Supporting Information

A Clock Reaction Based on Molybdenum Blue

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Contents

Cartesian coordinates of optimized intermediates

1

Mo	-0.00000	-0.29202	0.00000
O	1.43450	0.77474	-0.54242
C	2.70584	1.09001	0.01481
H	2.70166	2.13209	0.35201
H	2.94006	0.43492	0.86128
H	3.46707	0.96758	-0.76225
O	0.49652	-1.26749	1.29495
O	-0.49650	-1.26755	-1.29492
O	-1.43450	0.77475	0.54240
C	-2.70584	1.09001	-0.01483
H	-3.46706	0.96766	0.76226
H	-2.70165	2.13206	-0.35211
H	-2.94010	0.43487	-0.86125

2

Mo	0.04558	-0.19362	0.15509
O	-1.15716	1.23497	0.25639
C	-2.44277	1.49013	-0.28666
H	-2.42251	2.47260	-0.77057
H	-2.71456	0.72566	-1.02252
H	-3.17977	1.50073	0.52311
O	-1.38051	-1.24750	-0.60310
O	0.40920	-0.54238	1.75727
O	1.51360	0.55749	-0.71819
C	2.82152	0.99167	-0.36219
H	3.54323	0.49696	-1.01965
H	2.88280	2.07450	-0.51350
H	3.05056	0.75463	0.68223
O	-0.05344	-1.85055	-0.75481

3

Mo	0.325860	-0.064476	0.000070
O	1.259612	1.560988	0.223259
O	0.256417	-0.870078	1.486337
O	-1.411987	0.266984	-0.580589
C	-2.706107	0.174612	0.007050
H	-3.344260	-0.427767	-0.647013
H	-2.656790	-0.288502	0.998585
H	-3.127570	1.181264	0.094888
H	1.927476	1.842061	-0.417515
O	1.114919	-1.038734	-1.138282

4

Mo	-0.138971	-0.003654	0.345599
O	-1.848652	0.586114	-0.115635
C	-2.815293	0.259586	-1.087298
H	-3.795142	0.598146	-0.735694
H	-2.579123	0.757415	-2.036229
H	-2.823786	-0.827097	-1.233246
O	-0.910069	-1.718784	-0.159989
O	-0.052188	0.28762	1.99895
O	0.649975	1.386321	-0.678303
C	1.918869	1.997893	-0.518208
H	2.679022	1.248042	-0.264784
H	2.189987	2.490824	-1.457993
H	1.882282	2.746379	0.28269
H	-0.335349	-2.47528	0.02023
C	2.068835	-1.580626	-0.93847
H	2.245887	-0.863426	-1.752163
H	3.017748	-2.051002	-0.659788
H	1.386771	-2.356245	-1.316838
O	1.527688	-0.938199	0.192789

5

Mo	-0.501523	0.19697	-0.176859
O	-1.654853	-1.746611	0.536139
O	1.265164	-0.738151	-0.462149
O	-1.168756	0.889682	1.51549
O	-1.39414	0.121456	-1.612442
O	0.639033	1.77155	-0.300447
C	0.09947	3.065055	-0.119232
H	0.922414	3.788287	-0.029534
H	-0.518046	3.361162	-0.981303
H	-0.521299	3.120267	0.785776
C	-3.050667	-1.821456	0.170079
H	-3.472067	-2.779792	0.488842
H	-3.554457	-1.012689	0.700835
H	-3.173638	-1.670759	-0.905462
C	2.404604	-0.811301	0.061917
H	-1.887991	0.378745	1.912651
H	-1.189313	-2.476831	0.108324
C	2.633426	-0.268467	1.442515
H	2.05022	-0.846727	2.174419
H	3.685936	-0.309829	1.731064
H	2.274096	0.76478	1.486318
C	3.506691	-1.494192	-0.692492
H	3.900558	-2.348887	-0.125653
H	3.147394	-1.836586	-1.664323
H	4.347436	-0.805114	-0.843343

