459594021
,-0.8421150039,-1.3860028382\\Version=ES64L-G09RevD.01\HF=-616.0088217
\S2=0.621733\S2-1=0.\S2A=0.012683\RMSD=8.214e-09\RMSF=3.618e-06\Dipole
=-0.2774814,-0.3921716,0.19769\Quadrupole=6.4153226,-4.8971905,-1.5181
321,0.6329064,0.7188308,-1.2213802\PG=C01 [X(C8H18O4)]\\@

int-1 (^{s}Bu)

1\1\GINC-R1523\FOpt\UM11\6-31+G(d,p)\C8H18O4\ROOT\31-Aug-2015\0\\# um1
1/6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=mix
nosymm\\ROOO* + RO* caged complex (R = iso-Butyl)\\0,1\H,-1.5996045071
,-0.8227524648,0.9063610412\C,-1.914544697,-1.233690216,-0.0736191351\
O,-0.8003225448,-1.4924815845,-0.8458798099\O,0.1151645724,1.228152688
3,-0.1770479103\O,0.2526136006,1.073639686,1.0607276797\O,0.8144493502
,-0.2286184852,1.4248360299\C,1.85480724,-0.6307701246,0.5083715877\H,
1.447467466,-0.5950736542,-0.512194728\C,-2.8901381324,-0.2829272137,-
0.7776476711\H,-2.3268837021,0.618996107,-1.0582907191\H,-3.2230328089
,-0.7582649734,-1.7131238646\C,3.0700400663,0.2829441462,0.6533617967\
H,2.7491673399,1.3216366499,0.4829491343\H,3.4318756622,0.2227075174,1
.6913082652\C,-4.0834702909,0.0996258241,0.0993822417\H,-4.7451954497,
-0.7570343582,0.2884554905\H,-3.7483533864,0.4888208116,1.0724023547\C
,4.18443893,-0.0758661176,-0.3324811732\H,4.621597298,-1.0588638065,-0
.1107098033\H,3.8041238893,-0.0997726364,-1.3641682734\H,-4.687236855,
0.88107489,-0.3794855953\H,4.9953002112,0.662432963,-0.2926232995\C,2.
1005994261,-2.0831464506,0.8947614525\H,2.8389898294,-2.5263895174,0.2
150715718\H,2.4774222505,-2.1545237298,1.9243710373\H,1.1652168719,-2.
6491583067,0.8069739796\C,-2.5294751842,-2.6305957051,0.189412637\H,-3
.3846376045,-2.5191862554,0.8671748804\H,-2.8691665104,-3.0755640581,-
0.7547914079\H,-1.7910193306,-3.2923966254,0.6570952104\\Version=ES64L
-G09RevD.01\HF=-616.0144233\S2=1.002629\S2-1=0.\S2A=0.050556\RMSD=2.54
7e-09\RMSF=6.715e-06\Dipole=0.040061,-0.4041552,0.2048713\Quadrupole=6
.0289805,-1.2056745,-4.8233059,1.0428023,-0.063424,-1.3713651\PG=C01 [
X(C8H18O4)]\\@

TS2 (sBu)

```
1\1\GINC-R200\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\09-Sep-2015\0\\# um11/
6-31+G(d,p) opt=(calcfc,ts,noeigen,maxcyc=200) freq=noraman # guess=mi
x int=ultrafine scf=maxcyc=200 nosymm\\TS for 2nd O-O bond cleavage (R
 = sec-butyl)\\0,1\H,1.5600567502,0.9139120051,0.9160406003\C,2.056346
5983,1.3313786957,0.0065314527\O,0.985612765,1.4634429531,-0.849190542
7\O,-0.2996049539,-1.2743100171,-0.7806079417\O,0.0237263697,-1.184356
7128,0.3769085353\O,-0.7320040679,0.1813420195,1.2132023076\C,-1.72535
39249,0.6699400708,0.3607807934\H,-1.3464181883,0.6079578986,-0.681444
3857\C,3.0517285262,0.2768175535,-0.5105031587\H,2.4772183722,-0.62404
50659,-0.7689177187\H,3.4944297966,0.6530209117,-1.4459240245\C,-3.021
3934027,-0.134993696,0.4952449876\H,-2.7728788641,-1.198742257,0.35820
57567\H,-3.3905853169,-0.0275760798,1.5269385707\C,4.1506137372,-0.056
554653,0.4995571793\H,4.8098942303,0.8030722598,0.6811498567\H,3.72002
57821,-0.3621700317,1.4646873591\C,-4.0934935821,0.2824796163,-0.51267
0455\H,-4.4547120157,1.3024782732,-0.322656138\H,-3.7008532137,0.25054
48887,-1.5399040303\C,-1.8670754007,2.1612176193,0.6998453255\H,-2.577
858704,2.6323052845,0.0091386875\H,-2.2337781285,2.2861404838,1.727598
1391\H,-0.8950024212,2.6577193734,0.5943869392\C,2.6877790734,2.680084
1834,0.3632284411\H,3.3898744324,2.5829193017,1.2012844805\H,3.2327765
268,3.08419865,-0.501925331\H,1.9036825379,3.3938754997,0.6451304574\H
,4.7770710282,-0.8815898227,0.1367859923\H,-4.9613179919,-0.3878967761
,-0.4666328655\\Version=ES64L-G09RevD.01\HF=-616.0067408\S2=1.30472\S2
-1=0.\S2A=1.905886\RMSD=8.110e-09\RMSF=2.132e-06\Dipole=0.1595045,0.15
11007,0.099674\Quadrupole=5.3174276,-1.0189903,-4.2984374,0.1025268,0.
4650807,1.4256228\PG=C01 [X(C8H18O4)]\\@
```

