Supporting Information

Aluminum derivative peroxides in the $(t\text{-BuO})_3Al$ – 2t-BuOOH catalytic system as a source of electron-excited dioxygen: a quantum chemical study on a model

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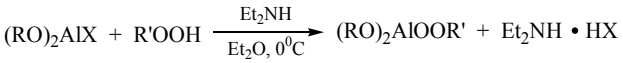
Additional Comment to Scheme 1: The content of the main product for R = $(CH_3)_2CH$-, $PhCH_2$- and *t*-Bu was 98-99%. According to the values of molecular masses (cryoscopy, benzene), these products are dimers. It is shown that (*tert*-butylperoxy)diisopropoxyaluminum is not stable at room temperature. It decomposes by 30-40% within an hour. The thermolysis of bis(benzyloxy)(tert-butylperoxy)aluminum in CCl_4 within the range of temperatures from 30-60°C at the initial concentration of 0.05 mol/L has been studied. The thermolysis is adequately described by the first-order kinetic equation to the conversion level of 50-60%. The temperature

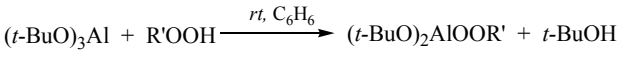
dependence of the reaction rate constant obeys Arrhenius' equation $k(T)=1.98\cdot10^{8}[\exp(-70300/RT)]$ s^{-1}. The thermolysis of individual $(RO)_2AlOOBu$-*t* with the primary and secondary alkyl group occurs intramolecularly to the corresponding aldehydes and ketones, *tert*-butyl alcohol and oxidized aluminum – alkoxo alumoxane $[ROAl–O–]_n$. No carbon- and oxygen-centered radicals have been detected by spin trapping using EPR in these reactions.[1]



R = $(CH_3)_2CH$, $PhCH_2$, *t*-Bu
R' = *t*-Bu, $PhC(CH_3)_2$, Ph_3C

Scheme 1. The high-yield synthesis of individual organoaluminum peroxides $(RO)_2AlOOR'$ under mild reaction conditions from $(RO)_2AlX$ (X=Cl, Br) and R'OOH

Additional Comment to Scheme 2. Thus, the oxidation of n-hexane by the $(t\text{-BuO})_3Al$–2*t*-BuOOH system at room temperature results in the mixture of isomeric ketones (2-hexanone and 3-hexanone) and, one order lower, the corresponding alcohols. In solid products there have been the carboxylic acids detected: acetic, propionic, butanoic at the 70:20:10 ratio, respectively. The oxidation of n-hexane indicates that the process occurs deeply and is accompanied by cleavage of the C-C bond[2,3]. Benzoic acid, esters, and peresters of benzoic acid have been identified in the products of the 1,2-diphenylethane oxidation[2,4,5].



R' = $PhC(CH_3)_2$, Ph_3C

Scheme 2. The high-yield synthesis of individual organoaluminum peroxides $(t\text{-BuO})_2AlOOR'$ from ready available $(t\text{-BuO})_3Al$

Additional Comment to Computational Details. The analytic calculation of the Hessian and vibrational spectrum have been carried out for the detected structures corresponding to the stationary points of the PES, which makes it possible to establish whether any detected stationary point is a local minimum (all frequencies are real) or a transition state (one vibrational

frequency is imaginary). The internal reaction coordinate (IRC) has been calculated for the located transition states (TS). The minimum energy pathways obtained this way make it possible to establish rearrangements of intermediates and, therefore, the mechanism of the reactions.

In case of the CCSD(T) method, the T_1 diagnostic and the T_2 maximum amplitude (hereinafter referred to as $T_{2,max}$) make it possible to establish the necessity of taking into account nondynamical correlation and the possibility of correct energy calculation with the help of the coupled cluster method and, therefore, to justify the results of B3LYP calculations.

1.1. Initial products of the thermolysis of peroxides and ozonides. It has been experimentally determined[1,6-9] that the elimination of O_2 in the t-BuOOH catalytic decomposition is the main reaction in benzene and CCl_4, i.e., in the absence of a reactive substrate. However, the formation of the precipitate consisting of polymeric alkoxo alumoxanes $[ROAlO–]_n$ and the detection of spin adducts of O–centered radicals, namely, *t*-BuO•, *t*-BuOO•, $(t\text{-BuO})_2$AlOO•, $(t\text{-BuO})_2$AlO•, by the EPR method for the organoaluminum compounds thermolysis indicate on the possibility of homolytic reactions.[1] The cleavage of the OO bond activated thermally is a common and well known phenomenon in the chemistry of peroxides.

The following compounds have been determined at the B3LYP/cc-pVTZ theory level: complex **16** (Fig. 1S) in the triplet electronic state corresponding to the $(MeO)_3Al$ and $O_2\left({}^3\Sigma_g^+\right)$ monomers; the products of ozonide decomposition, namely, the radical complexes $(MeO)_2AlO^{\bullet}$ and $MeOO^{\bullet}$ – **17**, **17*a*** and **18, 18*a*** (Fig. 1S) in the singlet and triplet electronic states, respectively. The η^1– and η^2–peroxides $(MeO)_2AlOO^{\bullet}$ (**20**) and $(MeO)_2AlO_2^{\bullet}$ (**21**) are formed in the initial stage of the homolysis together with MeO•.

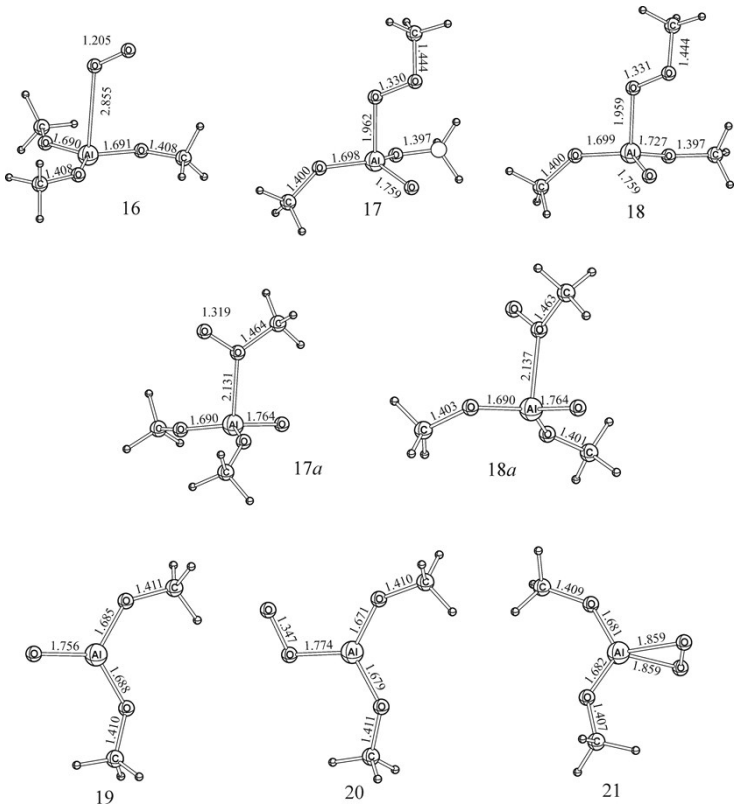


Figure 1S. Structures calculated by full geometry optimization at the B3LYP/cc-pVTZ theory level. Bond lengths are given in Å.

