Supporting information

Insights into the reversible oxygen reduction reaction in a series of phosphonium-based ionic liquids

Cristina Pozo-Gonzalo[*a], Patrick C. Howlett[a], Jennifer L. Hodgson,[b] Louis A. Madsen,[c] Douglas R. MacFarlane[b], Maria Forsyth[a]*

[a]ARC Centre of Excellence for Electromaterials Science, IFM-Institute for Frontier Materials, Deakin University, 221 Burwood Hwy, Burwood, Victoria 3125, Australia.

[b]ARC Centre of Excellence for Electromaterials Science, Monash University, Clayton, Victoria 3800, Australia.

[c] Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061 USA.

AUTHOR INFORMATION

Corresponding Author

* E-mail: cpg@deakin.edu.au; Tel.: +61 39244 6834; Fax: + 61 399054940.

Supporting information – 1D NMR spectroscopy

^{31}P and ^{1}H NMR on $P_{66614}NTf_2$ and its solutions with KO_2 and Na_2O_2:

All ^{31}P and ^{1}H NMR spectroscopy experiments were performed at 20℃ using a Bruker Avance III 11 T spectrometer equipped with 5 mm axial saddle coils tuned to their respective nucleus Larmor frequencies (202.4 MHz for ^{31}P and 500.1 MHz for ^{1}H). ^{31}P NMR was carried out using a single 90° pulse with duration 6.7 μs, relaxation delay time of 6 s, and 256 scans per spectrum. ^{1}H NMR was carried out using a single 90° pulse with duration of 15.0 μs, relaxation delay time of 5 s, and 32 scans per spectrum.

Figures S.1 and S.2 show representative results of these comparative spectral studies. No significant spectral changes are observed for the neat ILs relative to the ILs with KO_2 or Na_2O_2 dissolved. In other words, no new peaks or substantial changes in peak intensities or positions are observed. Relative to the main phosphorous peak or the main ^{1}H peaks, we would be able to see the appearance of new peaks down to the ~ 0.01 mol % level. The small impurity peaks in the ^{31}P and ^{1}H spectra are also no different in the pure IL spectra vs. the KO_2 or Na_2O_2 solution spectra. Comparative studies on these solutions using ^{19}F and ^{13}C spectroscopy showed the same null results.

Note that all spectra are only coarsely referenced in terms of chemical shift, due to the lack of a solvent (pure IL samples) or other internal standard. Minor differences in linewidths and peak shapes are attributed to differences in shimming (field homogeneity) since the individual samples were manually shimmed without a deuterated solvent.