int-2 (sBu)

```
1\1\GINC-R54\FOpt\UM11\6-31+G(d,p)\C8H18O4\ROOT\09-Dec-2015\0\\# um11/
6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=read g
eom=allcheck nosymm int=ultrafine\\RO* + 3O2 + RO* caged complex (R =
sec-Butyl)\\0,1\H,-1.3852447251,-0.0816118914,-0.6756910753\C,-1.87420
445,0.4033547954,0.1924790645\O,-0.9614333486,0.5022270428,1.221681257
3\O,-0.0206516632,-2.0995905948,0.6934712407\O,0.0573351141,-2.1431627
894,-0.5001438264\O,0.9339454609,0.4369566975,-1.217506686\C,1.8503489
472,0.4341107623,-0.1867932082\H,1.3758346845,-0.0008560744,0.71521496
98\C,-3.1398672889,-0.3497555227,0.6147581102\H,-2.8227587552,-1.31543
51609,1.037646419\H,-3.6244577048,0.208400589,1.4305963227\C,3.1340591
571,-0.3144408209,-0.5595979567\H,2.8409515241,-1.3165018039,-0.908783
0246\H,3.6006803258,0.1947910671,-1.416836154\C,-4.1118741599,-0.58318
76003,-0.5430008942\H,-4.5527858956,0.3567922256,-0.9022884914\H,-3.60
38045406,-1.0622409939,-1.3932941123\C,4.1161364195,-0.4370310904,0.60
67155891\H,4.5343908354,0.5377236832,0.892956498\H,3.6237396502,-0.864
4750197,1.4929924405\H,-4.9383780672,-1.2376754192,-0.2377428337\H,4.9
578692838,-1.0913618072,0.3460211729\C,2.0794541609,1.9305895033,0.136
0279196\H,2.7797765948,2.0101747619,0.9764197576\H,2.4999821755,2.4473
491402,-0.7366341838\H,1.1289029948,2.3958436438,0.4220485221\C,-2.140
7823532,1.8666995738,-0.2360372789\H,-2.8394143314,1.868226902,-1.0815
757252\H,-2.5781514512,2.4327862601,0.5968225088\H,-1.2015195937,2.335
4519411,-0.5519363424\\Version=ES64L-G09RevD.01\HF=-616.0205448\S2=1.9
88844\S2-1=0.\S2A=4.078779\RMSD=4.561e-09\RMSF=8.815e-06\Dipole=0.0013
893,0.1086827,-0.0056518\Quadrupole=5.0479506,0.8975607,-5.9455112,0.1
067184,1.6373947,-0.2240834\PG=C01 [X(C8H18O4)]\\@
```

int-2* (sBu, triplet)

```
1\1\GINC-R44\FOpt\UM11\6-31+G(d,p)\C8H18O4(3)\ROOT\11-Dec-2015\0\\# um
11/6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=rea
d geom=allcheck nosymm int=ultrafine\\RO* + 3O2 + RO* caged complex (R
 = sec-Butyl; triplet)\\0,3\H,-1.3725752403,-0.1810081463,-0.652572610
8\C,-1.8540054229,0.372780444,0.1782425081\O,-0.956917281,0.4998709553
,1.2176141182\O,-0.2178972278,-2.2090579868,0.932888385\O,0.0626885427
,-2.261033296,-0.2296995822\O,0.9367315737,0.5309083667,-1.2359381752\
C,1.8407261458,0.4444581136,-0.1988436545\H,1.3805882233,-0.0932157975
,0.6528068781\C,-3.1569686419,-0.3010762721,0.6223842143\H,-2.88864784
42,-1.2502912192,1.1108581224\H,-3.6307949145,0.3273733261,1.392074462
5\C,3.1510709814,-0.2185755545,-0.6393120198\H,2.8947207838,-1.1890996
449,-1.0905923717\H,3.6017569452,0.3929580655,-1.4359021094\C,-4.11849
68764,-0.5669005498,-0.537142127\H,-4.5138095676,0.3656318996,-0.96262
5824\H,-3.61710909,-1.1189273072,-1.3461110471\C,4.1319966783,-0.42679
79255,0.5156547081\H,4.5149950491,0.5269109653,0.9038024559\H,3.651656
8306,-0.9601278898,1.3495264346\H,-4.9765139259,-1.1666060002,-0.20730
84543\H,4.9967328827,-1.021552272,0.1945315521\C,2.0254757726,1.909995
2302,0.2676890061\H,2.7191880451,1.9245176449,1.1172257908\H,2.4357067
446,2.5188919914,-0.5485237566\H,1.061456074,2.318491546,0.5927751024\
C,-2.0573522739,1.8192873385,-0.3362466237\H,-2.7481995436,1.797982905
,-1.1879508591\H,-2.480380952,2.447601614,0.4585406764\H,-1.0977434708
```