Complex **16** (Fig. 1S) is weakly stabilized; the energy relative to the level of isolated $(MeO)_3Al$ and $O_2\left({}^3\Sigma_g^-\right)$ is –4.6 kJ/mol. The decomposition **16**→$(MeO)_3Al+O_2\left({}^3\Sigma_g^-\right)$ occurs with no transition state.

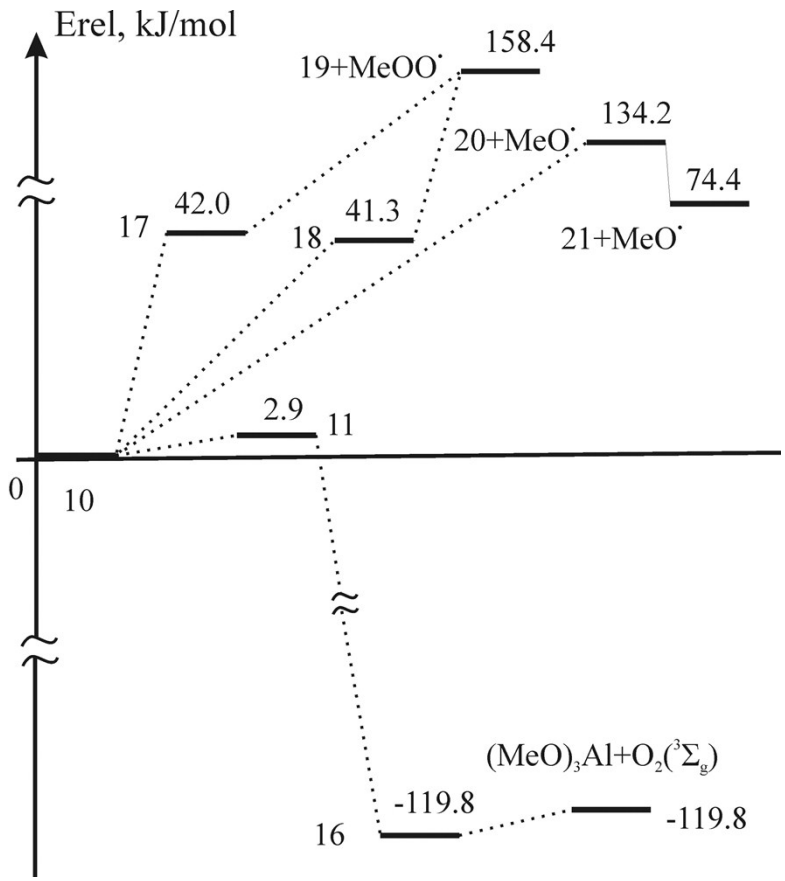


Figure 2S. Profile of the PES corresponding to the homolysis of $(MeO)_2AlOOOMe$ obtained at the B3LYP/cc-pVTZ theory level. The relative energies are in kJ/mol.

Structures **17** and **18** (Fig. 2S) are energetically quasi-degenerate (triplet complex **18** is 0.7 kJ/mol more energetically stable), which is explained by the delocalization of spin density onto two O atoms of the OOMe radical and the considerable spatial separation between O centers with high spin densities. In this case, the shortest distance between the O atoms in the AlO• and •OOMe fragments is approximately 3.0 Å. The energy of the dissociation of the OO bonds in ozonide **11** (Fig. 2S) with the formation of free radicals MeOO•+$(MeO)_2$AlO• or MeO•+$(MeO)_2$AlOO• is 158.4 and 134.2 kJ/mol, respectively. Then the energies of the complex formation **19**+MeOO•→**17** and **19**+MeOO•→**18** (Fig. 2S) are **-**116.4 and -117.1 kJ/mol, respectively, which exceed the energy of the complex formation $(MeO)_3Al$+MeOOH→**1*a*** in which the O atom of the peroxide group is similarly coordinated and the hydrogen bond is

additionally formed. The energy of the homolytic dissociation of **3** with the formation of **19**+MeO$^{\bullet}$ is 191.1 kJ/mol. In this case, the ozonide ring is strained, which lowers the energy of the dissociation reaction. **20** has an isomer (structures **21**, Fig. 2S) with the AlO_2 cyclic fragment that has a stabilizing influence on the structure during the delocalization of the AlOO$^{\bullet}$ unpaired electron onto the three atoms of AlO_2. The energy of the isomerization **20**→**21** is –59.8 kJ/mol. Previously[10-12], in case of aluminum, it was reported that in an inert matrix there were isolated $XAl(O_2)$ and $XAl(O_2)_2$ (X=F, Cl, Br) complexes with the AlO_2 fragments that are isosceles triangles, similarly to what has been established for **21** reported here for the first time. However, contrary to $(MeO)_2AlO_2$, η^2–$XAl(O_2)$ and bis–η^2–$XAl(O_2)_2$ are complexes, for example, the Al…O distances in $FAl(O_2)$ and $FAl(O_2)_2$ are 1.701 Å and 1.856 Å, respectively.[10-12]

References

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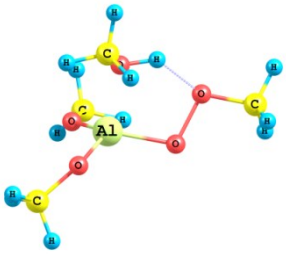
Cartesian Coordinates (in Å) for the intermediates and transition states located at the B3LYP/cc-pVTZ theory level

structure 1



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H	-0.171251000	-1.596156000	-1.299215000
H	0.110422000	-0.010403000	-2.037916000
H	1.424845000	-0.837341000	-1.195669000
C	-3.445070000	-2.072938000	1.411319000
H	-3.829540000	-2.767106000	0.657704000
H	-3.427194000	-2.602388000	2.370692000
H	-4.157751000	-1.245064000	1.499062000
O	-2.285993000	1.344701000	1.314832000
H	-1.014507000	0.720631000	3.239622000
O	-2.583969000	1.463778000	2.749135000
Al	-1.321514000	-0.155985000	1.095565000
C	-3.201605000	2.724923000	2.912340000
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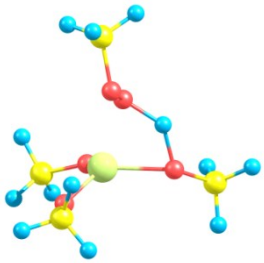
TS1



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H	1.371239000	0.282341000	4.155084000

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H	-0.242466000	0.661220000	-1.981346000
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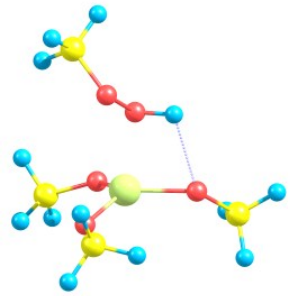
structure 2