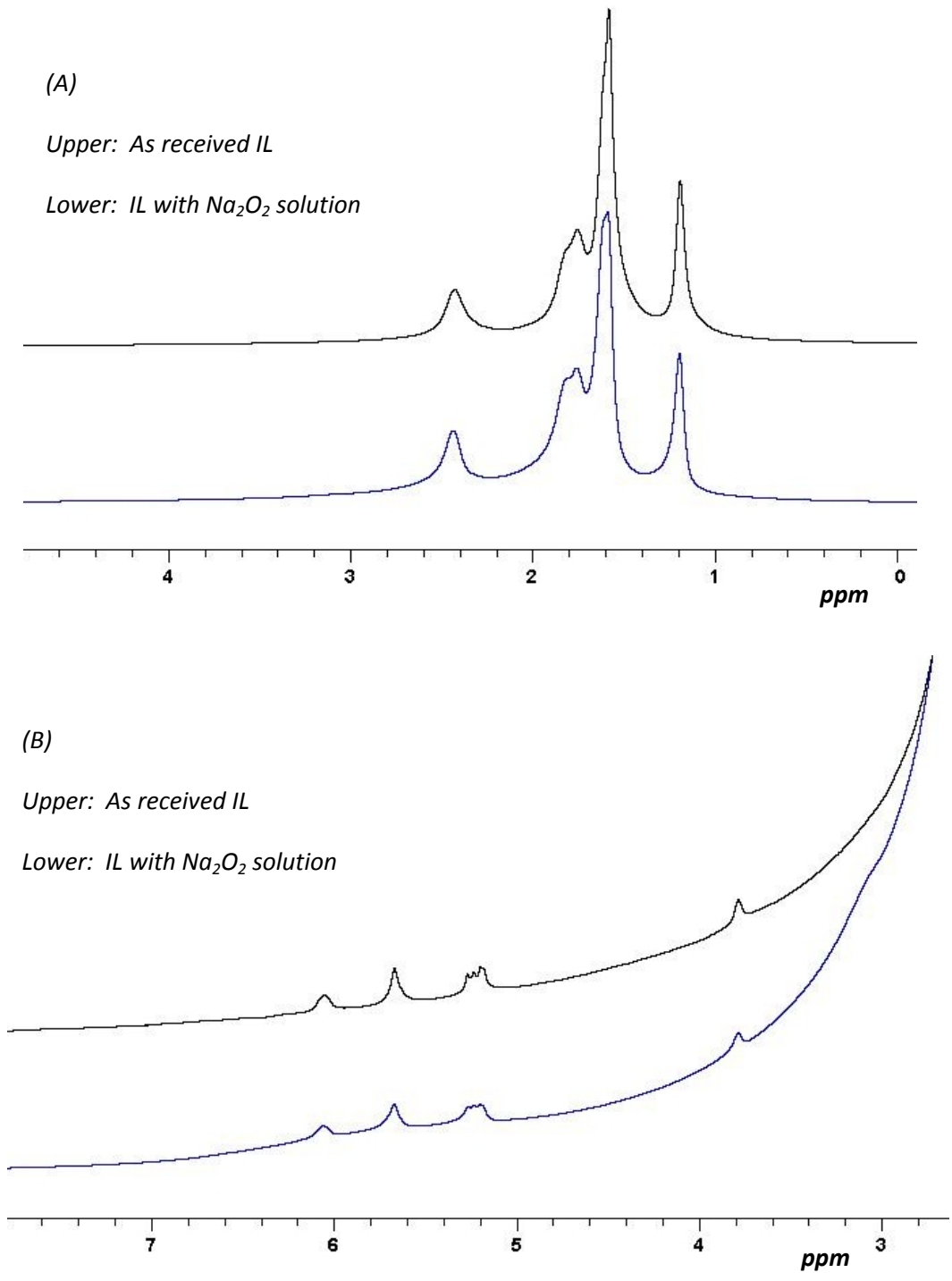
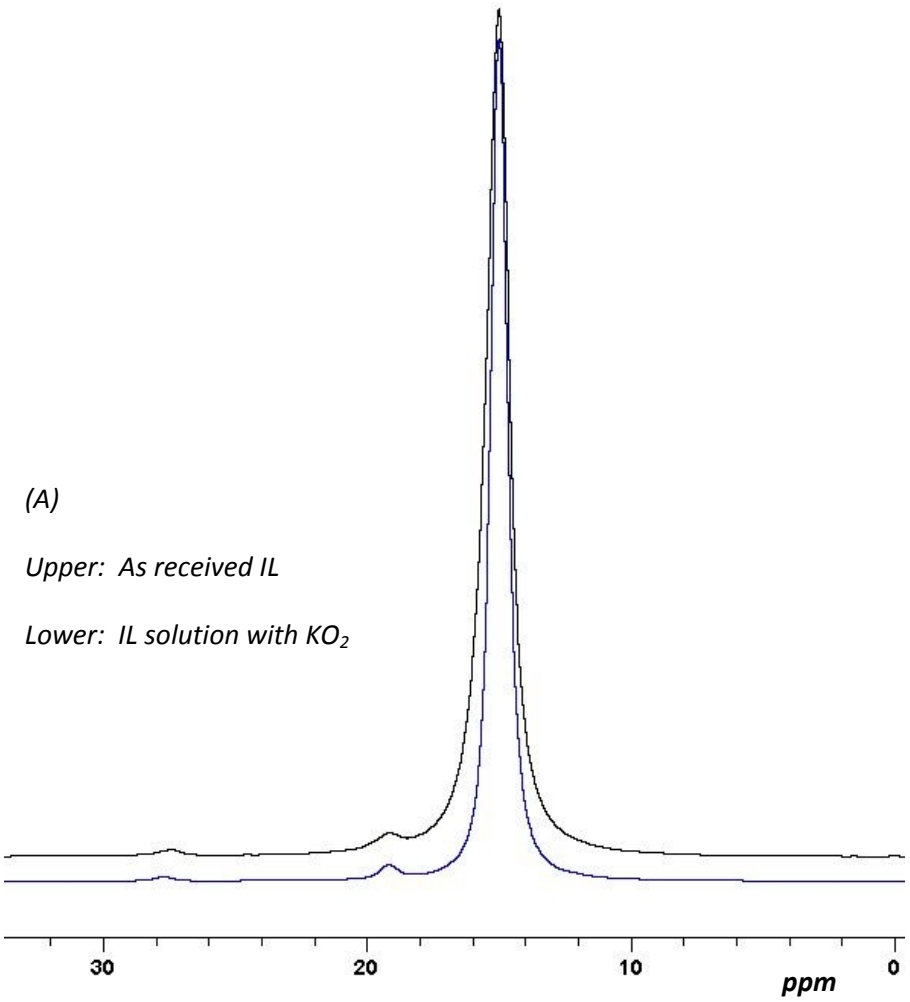