,2.2307614556,-0.6698551995\\Version=ES64L-G09RevD.01\HF=-616.0199948\
S2=3.000984\S2-1=0.\S2A=2.023121\RMSD=3.744e-09\RMSF=4.250e-06\Dipole=
0.0166025,0.0479857,-0.0040817\Quadrupole=5.0699636,0.821446,-5.891409
6,0.0891094,1.7512467,-0.0284973\PG=C01 [X(C8H18O4)]\\@

^{3}[^{t}BuO•]$_2$ (alkoxyl radical dimer, triplet)

1\1\GINC-R89\FOpt\UM11\6-31+G(d,p)\C8H18O2(3)\ROOT\11-Jan-2016\0\\# um
11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafin
e nosymm\\RO*--*OR dimer caged complex (R = sec-Butyl)\\0,3\H,-1.24705
06086,-0.1744417042,-0.449275267\C,-1.8112345486,0.4827236027,0.242912
814\O,-0.9999195593,0.8654246378,1.2884439694\O,0.9718095795,0.7998728
948,-1.3220253184\C,1.7870512693,0.510324846,-0.2499158418\H,1.2355509
008,-0.1109930816,0.4843693739\C,-3.096950117,-0.1948895337,0.73472201
87\H,-2.8071066302,-1.0320624336,1.3867897586\H,-3.6468910886,0.521853
1849,1.3634013129\C,3.0912019884,-0.1679229652,-0.6896321201\H,2.82471
62486,-1.0570869535,-1.2799126485\H,3.6246023387,0.5154136289,-1.36780
52123\C,-3.9744141471,-0.7074712209,-0.4085722487\H,-4.3991282406,0.11
64786871,-0.9979479271\H,-3.3975448489,-1.347552512,-1.0926606339\C,3.
9779172701,-0.5740117013,0.4887845436\H,4.3839943878,0.3009071846,1.01
42761735\H,3.4141241646,-1.1730997822,1.2193607858\H,-4.8124652136,-1.
3026691447,-0.0238260566\H,4.8291650155,-1.178180098,0.1497030661\C,2.
0281351771,1.8843312612,0.425989563\H,2.6167662396,1.7277427202,1.3382
114758\H,2.577840209,2.5462629987,-0.2558303876\H,1.0687388067,2.33642
70356,0.7007531852\C,-2.088359045,1.8007910757,-0.5243420168\H,-2.6741
194872,1.5677776014,-1.4219648529\H,-2.6537460847,2.4934182606,0.11268
20437\H,-1.1412879762,2.2575385107,-0.8320265526\\Version=ES64L-G09Rev
D.01\HF=-465.7486864\S2=2.006041\S2-1=0.\S2A=2.000022\RMSD=1.507e-09\R
MSF=2.890e-06\Dipole=-0.0014369,-0.2304329,0.0109288\Quadrupole=5.2332
708,0.2681685,-5.5014393,0.1228189,1.9206178,-0.1787032\PG=C01 [X(C8H1
8O2)]\\@

TS-H (^{s}Bu)

1\1\GINC-R48\FTS\UM11\6-31+G(d,p)\C8H18O2(3)\ROOT\05-Jan-2016\0\\# um1
1/6-31+G(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 freq=n
oraman int=ultrafine\\PES for H abstraction: sBuO*--*OsBu (diradical t
riplet)\\0,3\H,0.3286201465,-0.7363912634,-0.2359066691\C,1.2931109684
,-0.2041575822,0.214436472\O,0.9411686077,0.8981376399,0.9140451581\O,
-0.9785285062,-1.3090953904,-0.3615071715\C,-1.7870200349,-0.361375647
,0.2791762177\H,-1.3334448217,-0.0997410991,1.2586566627\C,-1.93489763
06,0.9168366589,-0.5544494088\H,-2.5347569469,0.6853775694,-1.44880404
18\H,-0.9324972596,1.2022656126,-0.9099647186\C,2.2302295689,0.1568532
724,-0.9582389286\H,2.3406681683,-0.7523464199,-1.5668201608\H,1.71234
76026,0.8995439529,-1.5817463098\C,1.8869660816,-1.2220455086,1.208488
0812\H,1.1189767099,-1.5285922754,1.9285579911\H,2.2131810501,-2.10321
41079,0.6415003083\H,2.7380510378,-0.7857468996,1.7463193221\C,3.58844
18127,0.6908264935,-0.5018357393\H,4.1848853671,-0.0908793097,-0.01244
26134\H,4.16442981,1.0593116595,-1.360419202\H,3.4600843702,1.52007760
05,0.2065297256\C,-3.1295194242,-1.0583288151,0.5491458139\H,-2.975809
5679,-1.9617618054,1.1511375517\H,-3.8046205389,-0.3815919262,1.089181
4182\H,-3.5985184188,-1.3438239493,-0.402149491\C,-2.5421591325,2.0762
589337,0.2355257407\H,-2.5878168618,2.9901672336,-0.3710050008\H,-3.56
47117834,1.8525029229,0.5710412368\H,-1.9318213744,2.2935509695,1.1246
711552\\Version=ES64L-G09RevD.01\State=3-A\HF=-465.7390295\S2=2.009432
\S2-1=0.\S2A=2.000043\RMSD=6.884e-09\RMSF=4.701e-07\Dipole=0.5458192,0
.0510773,0.0601102\Quadrupole=4.2800437,-3.4033704,-0.8766732,-2.30794
51,-1.6704393,-2.890102\PG=C01 [X(C8H18O2)]\\@