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H	-1.121278000	-0.495243000	-1.507516000
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H	-2.594966000	-2.326806000	2.944715000
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H	-1.358368000	1.332299000	3.290319000
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Al	-0.944352000	-0.173168000	1.485695000
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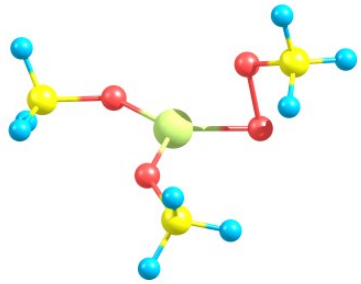
structure 3a



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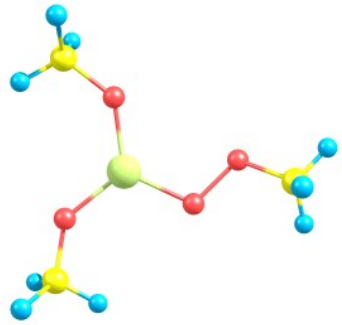
structure 3



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C	-1.038458000	-0.085720000	3.310411000
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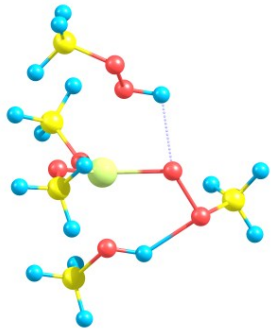
structure 4



symmetry c1

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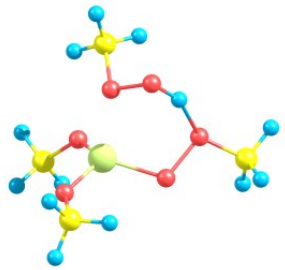
structure 5



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C	-0.151112000	1.359992000	3.254270000
H	-1.167504000	1.429023000	3.629577000
H	0.585820000	1.538590000	4.032492000
H	-0.011223000	2.033099000	2.411150000
O	-0.651311000	-1.256984000	0.344057000
O	-1.566409000	-2.616054000	2.697447000
C	-0.885919000	-3.842264000	2.634482000
H	-1.597404000	-4.658231000	2.475728000
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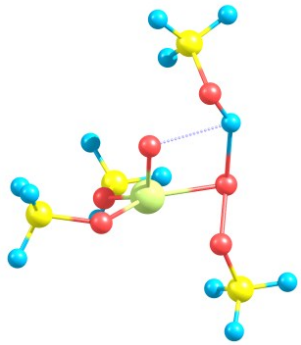
C	-4.050197000	-0.122674000	2.462007000
H	-4.405988000	0.670213000	3.126691000
H	-4.615409000	-0.049657000	1.526845000
H	-4.288154000	-1.084181000	2.928051000
Al	-1.416413000	-1.097523000	1.947242000

TS2

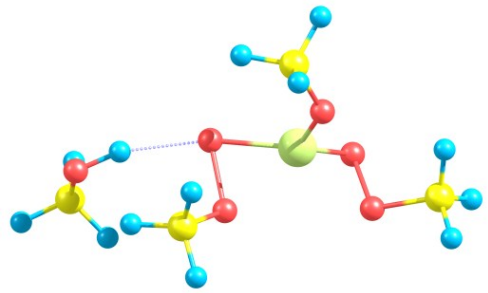


symmetry c1

O	0.529423000	-0.824809000	0.498550000
O	-0.016216000	0.180117000	3.837566000
C	1.774134000	-0.905750000	-0.203413000
H	2.620677000	-0.815709000	0.477016000
H	1.797609000	-1.873790000	-0.694026000
H	1.805727000	-0.109740000	-0.949535000

C	0.132818000	1.104625000	4.914599000
H	-0.582987000	0.780361000	5.669541000
H	1.146502000	1.080143000	5.312541000
H	-0.114961000	2.102464000	4.558397000
O	0.490339000	-2.021540000	1.856021000
O	2.784451000	-1.329638000	3.990387000
C	3.881119000	-0.457427000	4.010294000
H	4.693579000	-0.840272000	3.382220000
H	3.628029000	0.548847000	3.655664000
H	4.272752000	-0.365003000	5.028747000
O	0.979865000	0.535573000	2.770597000
H	0.537665000	-0.074300000	1.146212000
O	0.393047000	-2.774457000	3.728463000
C	0.987065000	-4.042851000	3.871807000
H	0.859433000	-4.367896000	4.909824000
H	0.483016000	-4.763252000	3.224373000
H	2.055820000	-4.033737000	3.644189000
Al	1.213664000	-1.244855000	3.303527000

structure 6

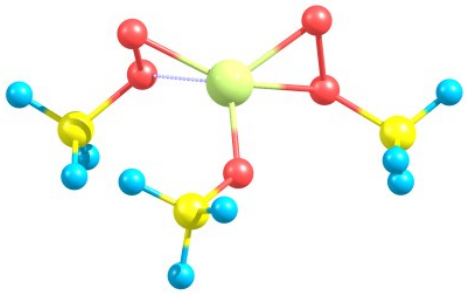


symmetry c1

O	0.637939000	1.521311000	0.365702000
O	0.485561000	-0.670559000	2.846196000
C	-0.051541000	0.964954000	-0.740915000
H	-0.690062000	0.122857000	-0.453164000
H	-0.684527000	1.747132000	-1.158826000
H	0.632911000	0.626036000	-1.526120000
C	0.122244000	0.548689000	3.509523000
H	-0.803980000	0.313545000	4.033341000
H	0.894913000	0.850684000	4.214758000
H	-0.044627000	1.311302000	2.752527000
O	1.928035000	-3.457430000	2.518534000
O	2.896047000	-1.519344000	4.619704000
C	3.788285000	-0.502567000	5.005234000
H	4.813546000	-0.883308000	5.031329000
H	3.764575000	0.356496000	4.326482000
H	3.538368000	-0.148283000	6.009329000
O	1.779175000	-0.458214000	2.089298000
H	1.179631000	0.828821000	0.771047000
O	1.014033000	-3.486142000	3.721736000
C	1.509105000	-4.459538000	4.642934000
H	0.802810000	-4.450385000	5.473146000
H	1.508030000	-5.432678000	4.156120000

H	2.505933000	-4.193858000	4.990231000
Al	1.976986000	-1.837349000	3.223961000

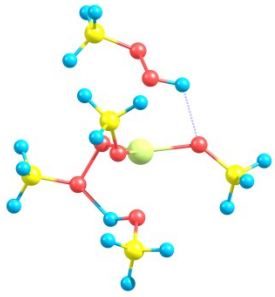
structure 7



symmetry c1

O	1.328054325	-1.196985363	-0.305734842
C	2.445238987	-0.840707951	-1.118112409
H	2.249721771	-1.289909450	-2.091745694
H	2.537478893	0.240933647	-1.207953886
H	3.344954213	-1.266048120	-0.678493062
O	-1.514081188	-0.770461938	1.038365616
O	-0.069159738	1.580726742	-0.161248115
C	0.766394847	2.697011970	0.015879923
H	0.279636877	3.444229482	0.650195955
H	1.724516856	2.436184511	0.478527205
H	0.973920500	3.166085658	-0.950553234
O	1.522269523	-0.598446990	1.071837021
O	-1.639176624	-0.790646597	-0.466571127
C	-2.792280412	-0.032285634	-0.832874324
H	-2.845166925	-0.100597639	-1.919602199
H	-3.670098282	-0.491431357	-0.382301044
H	-2.688499857	1.006134540	-0.523213174
Al	-0.037137179	-0.025414742	0.410572524

structure 4c

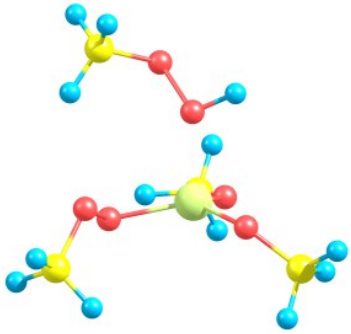


symmetry c1

O	-0.092656000	-0.173342000	0.272972000
O	-0.112572000	-0.232845000	2.973116000
C	1.306314000	0.001667000	2.918838000
H	1.785167000	-0.958874000	2.753345000
H	1.550147000	0.669562000	2.095970000
H	1.636354000	0.411144000	3.872522000
C	-0.021324000	-0.179869000	-1.123731000
H	-0.066826000	-1.193400000	-1.539849000
H	-0.832716000	0.398117000	-1.583407000