Figure S.1: Comparative ^{1}H NMR spectra of neat $P_{66614}NTf_2$ and saturated Na_2O_2 solution with this IL. (A) Main ^{1}H NMR peaks for P_{66614} in the range 0 – 5 ppm. (B) Vertically expanded view of small downfield impurity peaks (~ 0.1 mol % of main peaks).


(A)
Upper: As received IL
Lower: IL solution with KO_2
30
20
10
0
ppm

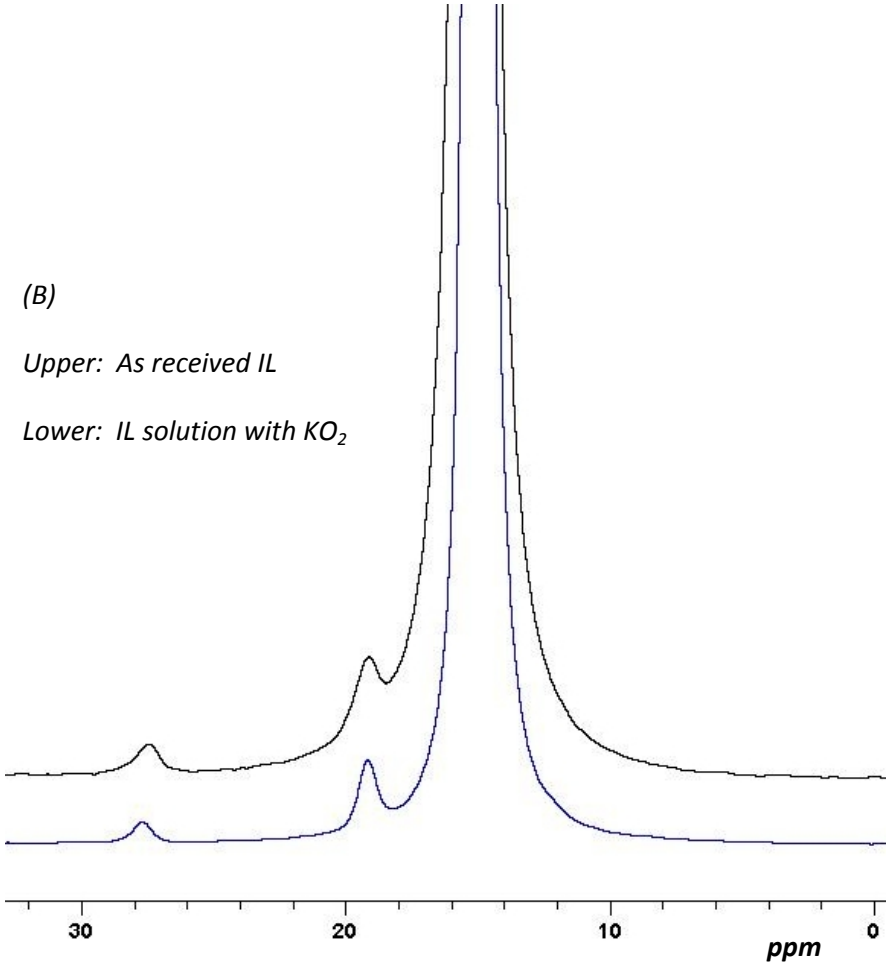


Figure S.2: Comparative ^{31}P NMR spectra of neat $P_{66614}NTf_2$ and saturated KO_2 solution with this IL. (A) ^{31}P NMR peaks for P_{66614}. (B) Vertically expanded view of ^{31}P peaks (< 1 mol % of main peaks).