===*tert*-Butyl===

^{t}BuO•

1\1\GINC-CA037\FOpt\UM11\6-31+G(d,p)\C4H9O1(2)\ROOT\11-Sep-2015\0\\# u
m11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafi
ne\\RO* R = tert-butyl\\0,2\C,0.0000000002,-0.0254230468,0.07769654\C,
-0.0000000993,1.3803491544,-0.5807609081\H,0.8947850238,1.9413632647,-
0.2849322166\H,0.0000000868,1.2470026309,-1.6710335675\H,-0.8947854986
,1.9413629624,-0.2849324965\C,-1.2721296909,-0.7896551961,-0.312963295
6\H,-1.3013396376,-0.9618831762,-1.398042168\H,-1.2989519906,-1.764161
4364,0.1929370321\H,-2.161068979,-0.2185068046,-0.0159598592\C,1.27212
98047,-0.7896550668,-0.3129633713\H,2.161068946,-0.2185064961,-0.01595
98332\H,1.2989521712,-1.764161332,0.1929368181\H,1.3013398534,-0.96188
26623,-1.3980423\O,0.00000001,0.2637932049,1.4316896257\\Version=AS64L
-G09RevD.01\State=2-A\HF=-232.8766948\S2=0.752925\S2-1=0.\S2A=0.750006
\RMSD=7.326e-09\RMSF=2.478e-05\Dipole=0.,-0.084354,-0.8916558\Quadrupo
le=0.7140784,1.500746,-2.2148243,-0.0000002,-0.0000001,-0.8846799\PG=C
01 [X(C4H9O1)]\\@

^{t}BuOO•

```
1\1\GINC-CA116\FOpt\UM11\6-31+G(d,p)\C4H9O2(2)\ROOT\11-Sep-2015\0\\# u
m11/6-31+g(d,p) opt=maxcyc=200 scf=maxcyc=200 freq=noraman int=ultrafi
ne\\ROO* R = tert-butyl\\0,2\O,0.6716318021,-0.1656402164,0.2137349369
\O,1.6425938833,-0.2994630067,-0.6382752364\C,2.97230648,-0.06864538,-
0.0262910267\C,3.9298116045,-0.2760884985,-1.1907125627\H,4.9628182807
,-0.1279842454,-0.8493522686\H,3.8356300316,-1.2937436822,-1.591772118
8\H,3.7203848124,0.4406778596,-1.9955277065\C,3.163962707,-1.100560395
3,1.0776928365\H,4.1590004792,-0.9778656312,1.5261165861\H,2.404691983
,-0.9671742307,1.8580118152\H,3.0846135639,-2.1180941377,0.6722620574\
C,3.0005609526,1.3586090576,0.5052233509\H,3.9895969241,1.5716299326,0
.9326201063\H,2.8059858551,2.075206923,-0.3038955221\H,2.2415646884,1.
4878646476,1.2865038852\\Version=AS64L-G09RevD.01\State=2-A"\HF=-308.0
229091\S2=0.752954\S2-1=0.\S2A=0.750005\RMSD=8.406e-09\RMSF=2.276e-05\
Dipole=1.2360158,0.1193871,0.1600538\Quadrupole=-2.4096797,1.6159749,0
.7937048,-0.3725591,-0.4284369,-0.2385753\PG=CS [SG(C2H1O2),X(C2H8)]\\
@
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TScomb (^{t}Bu)

```
1\1\GINC-R49\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\15-Dec-2015\0\\# um11/6
-31+g(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) scf=maxcyc=300 # freq=no
raman guess=read geom=allcheck nosymm iop(1/8=1) int=ultrafine\\TS for
 ROO-OOR symmetric O-O bond cleavage (R = t-Bu)\\0,1\C,-0.1588981703,2
.179741094,0.0122827659\O,-0.857432237,0.9210866005,-0.3226496189\O,-0
.7178586741,0.5867597682,-1.5873567657\O,0.7177744807,-0.5867471173,-1
.5874508283\O,0.8574260696,-0.9210900291,-0.3227522556\C,0.1589026089,
-2.1797395729,0.0122137314\C,0.2766517845,-2.2296336301,1.5291194449\H
,-0.1743530815,-3.1569332236,1.9066961853\H,1.3304797251,-2.2009722309
,1.8374976759\H,-0.2494475427,-1.3742154371,1.9750621144\C,-0.27667236
52,2.2296887517,1.5291842532\H,0.1743632508,3.1569830804,1.906737189\H
,-1.3305064182,2.2010794116,1.8375462037\H,0.2493861908,1.3742664052,1
.9751665596\C,-0.9215032102,3.3092166596,-0.6724550404\H,-0.4634836066
,4.2761308972,-0.4231549503\H,-0.8888691641,3.1751136552,-1.7617106593
\H,-1.9702308735,3.3203074104,-0.346336635\C,0.9215357505,-3.309228129
8,-0.6724722086\H,0.4635137296,-4.2761389721,-0.4231624905\H,0.8889334
989,-3.1751530237,-1.7617323352\H,1.9702537816,-3.3203057115,-0.346322
3525\C,1.2924356741,2.1179337927,-0.4469537998\H,1.3490909086,1.980834
972,-1.5332336404\H,1.7842365271,3.0638076461,-0.1802259853\H,1.821220
8892,1.2892193716,0.0394286802\C,-1.2924271524,-2.1179781121,-0.447042
4009\H,-1.7842367748,-3.0638100811,-0.180181033\H,-1.821205435,-1.2891
922588,0.0392240533\H,-1.3490801643,-1.9810319863,-1.533341857\\Versio
n=ES64L-G09RevD.01\HF=-616.041898\S2=0.358445\S2-1=0.\S2A=0.003526\RMS
D=9.222e-09\RMSF=1.117e-06\Dipole=0.0000193,0.0000157,0.9007243\Quadru
pole=-3.0694386,6.9806711,-3.9112325,0.3514974,-0.0000042,0.0000821\PG
=C01 [X(C8H18O4)]\\@
```

^{t}BuO$_4$^{t}Bu