H	0.924216000	0.267352000	-1.447784000
C	-0.597751000	-3.351160000	2.580832000
H	0.323240000	-3.679764000	2.084018000
H	-0.320752000	-2.883873000	3.532006000
H	-1.186378000	-4.243914000	2.810164000
O	-2.543265000	0.360994000	1.990796000
H	-0.611144000	0.566279000	3.268087000
O	-2.096337000	1.335661000	2.981599000
Al	-1.232828000	-0.761193000	1.437153000
C	-2.295535000	2.618629000	2.417247000
H	-1.686760000	2.756997000	1.520822000
H	-1.996038000	3.329136000	3.189372000
H	-3.349610000	2.760264000	2.174894000
O	-1.342148000	-2.484909000	1.767122000
O	-2.673536000	-1.503548000	-0.030262000
H	-2.575426000	-2.379026000	0.406432000
O	-4.109555000	-1.269712000	0.094832000
C	-4.387838000	-0.136631000	-0.704557000
H	-4.136073000	-0.319826000	-1.751289000
H	-5.464070000	-0.000792000	-0.599469000
H	-3.867004000	0.743837000	-0.326683000

structure 8

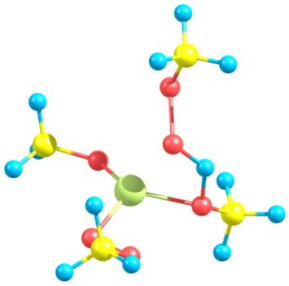


symmetry c1

O	0.053468000	0.448250000	0.260155000
O	-0.440982000	0.354229000	3.120854000
C	0.762373000	0.786730000	3.703015000
H	1.260744000	-0.034714000	4.228889000
H	1.463081000	1.189081000	2.963665000
H	0.558889000	1.572151000	4.437165000
C	0.233731000	0.112408000	-1.090977000
H	-0.270449000	-0.820707000	-1.363820000
H	-0.154312000	0.905794000	-1.738428000
H	1.299235000	-0.004958000	-1.311891000
C	-2.010345000	-3.321130000	2.862839000
H	-2.776071000	-3.569337000	3.599789000
H	-1.928793000	-4.123958000	2.126340000
H	-1.049107000	-3.181949000	3.364451000
O	-2.576351000	0.819805000	1.649515000
H	-2.477296000	1.749719000	1.901836000
O	-3.332231000	0.884862000	0.401858000

Al	-0.862681000	-0.186069000	1.551763000
C	-4.448619000	0.006804000	0.565151000
H	-4.115107000	-1.001875000	0.800353000
H	-4.924371000	0.034218000	-0.415089000
H	-5.132019000	0.383522000	1.326981000
O	-2.452373000	-2.125558000	2.258003000
O	-1.478212000	-1.804215000	1.211679000

TS3



symmetry c1

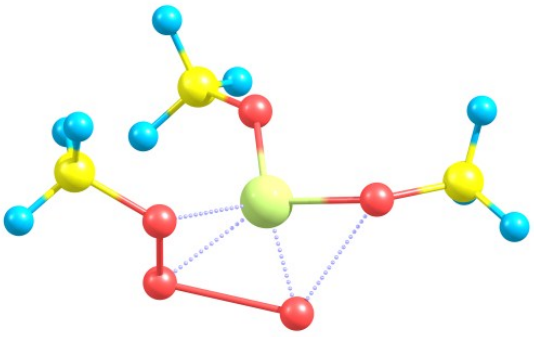
O	-0.091766000	-0.307690000	-0.073544000
O	0.491185000	-0.160410000	2.775218000
C	1.886026000	0.106649000	2.839152000
H	2.435597000	-0.831298000	2.762868000
H	2.198126000	0.768592000	2.029829000
H	2.118401000	0.569706000	3.797875000
C	-0.456894000	-0.561447000	-1.405197000
H	-1.057068000	-1.471280000	-1.508005000
H	-1.033238000	0.274026000	-1.815213000
H	0.441399000	-0.680906000	-2.016906000
C	-3.290599000	-2.430242000	3.111166000
H	-3.538311000	-2.486885000	4.172384000
H	-3.841603000	-1.607387000	2.647181000
H	-3.548729000	-3.370758000	2.619194000
O	-1.573424000	0.737117000	2.452256000
H	-0.439948000	0.645672000	2.903695000
O	-1.629268000	1.957695000	1.655971000
Al	-0.678853000	-0.668779000	1.473783000
C	-2.649253000	2.754090000	2.230164000
H	-3.616565000	2.250407000	2.186368000
H	-2.669947000	3.652138000	1.612213000
H	-2.412787000	3.020008000	3.262749000
O	-1.898275000	-2.208912000	3.070243000
O	-1.526533000	-2.190715000	1.649100000

structure 9

symmetry c1

O	-0.339683000	0.260146000	-0.059460000
O	-0.258226000	0.130129000	2.705074000
C	1.187118000	0.111589000	2.698123000
H	1.485712000	-0.919324000	2.536919000
H	1.567026000	0.736712000	1.893493000
H	1.545616000	0.449685000	3.667531000
C	-0.243703000	0.021058000	-1.439583000
H	-0.213523000	-1.049040000	-1.670629000
H	-1.085595000	0.458856000	-1.987786000
H	0.673912000	0.472546000	-1.827685000
C	-3.666395000	-2.654699000	2.275117000
H	-4.008697000	-2.949476000	3.268646000
H	-4.259332000	-1.807586000	1.919598000
H	-3.765583000	-3.495451000	1.584507000
O	-2.704248000	0.781295000	1.736727000
H	-0.629868000	0.997734000	2.977870000
O	-2.124988000	1.896051000	2.491664000
Al	-1.364718000	-0.277423000	1.206570000
C	-2.378179000	3.078760000	1.752678000
H	-1.873671000	3.055156000	0.784666000
H	-1.984611000	3.893028000	2.363198000
H	-3.451761000	3.206695000	1.610927000
O	-2.310296000	-2.301644000	2.444324000
O	-1.789770000	-1.977019000	1.111650000