Table S1. Gaussian archive entries for systems in this study.

$[N_{1111}^{+}]$—O_2

1\1\GINC-GN167\FOpt\UM062X\Aug-CC-pVDZ\C4H12N1O2(1+)\JLHODGSO\03-Aug-2
013\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol) freq=norama
n\\o2-nme4_2_accdm06cpcm\\1,1\C,0.060807748,-0.0000014452,1.4786908235
\N,-0.0206071451,-0.0000017102,-0.0124182803\C,-0.7507574792,1.2192984
051,-0.4714347138\C,1.3555527444,-0.000003828,-0.5919977375\C,-0.75076
13365,-1.2193003563,-0.4714337375\H,-0.9553819604,-0.0000119835,1.8805
147238\H,1.8770730864,0.8970782468,-0.2504710272\H,-0.2045394234,-2.10
07012017,-0.1271113925\H,-0.7982970796,1.2017302743,-1.5628599056\H,0.
5960873586,0.8973363192,1.7982552788\H,1.8770627842,-0.8970996509,-0.2
504911533\H,-0.7982756806,-1.2017476103,-1.5628604626\H,-1.7560746692,
1.2028386391,-0.0441086029\H,0.5961056912,-0.8973286336,1.7982543862\H
,1.2724209678,0.0000092765,-1.6815593486\H,-1.7560883212,-1.2028240598
,-0.0441305309\H,-0.204519015,2.1006981798,-0.1271361656\O,-0.03934757
61,0.0000033762,-3.8487794909\O,1.1252613058,0.0000301192,-4.091918663
\\Version=AM64L-G09RevA.02\State=1-A\HF=-364.3825685\S2=0.\S2-1=0.\S2A
=0.\RMSD=3.644e-09\RMSF=1.480e-05\Dipole=-0.2687162,-0.0000083,1.94832
29\Quadrupole=-1.7256566,-0.8400804,2.565737,-0.0000151,-0.804292,-0.0
00018\PG=C01 [X(C4H12N1O2)]\\@

$[N_{1111}^{+}]$—$O_2^{\bullet-}$

1\1\GINC-GN159\FOpt\UM062X\Aug-CC-pVDZ\C4H12N1O2(2)\JLHODGSO\06-Aug-20
13\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol) freq=noraman
\\o2_radan-nme4_5_accdm06cpcm\\0,2\C,-0.0598806539,-0.0041000478,1.432
7623125\N,0.0120531787,-0.000938589,-0.0537868575\C,-0.6692139048,1.21
29697676,-0.5980646608\C,1.4410404413,0.0026318855,-0.4904666036\C,-0.

664862213,-1.2151132019,-0.6028118383\H,-1.1111754461,-0.0062943976,1.
731041531\H,1.9209774304,0.8995185213,-0.0898888902\H,-0.136460674,-2.
0988752287,-0.2351948821\H,-0.6309481117,1.1450964724,-1.689476093\H,0
.4391615611,0.8933010666,1.8076437714\H,1.9243594036,-0.8941653034,-0.
0937887247\H,-0.6294053528,-1.1420996567,-1.6939948898\H,-1.7033955506
,1.2100264718,-0.2431790761\H,0.4418929484,-0.9015154795,1.8039220705\
H,1.4424576151,0.0051349922,-1.5841438166\H,-1.6983506207,-1.218546979
7,-0.2458770838\H,-0.1453517921,2.0971406058,-0.2250036207\O,0.1912060
95,0.0096953685,-3.4826125185\O,-1.1183803539,0.0061347327,-3.62749312
98\\Version=AM64L-G09RevA.02\State=2-A\HF=-364.5773657\S2=0.757528\S2-
1=0.\S2A=0.750025\RMSD=8.041e-09\RMSF=1.199e-05\Dipole=0.844899,-0.015
4208,6.0383342\Quadrupole=4.8266274,7.4227207,-12.249348,0.0019241,-2.
7404451,0.0463761\PG=C01 [X(C4H12N1O2)]\\@

