SUPPORTING INFORMATION

Figure 1:

The potential energy surface surrounding the transition state of MCO hydrolysis derived from an IRC calculation at the B3-LYP/6-31+G(d) level of theory. Relative energies have been calculated at the RMP2/6-311+G(3df,2p) and B3-LYP/6-31+G(d) levels of theory and plotted against the distance between the hydroxide nucleophile and electrophilic phosphorous.

![Graph showing the relationship between P-O distance and relative energy calculated at different levels of theory.](image-url)
Figure 2: B3-LYP/6-31+G(d) geometries of the reactants, intermediates, transition states and products formed during the gas phase reaction of OH- with MCS, MCO, MPS and MPO.
Figure 3: B3-LYP/6-31+G(d) optimised geometries of the reactants, intermediates, transition states and products formed during the gas phase reaction of OH$^-$ with TMP.
Figure 4: B3-LYP/6-31+G(d) optimized geometries of MCS, MCO, MPS and MPO with the aromatic rings sideways and upward, and the transition state between these conformations.
Figure 5:

The relative energy change as a function of the distance between Co\(^{2+}\) and the sulfur atom of MPS or OH.

Gaussian Archive Entries:

**Hydroxide:**

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\$\langle GINC-SC126\rangle\langle FOpt\rangle RB3LYP/6-31+G(d)\langle H1O1(1-)\rangle MLC501\langle 02-Aug-2004\rangle \# B3LYP/6-31+G(D) SCF=TIGHT OPT=TIGHT FREQ MAXDISK=39321600\langle OH-6dub3-bi\rangle g3b\langle -1,1\rangle O,0,0,0,0.1083189844\langle H,0,0,-0.866551875\rangle Version=DEC-AXP-O SF/1-G03RevB.03\langle State=1-SG\rangle HF=-75.79668095 RMSD=5.379e-10 RMSF=3.464e-08 Dipole=0,0,-0.75539755 PG=C*V [C*(H1O1)]\rangle \# @
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**Dimethyl Phosphate:**