```
1\1\GINC-R89\FOpt\RM11\6-31+G(d,p)\C8H18O2\ROOT\16-Jan-2016\0\\# m11/6
-31+g(d,p) int=ultrafine freq opt=maxcyc=200 scf=maxcyc=200\\tBuOOtBu\
\0,1\C,1.7476345794,-0.0268819543,-0.008914061\C,2.1635570714,-1.13710
10898,-0.9739105603\H,1.4646985287,-1.9804978104,-0.9144840228\H,2.168
4589193,-0.7569994202,-2.0043556742\H,3.1720454668,-1.4949644362,-0.72
29469035\C,1.6574555875,-0.5383856861,1.428374459\H,2.6379941816,-0.91
16393147,1.7556451927\H,1.3475715738,0.2711214312,2.1041619111\H,0.930
2186433,-1.3575090268,1.4974542193\C,2.6844550941,1.1745779674,-0.1103
255713\H,2.710595037,1.553604839,-1.1404397172\H,2.3468525198,1.981476
4649,0.554148931\H,3.7005167836,0.8786135138,0.1836967272\O,0.48112924
23,0.5277163558,-0.4236642647\O,-0.4810380002,-0.5301641306,-0.4205970
85\C,-1.7476211375,0.0269002138,-0.0094006013\C,-1.6577197673,0.546893
0662,1.4248542775\H,-0.9304035796,1.3663292546,1.4892334802\H,-2.63828
53444,0.9222026756,1.7496848966\H,-1.3480812568,-0.2586290316,2.105499
725\C,-2.1633403908,1.1313949981,-0.9810313123\H,-1.4646240064,1.97522
7490\2,-0.9263090825\H,-2.1678142755,0.7452502531,-2.0092289099\H,-3.17
19716115,1.4905773234,-0.7325361771\C,-2.6844384963,-1.1751252144,-0.1
038957115\H,-2.3468489635,-1.978159523,0.5652508675\H,-3.7005074285,-0
.8774679474,0.1883869949\H,-2.7105489704,-1.5601132618,-1.1317970274\\
Version=ES64L-G09RevD.01\State=1-A\HF=-465.8214855\RMSD=4.447e-09\RMSF
=3.241e-06\Dipole=-0.0000419,0.001064,0.3564264\Quadrupole=3.6196487,-
1.8097103,-1.8099383,-0.1431987,0.0009595,-0.000035\PG=C01 [X(C8H18O2)
]\\@
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TS1a (^{t}Bu)

```
1\1\GINC-R538\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\28-Aug-2015\0\\# um11/
6-31+G** opt=(TS,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 # int=ultra
fine freq=noraman guess=mix nosymm\\TS for single RO--O bond cleavage
(R = tert-butyl)\\0,1\C,-2.7671959208,0.0039307524,0.0625705947\O,-1.4
934831698,-0.5341935111,0.5222923095\O,-0.509132146,-0.339579513,-0.50
```

19938358\O,0.207062408,0.687252002,-0.2263382343\O,1.6778388569,0.0432
519455,0.9254711519\C,2.7956629872,-0.0399031064,0.081449126\C,3.87572
21373,-0.594947477,1.0376069774\H,4.8205403959,-0.6874942588,0.4844047
293\H,4.0224045713,0.0850660656,1.8861087122\H,3.5826447108,-1.5826550
978,1.415124337\C,-3.6686792263,-0.274229184,1.2629911973\H,-4.6883165
023,0.0676744127,1.0402479864\H,-3.6958648299,-1.3496673162,1.48118522
47\H,-3.3009927226,0.2579505034,2.1496438205\C,-3.2293106501,-0.761471
9895,-1.1755492308\H,-4.2268957085,-0.4140009396,-1.4777531784\H,-2.54
07800757,-0.5995879527,-2.0153682621\H,-3.2797839738,-1.8372105758,-0.
9614477859\C,3.1970481353,1.3466303758,-0.4299749074\H,4.1203926573,1.
2866788884,-1.0236466352\H,2.3999301511,1.7567560653,-1.0641576069\H,3
.3593900449,2.0282196682,0.4154151751\C,-2.6440162673,1.5025984441,-0.
2047538092\H,-2.0142589721,1.7024804795,-1.0820382335\H,-3.6413334757,
1.920943926,-0.3991396206\H,-2.2055131122,2.0104822377,0.6640344714\C,
2.5541960355,-1.022093995,-1.0696066102\H,3.4890561175,-1.2064518756,-
1.6177965388\H,2.1755585916,-1.9752366885,-0.6767098811\H,1.8155239529
,-0.6151112856,-1.7728984433\\Version=ES64L-G09RevD.01\HF=-616.01853\S
2=0.697062\S2-1=0.\S2A=0.016434\RMSD=4.101e-09\RMSF=5.013e-07\Dipole=-
0.4489541,0.0742425,-0.5588039\Quadrupole=8.4735549,-3.8331955,-4.6403
594,-1.3137775,-0.4162822,0.0679746\PG=C01 [X(C8H18O4)]\\@

int-1 (ᵗBu)

