Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information

## On the Instability of Iodides of Heavy Main Group Atoms in their Higher Oxidation State

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- Coordinates and Energies----------S2
- Scheme S1----------S4

Coordinates and energies (sum of electronic and zero point energies) of the structures calculated at the M06-2X/Def2-TZVPD level of theory.

$TeI_6$
E+ZPE: -2053.781373 a. u.

| | | | |
|---|---|---|---|
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | 2.786435000 |
| I | 0.000000000 | 2.786435000 | 0.000000000 |
| I | 2.786435000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | -2.786435000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | -2.786435000 |
| I | -2.786435000 | 0.000000000 | 0.000000000 |

$TeBr_6$
E+ZPE: -15713.147769 a. u.

| | | | |
|---|---|---|---|
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| Br | 0.000000000 | 0.000000000 | 2.531546000 |
| Br | 0.000000000 | 2.531546000 | 0.000000000 |
| Br | -2.531546000 | 0.000000000 | 0.000000000 |
| Br | 0.000000000 | -2.531546000 | 0.000000000 |
| Br | 0.000000000 | 0.000000000 | -2.531546000 |
| Br | 2.531546000 | 0.000000000 | 0.000000000 |

$SbI_5$
E+ZPE: -1728.461036 a. u.

| | | | |
|---|---|---|---|
| Sb | 0.000000000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 2.707087000 | 0.000000000 |
| I | -2.344406000 | -1.353543000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | 2.788750000 |
| I | 2.344406000 | -1.353543000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | -2.788750000 |

Transition state for the decomposition of $SbI_5$
E+ZPE: -3456.926242 a. u.

| | | | |
|---|---|---|---|
| I | 1.246032000 | 1.425429000 | -0.051887000 |
| I | 4.590897000 | -0.995413000 | 2.281270000 |
| I | 1.854003000 | -2.444469000 | -0.103215000 |
| I | -1.854006000 | 2.444447000 | -0.103990000 |
| I | -1.246020000 | -1.425427000 | -0.051532000 |
| I | -4.763375000 | 0.933153000 | -2.221425000 |
| I | 4.763460000 | -0.933792000 | -2.220955000 |
| I | -4.591018000 | 0.996059000 | 2.280779000 |
| I | -5.211303000 | -2.249221000 | 0.094070000 |
| I | 5.211327000 | 2.249230000 | 0.093660000 |
| Sb | -3.577194000 | -0.015218000 | 0.001600000 |
| Sb | 3.577196000 | 0.015224000 | 0.001751000 |

$PbI_4$
E+ZPE: -1383.430565 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000000000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 2.244679000 | 1.586829000 |
| I | -2.244679000 | 0.000000000 | -1.586829000 |
| I | 0.000000000 | -2.244679000 | 1.586829000 |
| I | 2.244679000 | 0.000000000 | -1.586829000 |

Transition state1 for the decomposition of $PbI_4$
E+ZPE: -2766.841917 a. u.

| | | | |
|---|---|---|---|
| Pb | 3.261365000 | 0.000023000 | 0.397707000 |
| I | 0.738957000 | 0.000100000 | 1.755492000 |
| I | 4.911763000 | -2.234818000 | 0.206824000 |
| I | 2.168539000 | -0.000142000 | -2.460265000 |
| Pb | -3.261365000 | -0.000023000 | -0.397707000 |
| I | -2.168539000 | 0.000142000 | 2.460266000 |
| I | -0.738956000 | -0.000100000 | -1.755492000 |
| I | -4.911764000 | 2.234818000 | -0.206824000 |
| I | 4.911761000 | 2.234844000 | 0.206568000 |
| I | -4.911761000 | -2.234844000 | -0.206568000 |

Transition state for the decomposition of $TeBr_6$
E+ZPE: -31426.278874 a. u.