$[N_{1111}^{+}]$—O_2^{2-}

1\1\GINC-NN104\FOpt\UM062X\Aug-CC-pVDZ\C4H12N1O2(1-)\JLHODGSO\04-Aug-2
013\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol) freq=norama
n\\o2_2an-nme4_3_accdm06cpcm\\-1,1\C,-1.6317199994,0.2809681846,1.7162
252057\N,-0.1876916918,0.1809460792,1.340570935\C,-0.0469187686,-0.289
4467346,-0.0621465266\C,0.437785731,1.5296426778,1.5027394907\C,0.4834
733696,-0.7695170494,2.2797469287\O,-0.5499501035,1.2770383502,4.34730
47836\O,-0.5995545682,1.6291025159,5.7971829223\H,-2.0818993912,-0.710
390972,1.6090273489\H,1.4980369693,1.4474122219,1.2456801839\H,0.33501
39369,-0.3531225627,3.2883214824\H,-0.5476823201,0.4238984105,-0.72242
99281\H,-1.654793187,0.6366633738,2.7597104954\H,-2.1126600734,0.98736
81174,1.0326398511\H,-0.0622843904,2.2208635388,0.8178773299\H,0.28813
46826,1.8124191228,2.5575659004\H,0.0144045565,-1.7514935998,2.1674299
172\H,1.5423377269,-0.8253880336,2.0108711042\H,1.0171730148,-0.347939
5868,-0.3068395646\H,-0.5091944939,-1.2763650539,-0.1504338605\\Versio
n=AM64L-G09RevA.02\State=1-A\HF=-364.6372076\S2=0.\S2-1=0.\S2A=0.\RMSD

=7.573e-09\RMSF=1.108e-04\Dipole=1.1845547,-3.866844,-11.2991608\Quadr
upole=19.1343722,13.7836579,-32.9180301,1.7658618,5.1440146,-17.482704
\PG=C01 [X(C4H12N1O2)]\\@

$[P_{1111}^{+}]$—O_2

1\1\GINC-GN139\FOpt\UM062X\Aug-CC-pVDZ\C4H12O2P1(1+)\JLHODGSO\07-Aug-2
013\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol) freq=norama
n\\o2-pme4_1cc_accdm06cpcm\\1,1\C,-0.001901282,0.0470686953,1.81398244
68\P,-0.0015721202,-0.0428545743,0.011024185\C,-0.8225568414,-1.565988
2634,-0.5058998948\C,-0.8847691589,1.3806632412,-0.6607419345\C,1.7042
418998,-0.0341825686,-0.5815372189\O,-0.0727786489,-0.1061638964,-3.66
69221107\O,-0.6543041816,0.8346499387,-4.1049433811\H,-1.0358502979,0.
0419562126,2.1735412134\H,2.1843318072,0.8981619588,-0.2663616645\H,-0
.291576962,-2.4216363248,-0.076026461\H,-0.8841855511,1.3264348241,-1.
7542179684\H,0.4958896683,0.9702744573,2.1274354655\H,2.2358675298,-0.
8897911109,-0.1524026399\H,-0.8095497226,-1.6294463469,-1.5983117373\H
,-1.9145559492,1.3686212315,-0.2886614175\H,0.5348949449,-0.8186650548
,2.2152472737\H,1.7068706744,-0.1031186891,-1.6736798899\H,-1.85675424
39,-1.5510086501,-0.1463619996\H,-0.3832195648,2.29746092,-0.333817266
4\\Version=AM64L-G09RevA.02\State=1-A\HF=-651.0089777\S2=0.\S2-1=0.\S2
A=0.\RMSD=6.420e-09\RMSF=8.848e-06\Dipole=0.1507349,-0.1665374,1.68413
33\Quadrupole=-0.7298974,-1.2065679,1.9364653,0.4131251,0.4324154,-0.5