TS4

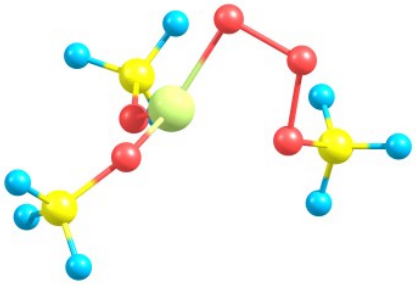


symmetry c1

O	1.322958823	-1.041529518	-0.493485079
C	2.584759210	-0.563464382	-0.971756305
H	2.549523882	-0.707380679	-2.051055965
H	2.722814539	0.488775777	-0.729785894
H	3.373305422	-1.169778075	-0.532431344
O	-0.725709585	-1.357573714	1.001512373
O	-0.015393120	1.657866838	-0.116543948
C	0.837818061	2.643180085	0.408697148
H	0.264481198	3.364218024	0.998087985
H	1.616609201	2.225272642	1.055462188
H	1.325746881	3.190619749	-0.403329520
O	1.289093863	-0.839481976	0.986855746
O	-1.834218493	-0.526524576	-0.580625989

C	-3.088194055	0.081685518	-0.397141262
H	-3.322463164	0.663689626	-1.296620965
H	-3.855642360	-0.683651811	-0.273249685
H	-3.108215246	0.760673305	0.459470085
Al	-0.228991128	-0.015852633	0.057751029

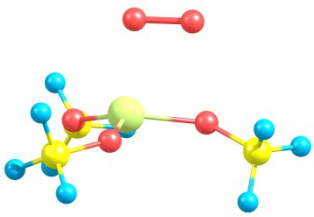
structure 10



symmetry c1

O	0.202459000	0.070175000	-0.144732000
C	0.149060000	0.093266000	1.293272000
H	1.038422000	0.641053000	1.600788000
H	-0.750433000	0.602055000	1.632836000
H	0.187192000	-0.929279000	1.659140000
O	-1.771732000	0.572616000	-1.161734000
O	-0.365723000	3.070196000	-0.312766000
C	-1.216331000	3.659695000	0.636242000
H	-1.590957000	4.618283000	0.266439000
H	-2.081708000	3.030737000	0.872541000
H	-0.671017000	3.853207000	1.565208000
O	-1.049721000	-0.553808000	-0.656325000
O	0.620199000	1.626633000	-2.652412000
C	1.476803000	2.515039000	-3.324436000
H	2.494006000	2.113295000	-3.347017000
H	1.144922000	2.644566000	-4.358243000
H	1.510830000	3.501596000	-2.851418000
Al	-0.337687000	1.663094000	-1.262860000

TS5

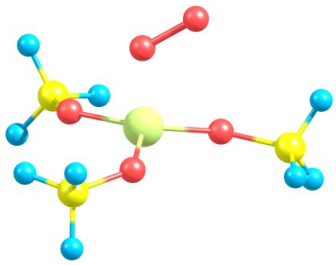


symmetry c1

O	0.388468000	-1.797021000	0.174540000
O	-1.790177000	0.242456000	0.178123000
O	0.976284000	0.985664000	0.766616000
O	0.601668000	0.156084000	-1.757074000
Al	-0.158762000	-0.186368000	0.068315000
C	-3.041727000	-0.371926000	0.000867000
H	-3.009645000	-1.446533000	0.206115000
H	-3.770311000	0.080284000	0.678418000
H	-3.403653000	-0.232587000	-1.022522000

C	1.567391000	-2.449872000	0.563977000
H	2.312703000	-1.758182000	0.968081000
H	1.339013000	-3.193263000	1.334137000
H	2.005898000	-2.977681000	-0.287552000
O	0.881632000	1.349452000	-1.466600000
C	0.693677000	2.174341000	1.457484000
H	0.072358000	2.845265000	0.854790000
H	0.142803000	1.962712000	2.381094000
H	1.626212000	2.678021000	1.715077000

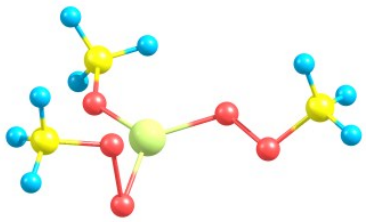
structure 11



symmetry c1

O	-0.007981000	0.147529000	0.022837000
O	0.037282000	0.113203000	2.934066000
O	2.571235000	-0.087184000	1.418993000
O	0.613742000	2.179014000	1.948224000
Al	0.920320000	0.271138000	1.439477000
C	-1.331599000	-0.020667000	3.218252000
H	-1.511966000	-1.015876000	3.640261000
H	-1.629501000	0.714849000	3.969488000
H	-1.957041000	0.093760000	2.329509000
C	0.249451000	-0.123104000	-1.332394000
H	1.303174000	-0.350001000	-1.520260000
H	-0.347307000	-0.978439000	-1.662023000
H	-0.030607000	0.736317000	-1.948565000
O	1.490157000	2.873057000	2.463520000
C	3.635368000	-0.212007000	2.327211000
H	4.271933000	0.677143000	2.297844000
H	3.290491000	-0.347525000	3.357349000
H	4.250134000	-1.075625000	2.060238000

structure 12

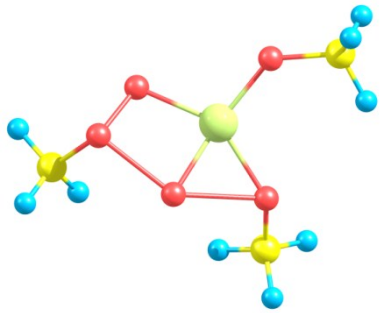


symmetry c1

O	-0.221423000	0.693995000	0.113876000
C	-0.324429000	0.334356000	1.471963000
H	0.651266000	0.263246000	1.961120000
H	-0.922218000	1.075476000	2.008800000
H	-0.823860000	-0.633847000	1.566433000

C	4.782549000	0.404155000	-1.007931000
H	5.527140000	0.707854000	-1.744988000
H	5.150589000	0.613858000	-0.000769000
H	4.575384000	-0.664565000	-1.110003000
O	0.674761000	1.821624000	-2.487866000
O	0.653020000	0.321311000	-2.724870000
Al	1.046782000	1.003582000	-0.963933000
C	-0.654161000	-0.044268000	-3.179160000
H	-1.407658000	0.206967000	-2.434605000
H	-0.610558000	-1.122268000	-3.333625000
H	-0.847889000	0.466444000	-4.119571000
O	3.644599000	1.181945000	-1.304408000
O	2.643651000	0.816660000	-0.301186000

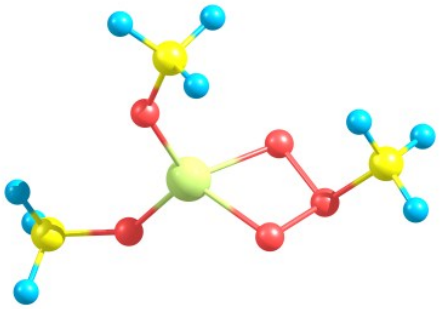
TS6



symmetry c1

O	-0.958616000	-0.101986000	0.491563000
C	-0.572145000	0.320393000	1.772857000
H	0.399670000	0.822721000	1.765264000
H	-1.323075000	1.021844000	2.152039000
H	-0.524207000	-0.534874000	2.448417000
C	3.030786000	0.345877000	-1.141057000
H	3.537912000	1.021124000	-1.828735000
H	2.748594000	0.861038000	-0.225192000
H	3.641969000	-0.527785000	-0.924824000
O	0.993262000	0.957574000	-2.094076000
O	-1.815211000	0.508552000	-2.181928000
Al	-0.452527000	0.280379000	-1.202136000
C	-3.199173000	0.363967000	-1.970597000
H	-3.441869000	0.110685000	-0.933475000
H	-3.596232000	-0.425415000	-2.614818000
H	-3.713460000	1.294876000	-2.224731000
O	1.867591000	-0.158915000	-1.797222000
O	0.703480000	-0.794939000	-0.430482000