| | | | |
|---|---|---|---|
| Te | -3.055727000 | -0.090821000 | -0.034639000 |
| Br | -3.970704000 | -0.453509000 | 2.328090000 |
| Br | -1.718093000 | 2.138011000 | 0.963789000 |
| Br | -4.919617000 | 1.535879000 | -0.451024000 |
| Br | -4.372881000 | -2.014602000 | -0.971310000 |
| Br | -2.072559000 | 0.512467000 | -2.319142000 |
| Br | -0.882139000 | -1.438155000 | 0.501065000 |
| Te | 3.055733000 | 0.090824000 | -0.034616000 |
| Br | 3.971035000 | 0.452882000 | 2.328092000 |
| Br | 4.372770000 | 2.014840000 | -0.970968000 |
| Br | 0.882207000 | 1.438033000 | 0.501676000 |
| Br | 1.718130000 | -2.138191000 | 0.963426000 |
| Br | 2.072280000 | -0.511883000 | -2.319140000 |
| Br | 4.919563000 | -1.535777000 | -0.451662000 |

Transition state for the decomposition of $TeCl_6$
E+ZPE: -6058.254196 a. u.

| | | | |
|---|---|---|---|
| Te | 2.973826000 | 0.094967000 | 0.008470000 |
| Te | -2.973827000 | -0.094967000 | 0.008476000 |
| Cl | 4.605599000 | -1.538098000 | 0.074541000 |
| Cl | 2.771836000 | -0.121238000 | 2.368600000 |
| Cl | 4.466651000 | 1.856072000 | 0.187314000 |
| Cl | 3.138945000 | 0.048398000 | -2.364494000 |
| Cl | 1.385220000 | -2.131403000 | -0.189155000 |
| Cl | 0.802485000 | 1.328573000 | -0.102703000 |
| Cl | -1.385224000 | 2.131407000 | -0.189235000 |
| Cl | -0.802472000 | -1.328562000 | -0.102595000 |
| Cl | -4.466646000 | -1.856069000 | 0.187381000 |
| Cl | -2.771902000 | 0.121368000 | 2.368599000 |
| Cl | -3.138884000 | -0.048542000 | -2.364497000 |
| Cl | -4.605606000 | 1.538094000 | 0.074408000 |

$TeCl_6$
E+ZPE: -3029.161126 a. u.

| | | | |
|---|---|---|---|
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| Cl | 0.000000000 | 0.000000000 | 2.333286000 |
| Cl | 0.000000000 | 2.333286000 | 0.000000000 |
| Cl | 2.333286000 | 0.000000000 | 0.000000000 |
| Cl | 0.000000000 | 0.000000000 | -2.333286000 |
| Cl | 0.000000000 | -2.333286000 | 0.000000000 |
| Cl | -2.333286000 | 0.000000000 | 0.000000000 |

$SbBr_5$
E+ZPE: -13111.277496 a. u.

| | | | |
|---|---|---|---|
| Sb | 0.000000000 | 0.000000000 | 0.000000000 |
| Br | 0.000000000 | 0.000000000 | 2.536862000 |
| Br | 0.000000000 | 2.478409000 | 0.000000000 |
| Br | -2.146365000 | -1.239204000 | 0.000000000 |
| Br | 0.000000000 | 0.000000000 | -2.536862000 |
| Br | 2.146365000 | -1.239204000 | 0.000000000 |

Transition state for the decomposition of $SbBr_5$
E+ZPE: -26222.519606 a. u.

| | | | |
|---|---|---|---|
| Sb | 3.293673000 | 0.106364000 | 0.000003000 |
| Sb | -3.293668000 | -0.106360000 | 0.000021000 |
| Br | 4.242224000 | -1.011385000 | -1.988146000 |
| Br | 4.242899000 | -1.011397000 | 1.987811000 |
| Br | 4.877171000 | 2.057782000 | -0.000228000 |

| | | | |
|---|---|---|---|
| Br | 1.023696000 | 1.349016000 | 0.000212000 |
| Br | 1.450387000 | -2.306843000 | 0.000374000 |
| Br | -1.023684000 | -1.349000000 | 0.000296000 |
| Br | -4.877152000 | -2.057791000 | -0.000124000 |
| Br | -4.242140000 | 1.011223000 | -1.988286000 |
| Br | -4.243022000 | 1.011551000 | 1.987701000 |
| Br | -1.450388000 | 2.306837000 | 0.000355000 |

