Mechanistic Insights into Li_2O_2-Solvent Reactions: Water-Induced Parasitic Chemistry in Li–Air Batteries

Leonardo H. Baumer [a], Carmen M. Sinitsyna [a] and Ana E. Torres* [a].

Supplementary Information

Coordinates of the optimized geometries for stationary points found along the reaction pathway.

LiOH Formation within the continuum solvent model (CH_3CN)

Li_2O_2
0 1

O	0.00006500	0.76033100	-0.13457900
O	-0.00007100	-0.76040700	-0.13453000
Li	-1.51494500	0.00019200	0.35881600
Li	1.51496200	0.00000900	0.35881000

H_2O

O	0.00000000	0.00000000	0.11723100
H	0.00000000	0.76676300	-0.46892200
H	0.00000000	-0.76676300	-0.46892200

Li_2O_2--H_2O

O	1.04386500	0.74794600	0.11339400
O	1.20846300	-0.76739800	0.03750500
Li	2.78661600	0.15034300	-0.18696400
Li	-0.45561300	-0.16197900	-0.16310400
O	-2.38281300	0.00390000	-0.07374600
H	-2.82516600	0.89282100	-0.07581500
H	-3.12396800	-0.73349600	0.50879000

TS

O	0.97838100	0.68581600	-0.14392800
O	0.60579500	-0.74416600	-0.32219000
Li	1.93768300	-0.42259300	0.85306700
Li	-0.70149300	1.36353100	0.08077400
O	-1.70055700	-0.14050800	0.04372000
H	-2.24665300	-0.58231500	0.69909700
H	-0.53086900	-0.64963200	-0.12143800

LiOOH--LiOH

O	0.97501600	0.68074100	-0.17807700
O	0.63768200	-0.75337500	-0.33267800

Li	1.90040700	-0.35607900	0.93177900
Li	-0.73390300	1.34010100	0.00006800
O	-1.69051500	-0.14013500	0.19821500
H	-2.48491200	-0.53935600	-0.16196800
H	-0.39205700	-0.71056200	-0.13325300

LiOOH

Li	0.72791400	1.24726400	0.06489100
O	-0.73561700	0.08040200	-0.11186000
H	-1.18241400	-0.23776600	0.68462200
O	0.61045100	-0.51840500	0.00194800

LiOH

O	0.00000000	0.00000000	-0.33599100
H	0.00000000	0.00000000	-1.29090800
Li	0.00000000	0.00000000	1.32627800

LiOOH reaction with ACN first stage

ACN

C	0.27799300	-0.00008900	-0.00001700
N	1.43485000	0.00004000	0.00001300
C	-1.18023600	0.00003100	0.00000600
H	-1.54357900	-0.36320900	0.96319700
H	-1.54343900	1.01587600	-0.16707200
H	-1.54347800	-0.65259800	-0.79614900

LiOOH--CH_3CN

Li	0.95270500	1.34163200	-0.16800300
O	1.46397300	-0.27523200	0.69130300
H	2.38041200	-0.43483700	0.95435200
O	1.54867800	-0.22760600	-0.78162000
C	-1.32147200	0.29327600	0.02729900
N	-1.13179800	1.43542500	0.07147500
C	-1.48947200	-1.14832600	-0.03749200
H	-1.82814500	-1.52299700	0.93018400
H	-2.21637200	-1.40003200	-0.81186600
H	-0.50696900	-1.56199300	-0.28528800

TS1

Li	-1.36666000	1.22153700	0.64448000
O	-1.73798600	-0.32293500	-0.35286800
H	-2.39070200	-1.00129300	-0.11773900
O	-0.55057900	-0.82577100	0.31383400
C	0.71766600	0.34788400	-0.03668300
N	0.40363800	1.49978200	-0.13844500
C	1.86810500	-0.59477400	-0.03526500
H	2.79753100	-0.02271800	-0.05404500
H	1.84293100	-1.21993800	0.86071700
H	1.81864900	-1.24814900	-0.90929000

RI_1'

Li	-1.54546900	0.87000000	-0.74341200
O	-0.85174700	-1.06806900	-0.63001800
H	-1.51141800	-1.20356300	0.09104600
O	0.38613800	-1.04506900	0.05583400
C	1.00449400	0.15852500	-0.07028300
N	0.43568900	1.13549800	-0.64840800
C	2.36254300	0.08552400	0.55210200
H	2.85444400	1.05477700	0.47084200
H	2.27257500	-0.19189800	1.60562600
H	2.96174500	-0.67527300	0.04538900
O	-2.42162200	0.40333700	0.70708900
H	1.04623100	1.95001800	-0.65366000
H	-3.14137600	0.72157700	1.25570300