937707\PG=C01 [X(C4H12O2P1)]\\@

$[P_{1111}^{+}]$—$O_2^{\bullet-}$

1\1\GINC-GN209\FOpt\UM062X\Aug-CC-pVDZ\C4H12O2P1(2)\JLHODGSO\07-Aug-20
13\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol) freq=noraman
\\o2_radan-pme4_5c_accdm06cpcm\\0,2\C,-0.148561,-0.047828,1.67908\P,-0
.019705,-0.048893,-0.12893\C,-0.848629,1.430537,-0.748241\C,1.725397,-
0.008419,-0.583673\C,-0.837227,-1.552249,-0.709128\H,-1.204501,-0.0873
51,1.967029\H,2.232153,0.722421,0.056253\H,-0.340719,-2.415741,-0.2530
01\H,-1.908978,1.388001,-0.478097\H,0.30922,0.863636,2.07739\H,2.15969
9,-1.00092,-0.423303\H,-0.757637,-1.589944,-1.797587\H,-0.384414,2.306
621,-0.282043\H,0.373197,-0.925763,2.0751\H,1.780388,0.287347,-1.63914
\H,-1.885671,-1.525024,-0.393241\H,-0.715347,1.45702,-1.833787\O,0.218
492,-0.14551,-3.246304\O,0.978561,0.892063,-3.521374\\Version=AM64L-G0
9RevA.02\State=2-A\HF=-651.204383\S2=0.757374\S2-1=0.\S2A=0.750025\RMS
D=8.331e-09\RMSF=1.409e-05\Dipole=-1.0763102,-0.7264266,5.5114023\Quad
rupole=6.2217502,6.1371497,-12.3588999,-1.4654098,3.5320865,2.6757295\
PG=C01 [X(C4H12O2P1)]\\@

$[P_{1111}^{+}]$—$O_2^{\bullet-}$ (gas phase)

1\1\GINC-NN108\FOpt\UM062X\Aug-CC-pVDZ\C4H12O2P1(2)\JLHODGSO\19-Feb-20

14\0\\# um062x/aug-cc-pVDZ opt freq=noraman\\o2_radan-pme4_2cc_accdm06

\\0,2\C,-0.0680014277,0.0460067012,1.4024037591\P,0.0191530136,-0.0339

804247,-0.4700798189\C,-0.8880383201,1.5149776447,-0.8273428553\C,1.84

28567473,-0.0718914407,-0.6284907693\C,-0.8896467358,-1.6147012953,-0.

6345332325\H,-1.1104244691,0.0851590205,1.7440938043\H,2.3218236552,0.