7

Mo	0.539705	-0.514603	-0.244099
O	-0.660728	1.657134	-0.064366
O	-1.353431	-1.114861	-0.461213
C	-0.605065	2.610317	-1.137527
H	-1.117246	3.53299	-0.844602
H	0.446905	2.816893	-1.329193
H	-1.053976	2.20945	-2.052163
O	1.17561	0.06922	1.409536
O	1.22347	0.309576	-1.556828
O	1.13252	-2.093893	-0.351013
O	-2.440324	-0.284085	-0.058452
H	-1.581435	1.365367	0.053572
O	-2.605131	-0.450628	1.359306
H	-3.007561	-1.33756	1.398625
C	1.678162	1.300006	1.913441
H	2.620344	1.555093	1.415537
H	0.948557	2.099188	1.754878
H	1.862347	1.170291	2.98426

8

Mo	-0.561625	-0.296855	0.03824
O	1.916328	0.248393	-0.460014
O	0.327802	-1.378771	-1.221267
C	2.924757	-0.400645	0.339262
H	3.885184	0.109036	0.208335
H	2.593063	-0.320212	1.37318
H	3.018275	-1.456162	0.06908
O	-0.758011	1.50283	-0.440707
O	0.047229	-0.486871	1.613795
O	-2.117418	- 0.987024	-0.024918
H	2.067644	0.042854	-1.394015
C	-0.144945	2.706166	0.004733
H	0.945581	2.610094	-0.004883
H	-0.446602	3.509244	-0.67519
H	-0.481215	2.95149	1.018347

Cartesian coordinates of optimized transition states

$TS_{2\text{-}3}$

Mo	0.64924800	-0.35279200	0.04490900
O	-0.92646500	0.71708400	0.51393800
C	-2.15116900	0.36868200	0.01235000
H	-1.91834000	-0.64145800	-0.64956900
O	-0.78623700	-1.25565800	-0.96092100
O	1.09159200	-0.91205600	1.57269200
O	1.76999100	1.02795700	-0.52237500
C	2.62181800	1.95625900	0.13871100
H	3.43510400	2.22038900	-0.54410400
H	2.05288400	2.85938200	0.38659100
H	3.03892100	1.52684300	1.05620100
O	0.93617000	-1.71162700	-1.08890400
C	-3.12196300	-0.08359000	1.09354200
H	-3.37572700	0.77207600	1.73058800
H	-4.04415700	-0.47553300	0.65601800
H	-2.66550500	-0.85316500	1.72030600
C	-2.68523000	1.36305500	-1.00951800
H	-3.60464400	0.99465800	-1.47229100
H	-2.90530400	2.31221400	-0.50681100
H	-1.94280000	1.54980300	-1.78905800

$TS_{4\text{-}5}$

Mo	-0.56268900	-0.38331900	-0.24300400
O	-1.95735500	0.80193700	0.34806600
C	-3.26898400	0.40622100	0.72518800
H	-3.23983300	-0.45431000	1.40195100
H	-3.75128600	1.25315500	1.22780600
H	-3.86037700	0.13962900	-0.16125800
O	-0.98745400	-0.91685700	-1.77747100
O	0.46626000	1.38792600	-0.41539000
O	1.30520700	-0.82288800	-0.05942300
C	2.39960000	-0.09584800	0.21739100
H	1.55365500	1.10767700	-0.22599000
O	-1.24638300	-1.59604300	1.09338600
C	0.11660400	2.76271300	-0.23865600
H	0.37585500	3.32403100	-1.14140400
H	-0.95991100	2.79252500	-0.06180700
H	0.64766700	3.17814700	0.62405500
H	-0.75004500	-2.42442500	1.15578200
C	2.67016600	0.16462900	1.68821200
H	3.41999600	0.95203300	1.81115500
H	1.75934500	0.46587700	2.21564700
H	3.05762000	-0.73877500	2.18331300
C	3.58928500	-0.39103900	-0.66806200
H	4.32880800	0.41349700	-0.60331800
H	4.09190000	-1.32288100	-0.36728700
H	3.27732000	-0.49946700	-1.71027600