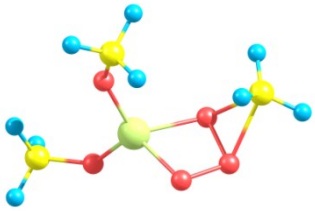
structure 13



symmetry c1

O	-1.408620000	0.314489000	1.037249000
C	-1.222866000	0.384289000	2.423342000
H	-0.722591000	-0.509824000	2.814492000
H	-0.628949000	1.258459000	2.718096000
H	-2.192728000	0.463568000	2.921669000
C	2.844979000	0.468265000	0.861986000
H	3.403015000	1.391780000	0.748876000
H	2.209722000	0.467827000	1.740727000
H	3.476890000	-0.411608000	0.801818000
O	1.044417000	1.509159000	-0.277438000
O	-1.180614000	0.219099000	-1.839338000
Al	-0.398571000	0.303282000	-0.336484000
C	-2.524472000	0.151335000	-2.242669000
H	-3.217788000	0.182653000	-1.395930000
H	-2.707010000	-0.774945000	-2.796232000
H	-2.761375000	0.988384000	-2.906534000
O	1.986563000	0.398346000	-0.320560000
O	1.135558000	-0.778978000	-0.208122000

TS7

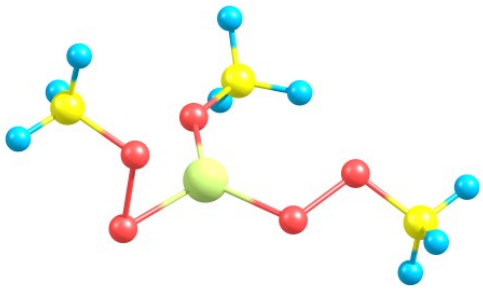


symmetry c1

O	-0.043437000	0.147947000	0.035894000
C	0.140106000	-0.049066000	1.407451000
H	1.166070000	0.167344000	1.732018000
H	-0.539717000	0.581081000	1.993555000
H	-0.072213000	-1.089529000	1.670404000
C	1.262234000	3.633900000	0.628278000
H	1.873063000	4.516239000	0.500393000
H	0.214040000	3.821525000	0.794235000
H	1.699321000	2.827722000	1.199196000
O	0.582374000	2.892529000	-1.110826000
O	0.351575000	0.462339000	-2.812274000
Al	0.695360000	1.002358000	-1.242422000
C	-0.393736000	-0.595494000	-3.357094000
H	-0.847258000	-1.228421000	-2.587207000
H	0.247252000	-1.225785000	-3.981064000

H	-1.196094000	-0.205773000	-3.991150000
O	2.092689000	2.923957000	-0.961632000
O	2.430595000	1.561171000	-0.907037000

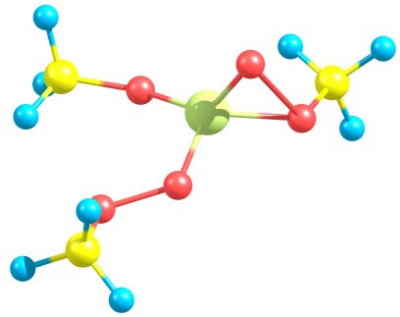
structure 12a



symmetry c1

O	0.026304000	0.324596000	0.009969000
C	0.067721000	0.087394000	1.397042000
H	1.089752000	-0.031555000	1.763005000
H	-0.399556000	0.918450000	1.932291000
H	-0.491420000	-0.821785000	1.633594000
C	4.489834000	0.427658000	0.412734000
H	4.767112000	-0.078895000	1.338215000
H	5.199787000	0.172784000	-0.377101000
H	4.483858000	1.509421000	0.568476000
O	0.468130000	1.321241000	-2.760300000
O	0.385028000	-0.189015000	-2.891131000
Al	1.091257000	0.595561000	-1.270445000
C	-0.984748000	-0.551807000	-3.090505000
H	-1.595386000	-0.241212000	-2.244444000
H	-0.980297000	-1.637801000	-3.182596000
H	-1.332580000	-0.094226000	-4.013809000
O	3.199854000	-0.054554000	0.105932000
O	2.829646000	0.591984000	-1.156580000

TS6a

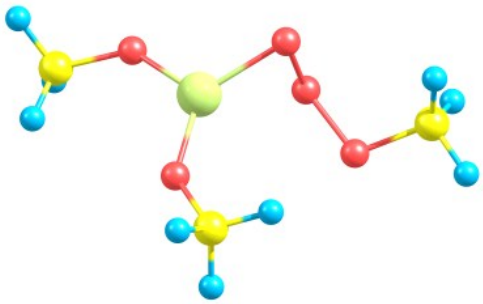


symmetry c1

O	-0.913672000	0.785530000	-0.150131000
C	-0.413370000	0.097484000	-1.264385000
H	-0.585430000	-0.980813000	-1.193683000
H	-0.876036000	0.455367000	-2.189932000
H	0.664393000	0.263005000	-1.344036000
C	-3.111370000	-3.052992000	1.085128000
H	-2.601917000	-3.885971000	0.605403000

H	-3.186626000	-3.210896000	2.160946000
H	-4.103872000	-2.910740000	0.655463000
O	-3.898761000	1.286357000	0.787709000
O	-2.095074000	2.094469000	2.110045000
Al	-2.239684000	0.815132000	0.902967000
C	-1.386611000	3.298725000	2.055174000
H	-0.854336000	3.438239000	1.111960000
H	-0.657923000	3.304030000	2.877320000
H	-2.067115000	4.136693000	2.230816000
O	-2.296501000	-1.916087000	0.812707000
O	-2.875363000	-0.818320000	1.432116000

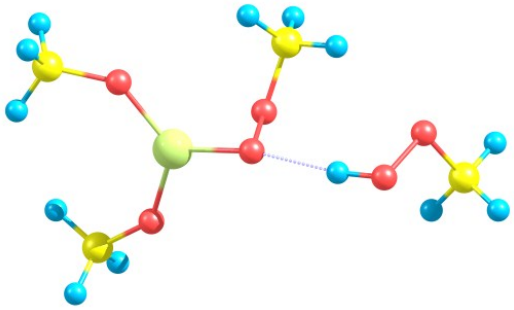
structure 13a



symmetry c1

O	-0.133422000	0.194275000	0.088029000
C	-0.051801000	0.164319000	1.492076000
H	0.854226000	0.647520000	1.868164000
H	-0.917917000	0.671470000	1.925430000
H	-0.055065000	-0.870712000	1.843627000
C	4.485095000	0.646444000	0.428649000
H	4.770622000	0.257531000	1.405054000
H	5.223963000	0.364516000	-0.321325000
H	4.369147000	1.728415000	0.475976000
O	2.182710000	1.833355000	-0.987964000
O	0.209931000	0.568919000	-2.784285000
Al	0.786613000	0.755966000	-1.209851000
C	-0.906296000	-0.070153000	-3.358831000
H	-1.613607000	-0.433284000	-2.607317000
H	-0.581730000	-0.921817000	-3.962964000
H	-1.432368000	0.627494000	-4.015296000
O	3.230133000	0.022701000	0.159704000
O	2.794086000	0.484469000	-1.129792000