$SbCl_5$

E+ZPE: -2541.291618 a. u.

| | | | |
|---|---|---|---|
| Sb | 0.000000000 | 0.000000000 | 0.000000000 |
| Cl | 0.000000000 | 0.000000000 | 2.345696000 |
| Cl | 0.000000000 | 2.301105000 | 0.000000000 |
| Cl | 1.992815000 | -1.150552000 | 0.000000000 |
| Cl | -1.992815000 | -1.150552000 | 0.000000000 |
| Cl | 0.000000000 | 0.000000000 | -2.345696000 |

Transition state for the decomposition of $SbCl_5$

E+ZPE: -5082.492321 a. u.

| | | | |
|---|---|---|---|
| Sb | -3.112760000 | -0.113737000 | 0.000309000 |
| Sb | 3.112803000 | 0.113809000 | -0.000325000 |
| Cl | -1.193928000 | 2.209701000 | 0.000581000 |
| Cl | 0.912922000 | 1.293654000 | 0.000216000 |
| Cl | -0.912843000 | -1.293816000 | 0.000154000 |
| Cl | 1.193855000 | -2.209887000 | 0.000003000 |
| Cl | 3.944969000 | -1.040754000 | 1.812787000 |
| Cl | 3.944028000 | -1.040279000 | -1.814160000 |
| Cl | 4.686916000 | 1.835701000 | -0.000505000 |
| Cl | -3.944564000 | 1.040705000 | -1.813063000 |
| Cl | -3.944584000 | 1.040407000 | 1.813865000 |
| Cl | -4.686901000 | -1.835649000 | 0.000168000 |

$PbBr_4$

E+ZPE: -10489.667323 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000000000 | 0.000000000 | 0.000000000 |
| Br | 0.000000000 | 2.073862000 | 1.466429000 |
| Br | 2.073862000 | 0.000000000 | -1.466429000 |
| Br | 0.000000000 | -2.073862000 | 1.466429000 |
| Br | -2.073862000 | 0.000000000 | -1.466429000 |

Transition state for the decomposition of $PbBr_4$

E+ZPE: -20979.282457 a. u.

| | | | |
|---|---|---|---|
| Pb | -3.017292000 | -0.424315000 | -0.000083000 |
| Pb | 3.017292000 | 0.424315000 | 0.000083000 |
| Br | -4.563290000 | -0.045241000 | 2.044378000 |
| Br | -4.563600000 | -0.044601000 | -2.044188000 |
| Br | 4.563603000 | 0.044601000 | 2.044185000 |
| Br | 4.563286000 | 0.045241000 | -2.044381000 |
| Br | 0.576848000 | 1.652639000 | 0.000346000 |
| Br | -1.892418000 | 2.305427000 | 0.000290000 |
| Br | -0.576848000 | -1.652639000 | -0.000344000 |
| Br | 1.892418000 | -2.305427000 | -0.000286000 |

$PbCl_4$

E+ZPE: -2033.657506 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000000000 | 0.000000000 | 0.000000000 |
| Cl | 0.000000000 | -1.943618000 | 1.373674000 |
| Cl | -1.943618000 | 0.000000000 | -1.373674000 |
| Cl | 1.943618000 | 0.000000000 | -1.373674000 |
| Cl | 0.000000000 | 1.943618000 | 1.373674000 |

Transition state for the decomposition of $PbCl_4$

E+ZPE: -4067.228866 a. u.