1\1\GINC-R2522\FOpt\UM11\6-31+G(d,p)\C8H18O4\ROOT\31-Aug-2015\0\\# um1
1/6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=mix
nosymm\\ROOO* + RO* caged complex (R = tert-Butyl)\\0,1\C,-3.045696955
2,0.1505471965,0.089159753\O,-2.0893332691,0.4613618497,1.0431398844\O
,-0.0202390083,-0.9554668324,0.0878059036\O,0.6365566645,0.0619268857,
-0.2703305307\O,1.681957217,0.3464910494,0.6861489755\C,2.9585470667,-
0.0258706195,0.0913143549\C,3.9354176438,0.3283643966,1.2100698512\H,4
.9604144827,0.1112606781,0.8806366547\H,3.8621367911,1.3947993059,1.45
93603852\H,3.7191421166,-0.2615143391,2.110002412\C,-4.2885250179,0.94
11641155,0.5775527523\H,-5.1138744965,0.7499970173,-0.1217441278\H,-4.
5806476728,0.6107484147,1.5818225193\H,-4.0751163143,2.017104956,0.597
7502087\C,-3.3440060089,-1.3546726788,0.0983999737\H,-4.1547897438,-1.
5898253801,-0.6058683244\H,-2.4467206054,-1.9132244818,-0.1988602819\H
,-3.6391558775,-1.6735887442,1.1064057013\C,3.2097917134,0.815558696,-
1.1583549753\H,4.2120429318,0.6017189284,-1.5545666626\H,2.4756040795,
0.5864523945,-1.9418638687\H,3.1465184606,1.8844926332,-0.9157431941\C
,-2.6207317772,0.6415229818,-1.3006315842\H,-1.7329345682,0.090388408,
-1.637908282\H,-3.4275149046,0.4839182603,-2.0306527905\H,-2.376655192
3,1.7113222642,-1.2613464005\C,2.9744409846,-1.5230991023,-0.210576528
6\H,3.9841187286,-1.8247600856,-0.5214886008\H,2.6906692536,-2.0943654
946,0.6830984601\H,2.2787572774,-1.7743876735,-1.0225996379\\Version=E
S64L-G09RevD.01\HF=-616.020827\S2=0.992261\S2-1=0.\S2A=0.045424\RMSD=4
.547e-09\RMSF=7.203e-06\Dipole=0.5449906,-0.1132354,-0.7834099\Quadrup
ole=10.039847,-4.263394,-5.776453,-0.7882763,0.9459766,-0.5310536\PG=C
01 [X(C8H18O4)]\\@

TS2 (ᵗBu)

1\1\GINC-R39\FTS\UM11\6-31+G(d,p)\C8H18O4\ROOT\14-Dec-2015\0\\# um11/6
-31+G** opt=(TS,calcfc,noeigen,maxcyc=200) scf=maxcyc=200 # int=ultraf
ine freq=noraman guess=read geom=allcheck nosymm\\TS for second RO--O
bond cleavage (R = tert-butyl)\\0,1\C,-2.5115032022,-0.2725031407,0.01
0592102\O,-1.3984183954,-0.7527855622,0.682233243\O,0.2036618822,2.402
9816557,-0.2057437026\O,0.4834696615,1.2778595805,0.1286059396\O,2.199
9792372,1.0101254549,-0.1488944418\C,2.4102517288,-0.3842109277,0.0151
378886\C,3.9273168555,-0.5075569712,-0.2114906032\H,4.2162825539,-1.56
27999413,-0.1098208108\H,4.1961470328,-0.1597098172,-1.2171715799\H,4.
4761810773,0.0857058694,0.5309018496\C,-3.5512797247,-1.4086077537,0.2
128049969\H,-4.480064468,-1.1124551282,-0.2931058157\H,-3.1849712718,-
2.3459851398,-0.2232348713\H,-3.7522574776,-1.5575302781,1.2806044659\
C,-2.2117293963,-0.094754671,-1.4841791255\H,-3.1158655065,0.222312318
5,-2.0223067176\H,-1.4379029028,0.6715243303,-1.6308242073\H,-1.854424
6187,-1.0403844595,-1.9135724991\C,1.6365700625,-1.1735848236,-1.04444
40131\H,1.9127251675,-2.2367456109,-1.0023716849\H,0.5555210012,-1.096
8826282,-0.8643714342\H,1.8685265671,-0.7857232024,-2.0457761711\C,-3.
016896272,1.0239151528,0.6566620629\H,-2.2670522407,1.8190636836,0.551
2398705\H,-3.9446818632,1.3576447911,0.1712445426\H,-3.2091248786,0.86
15733857,1.7250177953\C,2.0360829013,-0.8249896762,1.4331102232\H,2.32
26436382,-1.8746714531,1.5886678015\H,2.5596600187,-0.2017053064,2.170
4898361\H,0.9528418331,-0.7408747309,1.5930060604\\Version=ES64L-G09Re
vD.01\HF=-616.0138781\S2=1.374221\S2-1=0.\S2A=2.22189\RMSD=6.212e-09\R
MSF=1.459e-06\Dipole=-0.730872,-0.7089713,-0.2255081\Quadrupole=5.9321
507,-3.8847048,-2.0474459,-2.9461813,1.1871333,1.0157919\PG=C01 [X(C8H
18O4)]\\@

int-2 (ᵗBu)