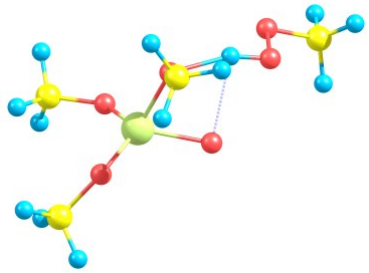
structure 14



symmetry c1

O	-0.085344000	0.100562000	0.105241000
O	-1.096951000	-1.337811000	5.864530000
C	0.086582000	0.325149000	-1.271070000
H	-0.672715000	1.020669000	-1.639570000
H	1.070359000	0.741419000	-1.510836000
H	-0.023599000	-0.614402000	-1.818776000
C	-0.604979000	-0.587760000	6.958988000
H	-1.471892000	-0.052276000	7.349687000
H	-0.200659000	-1.244294000	7.732169000
H	0.160727000	0.126388000	6.644954000
O	0.329134000	-0.702475000	2.908715000
O	-0.540882000	0.534759000	2.985966000
C	-1.920440000	0.136166000	2.916160000
H	-2.477496000	1.072417000	2.949847000
H	-2.116758000	-0.393810000	1.986455000
H	-2.141679000	-0.472667000	3.788920000
O	0.013955000	-2.121306000	5.360918000
H	0.205705000	-1.648351000	4.527590000
O	2.147845000	1.299390000	1.715831000
C	2.929667000	2.209778000	0.986895000
H	3.938417000	1.812089000	0.848108000
H	2.512865000	2.428280000	-0.001819000
H	3.011985000	3.152603000	1.534014000
Al	0.748895000	0.373548000	1.553410000

TS8

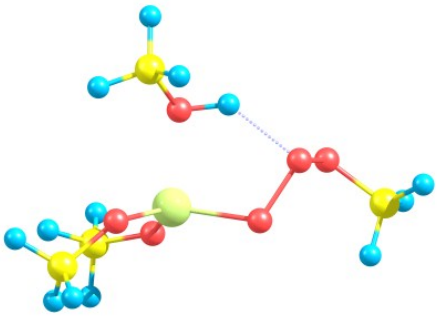


symmetry c1

O	0.051438000	-0.099890000	-0.020913000
O	-0.009988000	0.000768000	5.653683000
C	0.738086000	0.125185000	-1.218382000
H	0.046508000	0.487724000	-1.986864000
H	1.541114000	0.864122000	-1.117019000
H	1.181624000	-0.805226000	-1.589102000
C	0.727189000	-0.687810000	6.654871000
H	1.090576000	0.096902000	7.314723000
H	0.080352000	-1.376511000	7.200560000
H	1.561623000	-1.225088000	6.204110000
O	0.729506000	-0.983412000	2.740948000
O	-1.311189000	0.027582000	2.503657000
C	-2.345345000	-0.777977000	1.973970000
H	-3.220914000	-0.134780000	1.822549000

H	-2.064498000	-1.214120000	1.015119000
H	-2.619994000	-1.561137000	2.682324000
O	-0.533243000	-0.974110000	4.792544000
H	-0.875287000	-0.430778000	4.030875000
O	0.994389000	1.828446000	2.018467000
C	1.155129000	3.057691000	1.372439000
H	2.218944000	3.276929000	1.227714000
H	0.667989000	3.095778000	0.391016000
H	0.737663000	3.863779000	1.985789000
Al	0.260286000	0.325437000	1.633713000

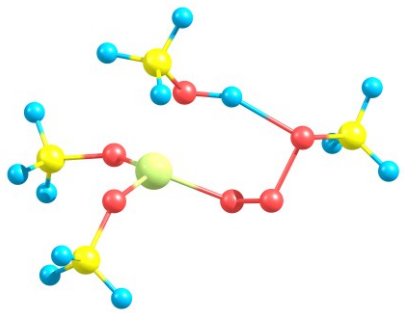
structure 15



symmetry c1

O	-0.091033000	-0.504759000	-2.167507000
O	-0.094124000	-0.276108000	2.795351000
C	0.604385000	-0.481967000	-3.387269000
H	0.023552000	0.052172000	-4.150669000
H	1.580580000	0.011196000	-3.307354000
H	0.773680000	-1.502689000	-3.751836000
C	0.690773000	-1.167737000	3.594219000
H	1.095733000	-0.536481000	4.385194000
H	0.065738000	-1.959365000	4.026052000
H	1.510798000	-1.594609000	3.006116000
O	0.312916000	-1.240810000	0.690238000
O	-1.534543000	0.622701000	-0.050401000
C	-2.724496000	0.367761000	-0.849348000
H	-3.531401000	0.997752000	-0.467246000
H	-2.486226000	0.622382000	-1.882684000
H	-2.994441000	-0.701974000	-0.797140000
O	-0.669018000	-1.049891000	1.719438000
H	-1.612286000	0.187276000	0.830944000
O	1.375184000	1.284226000	-0.318998000
C	1.871263000	2.383686000	-1.030523000
H	2.946091000	2.270611000	-1.208736000
H	1.385624000	2.519682000	-2.005046000
H	1.726431000	3.305970000	-0.457461000
Al	0.232019000	0.047035000	-0.577006000

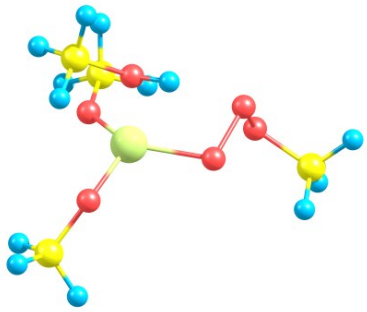
structure 15a



symmetry c1

O	0.032841000	-0.064324000	0.466634000
O	-0.712994000	-1.042771000	4.463228000
C	0.572416000	-0.746294000	-0.633398000
H	-0.194316000	-0.867625000	-1.404087000
H	1.412622000	-0.205901000	-1.084996000
H	0.927314000	-1.745338000	-0.357081000
C	-0.069910000	-1.115734000	5.736789000
H	-0.784197000	-0.690642000	6.441592000
H	0.133268000	-2.155806000	5.988716000
H	0.848778000	-0.531555000	5.732288000
O	1.216514000	-0.561371000	3.231607000
O	-1.020586000	0.979304000	2.801726000
C	-2.270159000	1.165019000	2.097516000
H	-3.039937000	1.432992000	2.817760000
H	-2.123746000	1.979741000	1.395899000
H	-2.534999000	0.260413000	1.555852000
O	0.218135000	-1.552984000	3.450390000
H	-1.114905000	0.347057000	3.556362000
O	1.647857000	1.935676000	1.964076000
C	2.165220000	2.813734000	1.003437000
H	3.258953000	2.765680000	0.988196000
H	1.806655000	2.593050000	-0.009121000
H	1.883335000	3.845619000	1.238561000
Al	0.638849000	0.562109000	1.942819000

structure 15b



symmetry c1

O	-0.244392000	-0.638528000	-0.012518000
O	0.219622000	0.376888000	4.664153000
C	0.876881000	-0.856737000	-0.828384000
H	0.553158000	-1.158488000	-1.829158000
H	1.494657000	0.042048000	-0.933360000