RI_1

Li	-1.75209900	1.40930200	-0.06470700
O	-1.67322900	-0.53128100	-0.05253700
H	-2.02376200	-1.03915700	0.69915200
O	-0.30111900	-0.92335600	-0.05836600
C	0.56985200	0.28712900	0.00886600
N	0.14775500	1.44117000	0.03563900
C	1.95338200	-0.32369600	0.00898800
H	2.69016700	0.47908400	0.04886300
H	2.09189200	-0.98213000	0.87190600
H	2.11908500	-0.91739800	-0.89517300

LiOOH reaction with ACN second stage

H_2O--RI_1

Li	1.37235400	-0.53178700	-0.00851500
O	0.53108100	1.23948900	-0.00386700
H	0.63406400	1.76483400	0.80818800
O	-0.88193200	1.05799300	-0.06378400
C	-1.21337200	-0.39821100	0.01198500
N	-0.37839800	-1.29648800	0.08327800
C	-2.72547000	-0.37385500	-0.03976000
H	-3.09254800	-1.40071500	-0.03414800
H	-3.13790900	0.15917000	0.82251000
H	-3.08056400	0.12870300	-0.94456200
O	3.24991500	-0.38069100	-0.04125500
H	3.89642900	-1.06037200	0.19796300
H	3.75279600	0.37721700	-0.36945800

TS2

Li	-2.16112300	0.74739800	1.08603500
O	-0.65524900	1.38425900	-0.25805900
H	-0.86439400	0.82067300	-1.02748100
O	0.70970300	1.09915100	-0.00234500
C	0.96270700	-0.33380900	-0.02849600
N	0.10592600	-1.20657300	-0.20991100
C	2.45546300	-0.43489100	0.18524400
H	2.73978600	-1.48615600	0.16781200
H	2.99988300	0.10241100	-0.59616200
H	2.73857200	-0.00055900	1.14838300
O	-2.34187000	-0.74338000	-0.02883400
H	-1.21641500	-0.99453000	-0.15820300
H	-2.86523500	-1.54606200	0.05034200

H_2O--RI_2

Li	1.76694600	0.71094600	-0.40870100
O	0.33141300	1.77889100	-0.25584900
H	1.83392800	-1.75121500	0.21146400
O	-0.20541700	0.53880000	-0.77643200
C	-1.01587600	-0.09245000	0.11034600
N	-1.31236400	0.34836100	1.26587200
C	-1.51668800	-1.38288200	-0.46182400
H	-2.16519700	-1.87685900	0.26171600
H	-2.07466500	-1.19479500	-1.38344800
H	-0.67650100	-2.04036800	-0.70615300
O	2.35987100	-0.93954300	0.26422900
H	-0.82663700	1.24411400	1.38031800
H	3.10322500	-1.12543400	0.85439500

RI_2

Li	2.03307400	-1.13971500	0.88826900
O	1.74612500	0.20483500	-0.25391500
O	0.51937600	-0.56796400	-0.26943200
C	-0.57905100	0.18626200	-0.00372100
N	-0.56368400	1.44050500	0.19888900
C	-1.81139800	-0.66404500	0.00195100
H	-2.68275700	-0.04172300	0.20548000
H	-1.93328100	-1.15745300	-0.96644600
H	-1.73119100	-1.44044700	0.76840500
H	0.41247900	1.74697000	0.13292200

LiOOH reaction with ACN third stage

$LiOH--RI_2$

Li	-1.74267100	-0.64367200	1.00064400
O	-0.72987400	0.97632700	0.79000300
O	0.21110200	-0.11631900	0.77885700
C	1.24595800	0.07202900	-0.07694700
N	1.45575000	1.13194500	-0.74761600
C	2.11580700	-1.14504500	-0.11871000
H	2.95466500	-0.96883500	-0.79160300
H	2.49213600	-1.37167100	0.88276300
H	1.54002500	-2.00701500	-0.46754100
H	0.73695500	1.82056500	-0.50808600
O	-2.56887300	-0.64863000	-0.57163700
H	-3.15140100	-1.23539800	-1.05404900
Li	-1.66801600	0.83894100	-0.87798100