1\1\GINC-R53\FOpt\UM11\6-31+G(d,p)\C8H18O4\ROOT\09-Dec-2015\0\\# um11/
6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=read g
eom=allcheck nosymm int=ultrafine\\RO* + 3O2 + RO* caged complex (R =
tert-Butyl)\\0,1\C,-2.5487888788,-0.2648873853,-0.0269345331\O,-1.3841
367084,-0.3319154907,0.719949852\O,-0.2099069724,2.2001823708,-0.02879
82355\O,0.4745868652,1.9727642394,0.925395721\O,2.8930624597,1.0200242
616,0.1685576611\C,2.6266261764,-0.3349520964,0.0413457876\C,4.0203848
002,-0.9264876167,-0.3003580516\H,3.9096004686,-2.0123223624,-0.423934
019\H,4.4025740432,-0.494518565,-1.2336032096\H,4.7306128919,-0.724611
897,0.5107500547\C,-3.2671133083,-1.5948173698,0.3305416345\H,-4.21205
13998,-1.63127705,-0.2280888165\H,-2.6464321548,-2.4535062632,0.046997
306\H,-3.4796610271,-1.6380788671,1.4055494045\C,-2.2306205506,-0.2242
357088,-1.5274468371\H,-3.1569839484,-0.2233058103,-2.1186790638\H,-1.
6641593421,0.6860242712,-1.768969412\H,-1.6261979723,-1.0966181954,-1.
8101554022\C,1.6408987762,-0.5967728031,-1.1040908613\H,1.5129776276,-
1.6774129812,-1.2629590964\H,0.6580758778,-0.1752560621,-0.8549220597\
H,2.008316938,-0.1371664042,-2.0312984004\C,-3.4055472008,0.9295961504
,0.4133635963\H,-2.8843469222,1.8707408209,0.1925046048\H,-4.365896416
3,0.9312092028,-0.1209322022\H,-3.5952346822,0.879023575,1.49323198\C,
2.1179077507,-0.9128193393,1.3690898737\H,2.0052542247,-2.003488894,1.
2900441271\H,2.8252400818,-0.6812069709,2.1761028288\H,1.1366175026,-0
.4852507593,1.6149757683\\Version=ES64L-G09RevD.01\HF=-616.0289831\S2=
1.999392\S2-1=0.\S2A=4.0984\RMSD=3.660e-09\RMSF=7.383e-06\Dipole=-0.98
28954,-0.9042866,-0.4469414\Quadrupole=3.9570415,-1.8892496,-2.0677919
,-3.7814786,0.0150096,0.0428362\PG=C01 [X(C8H18O4)]\\@

int-2* (ᵗBu, triplet)

1\1\GINC-R50\FOpt\UM11\6-31+G(d,p)\C8H18O4(3)\ROOT\09-Dec-2015\0\\# um
11/6-31+G** opt=(maxcyc=200) scf=(maxcyc=200) # freq=noraman guess=rea
d geom=allcheck nosymm int=ultrafine\\RO* + 3O2 + RO* caged complex (R
= tert-Butyl)\\0,3\C,-2.5440956482,-0.2628818956,-0.0264304865\O,-1.3
716808841,-0.351693284,0.7060244072\O,-0.1881110358,2.1807319136,-0.11
30543382\O,0.3987662244,1.9076670489,0.8931439471\O,2.8471811844,1.023
9385064,0.1872303948\C,2.6184049259,-0.3365853868,0.046360693\C,4.0321
012377,-0.8882564853,-0.2800064588\H,3.9524527388,-1.9758845194,-0.411
4332312\H,4.4148776767,-0.4404110685,-1.2055164238\H,4.725715632,-0.67
2204639,0.5417498036\C,-3.2795428966,-1.5815950495,0.3387233822\H,-4.2
323532252,-1.6012054858,-0.2072529098\H,-2.6772685025,-2.4499466269,0.
0450617329\H,-3.4778093772,-1.6233287813,1.4164768972\C,-2.2479114081,
-0.223588451,-1.5313010099\H,-3.1826851224,-0.2088406048,-2.1089876856
\H,-1.6722862051,0.6786935002,-1.7802816142\H,-1.6603576915,-1.1040973
883,-1.8242831395\C,1.6556271583,-0.6171373619,-1.1141086116\H,1.56679
30867,-1.6993844988,-1.2877502587\H,0.6560340189,-0.2320157209,-0.8724
064713\H,2.018819388,-0.134110092,-2.0310470703\C,-3.3748090579,0.9439
228041,0.4305289412\H,-2.8421376371,1.8774557912,0.2047841007\H,-4.342
451687,0.9624711804,-0.0900590535\H,-3.5495794758,0.892467571,1.512835
7317\C,2.1074366894,-0.9367932239,1.3633655501\H,2.0245869293,-2.02946
0177,1.2751069747\H,2.7978653594,-0.6928586383,2.1813022816\H,1.112076
6045,-0.5364159367,1.5984519246\\Version=ES64L-G09RevD.01\HF=-616.0292
96\S2=3.000495\S2-1=0.\S2A=2.022791\RMSD=8.615e-09\RMSF=5.404e-06\Dipo
le=-0.9714731,-0.8897303,-0.4386078\Quadrupole=4.2131716,-2.0325714,-2
.1806001,-3.7392723,-0.0505321,0.0450699\PG=C01 [X(C8H18O4)]\\@