H	1.511134000	-1.657100000	-0.431358000
C	0.514278000	-0.750203000	5.482066000
H	1.438348000	-0.486612000	5.996095000
H	-0.281619000	-0.921680000	6.208857000
H	0.671072000	-1.638279000	4.869935000
O	-0.680261000	-0.753383000	2.839355000
O	-2.434198000	0.559163000	1.180995000
C	-2.997281000	0.967864000	-0.091727000
H	-4.059222000	1.163290000	0.036903000
H	-2.482104000	1.882264000	-0.367191000
H	-2.818247000	0.200016000	-0.840215000
O	-0.996037000	0.105834000	3.961162000
H	-2.916606000	-0.185749000	1.559304000
O	0.155936000	1.853510000	1.426598000
C	0.404975000	2.892921000	2.336672000
H	0.688576000	2.517499000	3.322845000
H	1.218160000	3.520411000	1.960427000
H	-0.477450000	3.531260000	2.460013000
Al	-0.513873000	0.291977000	1.402321000

Cartesian Coordinates (in Å) for the structures corresponding to minimum energy crossing points for singlet and triplet PESs located at the B3LYP/cc-pVTZ theory level

3a-MECP
symmetry c1

O	-1.621056000	-1.159226000	0.416298000
C	-2.909624000	-0.850503000	0.888613000
H	-2.965385000	-1.233740000	1.913085000
H	-3.101805000	0.223281000	0.900096000
H	-3.657978000	-1.363295000	0.284651000
O	1.207259000	-1.211413000	-0.149049000
O	-0.013969000	1.415485000	0.286034000
C	-0.731099000	2.619429000	0.245198000
H	-0.145717000	3.389963000	-0.265213000
H	-1.686930000	2.523859000	-0.281979000
H	-0.938076000	2.974419000	1.259624000
O	-1.429963000	-0.527030000	-1.441966000
Al	-0.159050000	-0.215972000	-0.161891000
C	2.593125000	-1.052410000	0.008326000
H	2.933678000	-1.579383000	0.905305000
H	3.119267000	-1.481705000	-0.849686000
H	2.887662000	-0.002031000	0.099993000

7-MECP
symmetry c1

O	-1.265495000	-1.266904000	0.313535000
C	-2.419025000	-1.056278000	1.091381000
H	-2.256158000	-1.587347000	2.035914000

H	-2.587898000	0.000289000	1.303279000
H	-3.286041000	-1.492370000	0.595131000
O	1.439619000	-0.822074000	-1.004339000
O	-0.068730000	1.506830000	0.235414000
C	-0.707600000	2.724271000	-0.044178000
H	-0.126697000	3.320309000	-0.756350000
H	-1.709971000	2.585753000	-0.463958000
H	-0.807523000	3.308147000	0.875643000
O	-1.488801000	-0.366953000	-1.481132000
O	1.616943000	-0.824849000	0.491840000
C	2.775688000	-0.056206000	0.806045000
H	2.865674000	-0.107153000	1.891850000
H	3.642641000	-0.514577000	0.332943000
H	2.657329000	0.977999000	0.485059000
Al	-0.039986000	-0.087342000	-0.371845000

10-MECP
symmetry c1

O	0.068395000	0.036361000	-0.122427000
C	0.427356000	-0.001811000	1.233768000
H	1.523723000	0.028235000	1.270892000
H	0.041387000	0.859133000	1.783199000
H	0.090589000	-0.937747000	1.679421000
O	-1.811948000	0.666700000	-1.670828000
O	-0.463844000	3.021180000	-0.266033000
C	-1.426263000	3.605626000	0.570127000
H	-1.942499000	4.419897000	0.052082000
H	-2.183471000	2.888177000	0.906197000
H	-0.945137000	4.028932000	1.457195000
O	-1.865418000	0.359588000	-0.394333000
O	0.935927000	1.542950000	-2.367216000
C	1.560584000	2.482403000	-3.203882000
H	2.607771000	2.204515000	-3.352784000
H	1.079696000	2.505686000	-4.187492000
H	1.532485000	3.495246000	-2.788040000
Al	-0.240750000	1.587345000	-1.145324000

11-MECP
symmetry c1

O	-1.831561000	0.102073000	0.189040000
O	0.441774000	-1.311311000	-0.883171000
O	0.532269000	1.686821000	-0.626675000
O	0.768823000	-0.937990000	0.997151000
Al	-0.185678000	0.231208000	-0.184896000
C	-0.183464000	-2.569549000	-0.991636000
H	-0.324493000	-2.765335000	-2.060653000
H	0.472459000	-3.339968000	-0.584380000
H	-1.155957000	-2.588247000	-0.498916000
C	-2.910463000	0.970548000	0.435210000
H	-2.644157000	2.020685000	0.279563000
H	-3.743992000	0.728640000	-0.229831000

H	-3.258398000	0.856509000	1.466195000
O	1.946889000	-0.617137000	1.271953000
C	1.810625000	2.205787000	-0.907600000
H	2.365922000	2.397393000	0.013440000
H	2.403578000	1.521168000	-1.522262000
H	1.704392000	3.147810000	-1.450776000

Table 1S. Focal point analysis for the reaction $2H_3COOH \rightarrow 2H_3COH+O_2$

	cc-pVDZ			
	CCSD	CCSD(T)	CCSDT	CCSDT(Q)
H_3COOH	-190.368187	-190.382701	-190.3832008	-190.384979
H_3COH	-115.412466	-115.420205	-115.4206500	-115.421363
$^1O_2$	-149.922723	-149.937141	-149.9424714	-149.949966
$^3O_2$	-149.975978	-149.985811	-149.9859998	-149.987962
Erel, kJ/mol	-169.4	-159.7	-159.9	-159.45
Delta, kJ/mol	-	9.8	-0.2	0.44

	cc-pVTZ			
	CCSD	CCSD(T)	CCSDT*	CCSDT(Q)*
H_3COOH	-190.561367	-190.587674	-	-
H_3COH	-115.535996	-115.550786	-	-
$^1O_2$	-150.058380	-150.081394	-	-
$^3O_2$	-150.111076	-150.129036	-	-
Erel, kJ/mol	-158.4	-145.1	[-144.9]	[-144.4]
Delta, kJ/mol		13.3	[-0.2]	[0.44]

* the estimated values are given in square brackets; the basis set (cc-pVDZ vs. cc-pVTZ) error is ±3.5 kJ/mol; total error of the focal point estimation for the CCSDT(Q)/cc-pVTZ is about ±4.0 kJ/mol