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\$\langle GINC-SC49\rangle FOpt\langle RB3LYP\rangle 6-31+G(d)\langle C2H7O4P1\rangle MLC501\langle 30-Aug-2004\rangle \# B3LYP/6-31+G* OPT FREQ MAXDISK=134217728\langle OHO-6+dub3\rangle \langle C,0.3893174154,2.2719552,-1.1950599595\rangle \langle H,0.6498856595,-0.03856106,-1.844893\rangle \langle H,-0.667746915,2.551891805,-1.0680755023\rangle \langle H,0.54106409,-1.9698691462\rangle \langle H,-1.2768309222\rangle \langle Version=DEC-AXP-OSF/1-G03RevB.03\rangle \langle State=1-AH\rangle HF=-
```

Dimethyl Thiophosphate:
\$
\begin{align*}
\text{RMSD} &= 7.382 \times 10^{-9} \\
\text{RMSF} &= 2.239 \times 10^{-5} \\
\text{Dipole} &= 0.2500141, -0.3293539, -0.4169611
\end{align*}
\$
PG=C01 [X(C2H7O4P1)]

Trimethyl Phosphate reaction with hydroxide:
\$
\begin{align*}
\text{RMSD} &= 3.218 \times 10^{-9} \\
\text{RMSF} &= 2.899 \times 10^{-6} \\
\text{Dipole} &= 0.3696425, 0.5134713, -0.1387684
\end{align*}
\$
PG=C01 [X(C3H9O4P1)]

INT1
\$
\begin{align*}
\text{RMSD} &= 3.314 \times 10^{-9} \\
\text{RMSF} &= 1.910 \times 10^{-5} \\
\text{Dipole} &= 3.7428273, -0.1758144, 0.3052228
\end{align*}
\$
PG=C01 [X(C3H10O5P1)]

TS1
TMPTS3
\[\text{Version=Al64T-G03RevC.02}\ \text{State=1-A}\ \text{HF}=-837.9148959\ \text{RMSD}=3.887e-09\ \text{RMSF}=2.270e-05\ \text{Dipole}=-0.306095, -0.0811224, -0.2752485\ \text{PG}=\text{C01}\ [X(\text{C3H10O5P}1)archs]
\]

TMPTINT4
\[\text{Version=Al64T-G03RevC.02}\ \text{State=1-A}\ \text{HF}=-837.9123161\ \text{RMSD}=4.067e-09\ \text{RMSF}=3.467e-06\ \text{Dipole}=0.2927716, -0.1908961, 0.00988\ \text{PG}=\text{C01} [X(\text{C3H10O5P}1)]\]

TMP leaving group: Methoxide
\[\text{Version=Al64T-G03RevC.02}\ \text{State=1-A}\ \text{HF}=-837.9123161\ \text{RMSD}=4.067e-09\ \text{RMSF}=3.467e-06\ \text{Dipole}=0.2927716, -0.1908961, 0.00988\ \text{PG}=\text{C01} [X(\text{C3H10O5P}1)]\]
Dimethoate reaction with hydroxide:

**Dimethoate**

\[\text{Dimethoate} \rightarrow \text{Dimethoate INT1} \rightarrow \text{Dimethoate TS1}\]

**Dimethoate INT1**

**Dimethoate TS1**
Dimethoate INT2

\[ \text{Dimethoate TS2} \]

\[ \text{Dimethoate INT2} \]
Dimethoate LEAVING GROUP
\[ \text{Dimethoate LEAVING GROUP} \]

\[ \text{MCO, MCS reactions with hydroxide:} \]

\[ \text{MCO} \]

\[ \text{MCOINT1} \]

\[ \text{MCOINT} \]
\[ H, -6.3821941481, -1.6342377012, 0.9825725044 \]
\Version=Al64T-G03RevC.02\State=1-A\HF=-2424.4784834\RMSD=8.911e-09\RMSF=1.099e-05\Dipole=6.5954904, 1.4006293, 0.0337788\PG=C01 \[X(C7H8Cl3N1O5P1)\]@}

MCOTS1
\Version=DEC-AXP-OSF/1-G03RevB.03\State=1-A\HF=-2671.5896612\RMSD=6.726e-09\RMSF=4.604e-05\Dipole=-0.0871899, 0.5814402, -0.4296467\PG=C01 \[X(C7H7Cl3N1O3P1S1)\]@}

MCS
\Version=DEC-AXP-OSF/1-G03RevB.03\State=1-A\HF=-2424.4761836\RMSD=4.002e-09\RMSF=2.306e-06\}

MCSINT1
\Version=DEC-AXP-OSF/1-G03RevB.03\State=1-A\HF=-2671.5896612\RMSD=6.726e-09\RMSF=4.604e-05\Dipole=-0.0871899, 0.5814402, -0.4296467\PG=C01 \[X(C7H7Cl3N1O3P1S1)\]@}
\begin{verbatim}
MPO
\end{verbatim}

\begin{verbatim}
MPOINT1
\end{verbatim}

\begin{verbatim}
MPOTS
\end{verbatim}
Diethyl benzylphosphonate Ring ‘sideways’:

\[ \text{Diethyl benzylphosphonate Ring ‘sideways’:} \]
Diethyl benzylphosphonate Ring 'up':

\[
\begin{align*}
\text{B3LYP/6-31+G* OPT=debpup/O} & \quad \text{C12H19O3P1/CJJ506/05-Apr-2005/O} \\
\end{align*}
\]

Diethyl benzylphosphonate Transition State:

\[
\begin{align*}
\text{B3LYP/6-31+G* OPT=(TS,CALFC,NOEIGENTEST) DEBPTS/O} & \quad \text{C12H19O3P1/CJJ506/05-Apr-2005/O} \\
\end{align*}
\]

Diethyl benzylphosphonate
MCS ring ‘up’:
\[\text{\# B3LYP/6-31+G* OPT}\]
\[\text{mcs-up}\]
\[\text{0,1}\]
\[\text{O},-2.061216112,-0.6113995103,-C.,-2.27303813,-2.1008659551,1.59448825161\]
\[\text{H},-2.1064893523,-0.6881451947,1.3464710146\]
\[\text{O},-3.977876341,1.9296111842,2.246303425,2.69143629-H.,-1.4460313758,-2.6515902225,1.14002154799,-2.4344799514,1.1995836254\]
\[\text{Cl},0.3861585012,1.7943758086,1.9664764516\]
\[\text{Version}=\text{Al64T-G03RevC.02}\]
\[\text{State}=1-A\]
\[\text{HF}=-2671.5859725\]
\[\text{RMSD}=6.940e-09\]
\[\text{RMSF}=3.208e-06\]
\[\text{Dipole}=0.4806552,0.634292,0.823877\]
MCO Transition State:

\[ \text{Version=Al64T-G03RevC.02\ State=1-A\ HF=-2348.632589\ RMSD=6.788e-09\ RMSF=6.552e-06\ Dipole=0.5081652,0.6683177,0.8390189\ PG=C01 [X(C7H7Cl3N1O4P1)]} \]

\[ \text{MPS Transition State:} \]

\[ \text{Version=Al64T-G03RevC.02\ State=1-A\ HF=-2348.6287277\ RMSD=8.431e-09\ RMSF=4.687e-06\ Dipole=-0.2861033,-0.2153083,0.1201229\ PG=C01 [X(C8H10N1O5P1S1)]} \]

\[ \text{MPS ring 'up':} \]

\[ \text{Version=Al64T-G03RevC.02\ State=1-A\ HF=-1481.2776015\ RMSD=2.966e-09\ RMSF=8.866e-05\ Dipole=-1.737421999,-3.4179130732\ PG=C01 [X(C8H10N1O5P1S1)]} \]
6170584.0.4409044796,0.8194908734\Version=Al64T-G03RevC.02\State=1-A
\HF=-1158.3227732\RMSD=7.429e-09\RMSF=2.671e-06\Dipole=-1.9968377,-0.3997861,0.7033998\PG=C01 [X(C8H10N1O6P1)]\@