===Complexation===

***sec*-tetroxide-ether complex**

E(M11/6-311+G**//M11/6-31+G*) = -771.1844763810
1\1\GINC-R140\FOpt\RM11\6-31+G(d,p)\C10H24O5\ROOT\16-Feb-2016\0\\# m11
/6-31+G** opt=maxcyc=200 scf=maxcyc=200 freq int=ultrafine\\ROOOOR'(H)
---OMe2 complex (R = sec-Bu)\\0,1\H,-1.9662974119,1.8933550227,-1.2354
881811\C,-2.3878034051,1.9966507923,-0.2221886186\O,-1.2982039996,2.36
99901037,0.6579802158\O,-0.2295199856,1.4916227272,0.4478882486\O,0.44
72770835,1.9293760153,-0.703248207\O,1.2496197245,3.0167541697,-0.3277
021069\C,2.4710114518,2.5085622194,0.2537343336\H,2.1831137957,1.78301
27547,1.0336174253\C,3.1241758215,3.727274194,0.8869570575\H,4.0326327
976,3.4338988777,1.4278471075\H,3.3970094359,4.4581984304,0.1129958673
\H,2.4344506031,4.2039819569,1.5936393529\C,-3.343087393,3.177652227,-
0.1497958822\H,-4.1939790459,3.0165969581,-0.8237256585\H,-3.726119545
6,3.2959612514,0.8735279471\H,-2.8333224555,4.1032263051,-0.4436876308
\C,-2.9990215354,0.6707054418,0.2185341896\H,-2.1799841235,-0.05212407
1,0.3331914778\H,-3.4669284365,0.8076999158,1.2064325986\C,3.325978643
8,1.8325318313,-0.816604554\H,2.7050762277,1.0828770545,-1.3291349285\
H,3.6025416219,2.5889162577,-1.5675171025\C,-4.0064253105,0.1348132413
,-0.7998561662\H,-4.3875678526,-0.8484101778,-0.494487723\H,-4.8720644
11,0.8027809471,-0.9132863428\H,-3.5222480413,0.0155074241,-1.77964315
03\C,4.5749189396,1.1641243447,-0.237782189\H,5.1172921092,0.607781287

,-1.0128507866\H,5.2707950555,1.900328625,0.1870924867\H,4.3091720468,
0.4535863799,0.558920276\O,-0.8896542061,-0.3278942916,-1.930631621\C,
-0.3641496197,0.1694152963,-3.141824182\H,0.5561389703,0.7522192119,-2
.9598623136\H,-1.1215635548,0.8257687348,-3.588500542\H,-0.1388451086,
-0.6540559069,-3.8434641088\C,0.0354834188,-1.1453043678,-1.2487032273
\H,0.9576906912,-0.5828644138,-1.0161517975\H,0.2957932794,-2.03451082
13,-1.8508967557\H,-0.4303862758,-1.4670059484,-0.3093248082\\Version=
ES64L-G09RevD.01\State=1-A\HF=-771.0040293\RMSD=4.608e-09\RMSF=5.859e-
06\Dipole=0.6626081,-0.422175,-0.3488615\Quadrupole=4.290292,-2.650800
9,-1.6394911,-0.9339771,1.1528536,0.0433351\PG=C01 [X(C10H24O5)]\\@

***tert*-tetroxide-ether complex**

E(M11/6-311+G**//M11/6-31+G*) = -771.1940559920
1\1\GINC-R89\FOpt\RM11\6-31+G(d,p)\C10H24O5\ROOT\16-Feb-2016\0\\# m11/
6-31+G** opt=maxcyc=200 scf=maxcyc=200 freq int=ultrafine\\ROOOOR'(H)-
--OMe2 complex (R = tert-Bu)\\0,1\C,0.0361927149,3.6612406371,0.855141
8866\O,0.444354072,2.3534322163,1.3503426617\O,-0.485351851,1.38359092
69,0.9559294572\O,0.0132960083,0.7728631833,-0.2121292272\O,0.94978420
81,-0.1835973371,0.1931146098\C,0.3299673438,-1.5055731851,0.238052243
5\C,1.4581370885,-2.3577291807,0.8120135037\H,1.133480073,-3.405283147
3,0.86947048\H,2.3470119972,-2.2999114675,0.1698068386\H,1.726769459,-
2.0124791267,1.8188598224\C,1.1670468159,4.5557201333,1.3545927795\H,0
.9631659217,5.5981755035,1.0755544982\H,1.2503198823,4.4925826181,2.44
74630429\H,2.1226210776,4.2491061892,0.9098480051\C,-1.3021572113,4.04
08955982,1.4848460947\H,-1.592742171,5.0525684672,1.1693777989\H,-2.08
84441542,3.3415401584,1.1700530652\H,-1.2283656102,4.0192403064,2.5802
661035\C,-0.0400492271,-1.9322973291,-1.1795705762\H,-0.3944759353,-2.
9727446116,-1.1750489173\H,-0.8507292405,-1.3015294515,-1.5666102978\H
,0.8364712779,-1.8612061852,-1.8380708437\C,-0.0415112823,3.659077401,

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