$TS_{2\text{-}7}$

Mo	0.44554900	-0.35972400	-0.20758600
O	-0.66233500	1.30028800	-0.07756300
O	-1.39144500	-1.12116000	-0.11774800
C	-0.15855700	2.57456800	-0.47175100
H	-0.95243600	3.31676500	-0.34190900
H	0.69344900	2.85764000	0.15686800
H	0.16007100	2.55986200	-1.52097600
O	1.67551000	0.08457900	1.12294400
O	1.16298600	-0.10394800	-1.71324000
O	0.18235100	-2.10230300	-0.05810700
O	-2.76050500	0.11081600	-0.15968000
H	-2.01008000	0.84358200	-0.12139900
O	-3.28020200	0.16278400	1.17275100
H	-3.59451200	-0.75356600	1.25903000
C	3.05163300	0.43572700	1.18614400
H	3.44709400	0.67237300	0.19213800
H	3.16161600	1.30510200	1.84253600

H	3.61240000	-0.40355800	1.61110900

Equations used for modeling the steps 1→4 and 4→5

For MB formation, **4**→**5** is the most important reaction. However, first **4** needs to be made from **1**, a reaction which is reversible. Since **1**→**4** is calculated to be thermoneutral and is isentropic under fixed solvation shell conditions, it can be roughly assumed that $K_{1\text{-}4} \approx 1$. As ROH is the solvent, its concentration can be directly included in the equilibrium constant (equation S1). Instead of modeling this equilibrium dynamically, we assumed fast equilibration and thus expressed the overall rate of reaction **4**→**5** as a function of [**1**] (equation S4).

The subtle distinction of the reactive part of the [**1**] pool (i.e. [**4**]) and the unreactive part of the [**1**] pool (i.e. [$\mathbf{1}_{nr}$]) is only relevant for this case, due to the quantum chemically found lowering of the barrier by solvolysis. The other elementary steps are most likely not affected by the catalyst being in state **4** or $\mathbf{1}_{nr}$, and therefore we opted for the simple notation given in Table 1. Furthermore, treating **1** by lumping together $\mathbf{1}_{nr}$ and **4** keeps the model complexity at a reasonable level.

Equilibrium	$[\mathbf{4}] = K'_{1\text{-}4}\,[\mathrm{ROH}]\,[\mathbf{1}_{nr}] = K_{1\text{-}4}\,[\mathbf{1}_{nr}]$	(eq. S1)
Distinction	$[\mathbf{1}_{nr}] + [\mathbf{4}] = [\mathbf{1}]$	(eq. S2)
(S1 in S2)	$[\mathbf{4}]\,(1 + K_{1\text{-}4}^{-1}) = [\mathbf{1}]$	(eq. S3a)
	$[\mathbf{4}] = (1 + K_{1\text{-}4}^{-1})^{-1}\,[\mathbf{1}]$	(eq. S3b)
Rate	$r_{4\text{-}5} = k_{4\text{-}5}\,[\mathbf{4}] = k_{4\text{-}5}\,(1+ K_{1\text{-}4}^{-1})^{-1}\,[\mathbf{1}]$	(eq. S4)

Equation used for modeling the step 3→1

Reaction **3**→**1** is a mere solvent coordination event and supposedly very fast, compared to the other steps in the catalytic cycle. Thus, in the kinetic model we directly substituted any formation of **3** by quasi instantaneous formation of **1**.

Substitution	$\mathrm{d}[\mathbf{1}]/\mathrm{d}t = \mathrm{d}[\mathbf{3}]/\mathrm{d}t$	(eq. S5)

Mulliken and bond length analysis of 8

The electronic configuration of **8** was invesigated by Mulliken and bond length analysis (Figure S1). Both bond lenghts and Mulliken spin densities consistently revealed a structure that is best described by a localized oxyl radical rather than a mesomerically diffuse form.

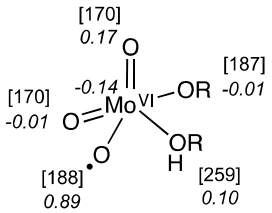

Figure S1. Bond lengths to ligands (square brackets, in pm) and Mulliken spin densities (italic, atomic units) on Mo and O atoms in the Mo^{VI} oxyl species **8**.