0303249176,0.3484642307\H,-0.3164063545,-2.3859634494,-0.1069714138\H,

-1.8321206737,1.2376164881,-1.3094594675\H,0.4479488493,0.9468143971,1

.7601792244\H,2.1156979036,-1.023752251,-1.0966553932\H,-1.0315901968,

-1.8941651771,-1.6790514952\H,-1.0790801383,2.0774358137,0.0901691164\

H,0.4161632222,-0.8311373663,1.8513383792\H,2.1412082419,0.7297289362,

-1.309857473\H,-1.8553852727,-1.5021765591,-0.1287060737\H,-0.30259327

51,2.0967536392,-1.5445942093\O,0.078781829,-0.1868634186,-2.531046844

9\O,0.7153764017,0.7798158237,-3.1128564673\\Version=AM64L-G09RevA.02\

State=2-A\HF=-651.1867429\S2=0.756266\S2-1=0.\S2A=0.750022\RMSD=4.811e

-09\RMSF=3.757e-05\Dipole=-0.3400931,-0.3262506,1.9050515\Quadrupole=3

.5946635,3.1314492,-6.7261127,-0.6589698,1.4170266,0.9970583\PG=C01 [X

(C4H12O2P1)]\\@

$[P_{1111}^{+}]—O_2^{2-}$

1\1\GINC-GN115\FOpt\UM062X\Aug-CC-pVDZ\C4H12O2P1(1-)\JLHODGSO\04-Aug-2

013\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol) freq=norama

n\\o2_2an-pme4_3_accdm06cpcm\\-1,1\C,-1.6994939737,-0.1929750914,2.705

4910075\P,-0.3765113198,0.54119826,1.6526500038\C,0.6310850463,-1.1327

45502,1.7180481123\C,-0.4764228772,0.3914373158,-0.193976744\C,1.03881

80109,1.4410410928,2.4176339317\O,-1.5307700248,2.6897540211,2.7329958

051\O,-1.3048203934,2.0549987622,1.4527748646\H,-2.2026824166,-0.94757

35551,2.0860948234\H,1.8533847548,1.4205757394,1.6814890587\H,0.907249

3297,-1.3801594814,2.7531977096\H,-1.0483828711,1.2047349544,-0.643518

6571\H,-1.2620616746,-0.7032440207,3.5709615413\H,-2.3887639108,0.5930

241612,3.0188642419\H,0.734313052,2.4612090739,2.6567934582\H,1.382779

3857,0.9148508866,3.3154523981\H,0.0373497454,-1.968112624,1.317661545

4\H,1.5575455915,-1.0614951907,1.1286325377\H,0.5480108694,0.386485666

4,-0.5859140792\H,-0.9321743236,-0.5759524685,-0.435905559\\Version=AM

64L-G09RevA.02\State=1-A\HF=-651.309509\S2=0.\S2-1=0.\S2A=0.\RMSD=4.62

2e-09\RMSF=1.660e-05\Dipole=2.0250455,-3.6328359,-1.254569\Quadrupole=

3.0194949,-8.7830117,5.7635168,9.8035977,2.5510599,-4.8184823\PG=C01 [

X(C4H12O2P1)]\\@

$[P_{2222}^{+}]—O_2^{\bullet-}$

1\1\GINC-NN103\FOpt\UM062X\Aug-CC-pVDZ\C8H20O2P1(2)\JLHODGSO\10-Sep-20

13\0\\# um062x/aug-cc-pVDZ opt SCRF(CPCM,solvent=ethanol)\\o2_radan-pe

th4_11cccc_accdm06cpcm\\0,2\P,-0.074057604,-0.026301436,-0.3735611611\

C,1.7104484292,-0.020715264,-0.0163634587\C,2.3415412248,1.3556392076,

-0.2339769054\C,-0.2284165377,0.1857015122,-2.1840165466\C,-1.65513433

16,0.4821838828,-2.649034232\C,-0.8607225487,-1.6330037731,0.003550523

\C,0.1620737868,-2.7684629628,0.0634149208\C,-0.8923438444,1.394809731

4,0.4219689487\C,-2.3400862471,1.1139870052,0.8256145027\O,0.777088230

5,0.5072007427,2.958327133\O,0.025740074,-0.4602570813,2.4836336453\H,

1.8089761272,-0.3327444144,1.0264348422\H,2.1637208667,-0.7741006507,-

0.6723658505\H,3.4149287139,1.2942019717,-0.0250944674\H,2.2215425801,

1.7096369886,-1.2643333415\H,1.9070339931,2.0956571415,0.4467664053\H,

0.1517580129,-0.7378926303,-2.6405094424\H,0.4471295114,0.9981875842,-

2.4763291462\H,-1.6736218092,0.5763948086,-3.7396053428\H,-2.348971365

3,-0.3194343687,-2.3704000301\H,-2.0227747364,1.4231852994,-2.22383350

51\H,-1.3774690941,-1.5264506188,0.959137558\H,-1.6011823138,-1.813933

0155,-0.7849350493\H,-0.3581943354,-3.715523282,0.2413100333\H,0.86799

33481,-2.6010164879,0.8842386322\H,0.721804091,-2.8633805792,-0.875082

7004\H,-0.2801097306,1.623477881,1.3017280924\H,-0.8253777019,2.227857

6187,-0.289536142\H,-2.8047074525,2.0403627064,1.1802256667\H,-2.36570

85856,0.3832141392,1.6409531786\H,-2.9396997515,0.7334183435,-0.010025

7608\\Version=AM64L-G09RevA.02\State=2-A\HF=-808.3904836\S2=0.757321\S

2-1=0.\S2A=0.750026\RMSD=8.766e-09\RMSF=1.053e-05\Dipole=-0.7909898,-0

.104262,-5.0515479\Quadrupole=7.1753438,7.6393891,-14.8147329,-0.95933

95,-4.453191,-0.3090968\PG=C01 [X(C8H20O2P1)]\\@