TS3

Li	-1.03246700	0.13023500	1.51718400
O	-1.01423800	1.40503200	-0.19511700
O	0.35265500	1.16247200	0.15669100
C	0.87997900	0.03594900	-0.28321800
N	0.22599000	-0.80860600	-1.04400800
C	2.17565700	-0.30351400	0.36262500
H	2.93716400	-0.44998600	-0.40703900
H	2.49053800	0.46801100	1.06525600
H	2.04603000	-1.25532000	0.89066200
H	-0.44076400	-0.26961900	-1.60286100
O	-1.40222200	-1.32162100	0.52989900
H	-0.47348200	-1.25205900	-0.33714100
Li	-2.28913100	-0.11105700	-0.42019700

Li_2O_2--acetamide

Li	1.16954300	-1.43596300	0.68991800
O	1.77853200	-0.12944400	-0.51567600
O	0.43389800	-0.59492200	-0.85659900
C	-0.50646900	0.05230300	0.05791800
N	-0.62965000	1.44693200	-0.41337600
C	-1.82135300	-0.68489500	-0.15366000
H	-2.11298900	-0.67423100	-1.20740800
H	-1.73279600	-1.71863700	0.19336300
H	-2.59820200	-0.18279500	0.43048500
H	0.22133700	1.73872500	-0.89088300
O	-0.02432700	-0.05775800	1.32409400
H	-0.80505100	2.06887900	0.37239600
Li	1.46291200	0.99998900	0.96194200

Acetamide

N	-1.02460000	-0.82693600	0.00001400
C	-0.07693900	0.13533700	-0.00000400
O	-0.36050600	1.33396100	-0.00000100
H	-2.00161900	-0.56455900	-0.00004000
H	-0.78566100	-1.80800100	-0.00001800
C	1.35724000	-0.33846300	0.00000800
H	1.85692800	0.06731900	0.88343200
H	1.44794400	-1.42621700	0.00010000
H	1.85684600	0.06707900	-0.88358300

LiOH formation in a cluster model

--Reactants--

Charge = 0 Multiplicity = 3

O	-2.30341	0.73633	0.53513
O	-1.647	0.76516	-0.8127
Li	-2.86802	-0.56088	-0.58879
Li	-0.74729	1.79137	0.77646
O	-1.92302	-2.22736	-0.34522
O	-1.23909	-2.18122	0.78628
Li	-0.07684	-2.6945	-0.76853
Li	-1.09458	-0.34305	1.51951
Li	0.12573	0.00049	-0.66172
O	1.16342	-1.49334	-0.93977
Li	2.74636	-0.86936	-1.31079
O	0.48513	0.49666	1.18473
Li	2.05883	1.29893	1.13367
Li	1.40948	-1.03956	0.8049
O	3.35326	-0.04153	0.45187
O	3.10393	0.88522	-0.46663
O	-1.14994	3.2037	-0.56771
H	-1.89856	3.79304	-0.42046
H	-1.50872	2.3076	-0.90155

--TS--
Charge = 0 Multiplicity = 3

O	-2.1835	1.10225	0.54357
O	-1.61883	0.98494	-0.82357
Li	-3.08567	-0.09781	-0.49499
Li	-0.41928	1.9947	0.94029
O	-2.29522	-1.84906	-0.35753
O	-1.60369	-1.92871	0.76721
Li	-0.52894	-2.55569	-0.81524
Li	-1.15575	-0.15597	1.5282
Li	0.15647	0.0754	-0.63807
O	0.89575	-1.57226	-0.93601
Li	2.56175	-1.21619	-1.29999
O	0.52136	0.44165	1.22191
Li	2.19783	1.00552	1.15153
Li	1.19624	-1.21649	0.82195
O	3.28491	-0.50186	0.46439
O	3.17323	0.45993	-0.44517
O	-0.30322	2.95084	-0.6553
H	-0.60358	3.83008	-0.90096
H	-1.13083	1.96771	-0.91615

--Products--
Charge = 0 Multiplicity = 3

O	-2.32054	0.73077	0.78517
O	-2.13144	0.68561	-0.68224
Li	-3.21422	-0.66988	0.03843
Li	-0.65733	1.84799	1.10052
O	-1.88515	-2.03354	-0.33846
O	-0.99801	-1.99453	0.63599
Li	-0.88353	-0.75393	-1.55074
Li	-0.98802	-0.34517	1.64217
Li	0.73542	1.03666	-0.59122
O	0.84467	-0.53328	-1.51043
Li	2.57683	-0.64475	-1.55767
O	0.55197	0.47643	1.28848
Li	2.27248	0.50901	1.59936
Li	0.83399	-1.07589	0.22059
O	3.12184	-0.81187	0.38224
O	3.33611	0.42369	-0.05662
O	-0.49924	2.46481	-0.63938
H	-0.57287	3.29031	-1.12189
H	-1.50704	1.55845	-0.82155