| | | | |
|---|---|---|---|
| Pb | -2.814437000 | 0.309723000 | -0.000134000 |
| Pb | 2.814437000 | -0.309723000 | 0.000136000 |
| Cl | 0.524225000 | -1.546221000 | 0.000593000 |
| Cl | -1.643838000 | -2.239583000 | 0.000808000 |
| Cl | -4.264665000 | -0.155611000 | 1.898832000 |
| Cl | -4.264799000 | -0.157116000 | -1.898628000 |
| Cl | -0.524227000 | 1.546219000 | -0.000596000 |
| Cl | 1.643837000 | 2.239582000 | -0.000816000 |
| Cl | 4.264799000 | 0.157124000 | 1.898628000 |
| Cl | 4.264667000 | 0.155606000 | -1.898831000 |

Transition state for the decomposition of $PbI_4$ on reaction with $PbI_2$.

E+ZPE: -2171.576294 a. u.

| | | | |
|---|---|---|---|
| Pb | -1.911150000 | -0.202478000 | -0.240439000 |
| Pb | 2.420821000 | 0.126971000 | 1.104636000 |
| I | -3.010737000 | 1.845783000 | -1.759053000 |
| I | -3.992888000 | -1.717525000 | 0.817007000 |
| I | -0.737450000 | 1.122995000 | 2.062479000 |
| I | 0.573581000 | -1.448449000 | -1.001673000 |
| I | 2.801926000 | 2.372960000 | -0.543048000 |
| I | 3.577022000 | -2.058942000 | -0.912771000 |

Transition state for the decomposition of $PbBr_4$ on reaction with $PbBr_2$.

E+ZPE: -15830.924724 a. u.

| | | | |
|---|---|---|---|
| Pb | -1.825572000 | -0.251738000 | -0.279445000 |
| Pb | 2.302506000 | 0.287222000 | 0.923314000 |
| Br | 0.539048000 | -1.478136000 | -0.921719000 |
| Br | -3.746183000 | -1.377385000 | 1.052029000 |
| Br | -2.919514000 | 1.746537000 | -1.502948000 |
| Br | 3.059985000 | -2.113096000 | -0.974255000 |
| Br | 2.414450000 | 2.096103000 | -0.956614000 |
| Br | -0.465174000 | 1.042843000 | 1.795011000 |

Transition state for the decomposition of $PbCl_4$ on reaction with $PbCl_2$.

E+ZPE: -3146.899527 a. u.

| | | | |
|---|---|---|---|
| Pb | -1.842343000 | 0.204382000 | 0.179826000 |
| Cl | -2.839610000 | -1.722303000 | 1.277929000 |
| Cl | 0.279644000 | 1.605075000 | 0.767188000 |
| Cl | -3.569954000 | 0.883579000 | -1.407446000 |
| Cl | -0.199186000 | -1.035435000 | -1.539260000 |
| Pb | 2.255175000 | -0.308139000 | -0.507972000 |
| Cl | 1.887396000 | -1.582621000 | 1.564677000 |
| Cl | 2.450399000 | 2.352180000 | 0.919732000 |

$PbI_5^-$

E+ZPE: -1681.205057 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000000000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | 2.932691000 |
| I | 0.000000000 | 2.844208000 | 0.000000000 |
| I | -2.463157000 | -1.422104000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | -2.932691000 |
| I | 2.463157000 | -1.422104000 | 0.000000000 |

$PbI_6^{2-}$

E+ZPE: -1978.873735 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000000000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | 2.984367000 |
| I | 0.000000000 | 2.984367000 | 0.000000000 |
| I | -2.984367000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | -2.984367000 |
| I | 0.000000000 | -2.984367000 | 0.000000000 |
| I | 2.984367000 | 0.000000000 | 0.000000000 |

$PbF_4$

E+ZPE: -592.157805 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000033000 | -0.000002000 | -0.000005000 |
| F | -0.580708000 | -1.595466000 | -0.995064000 |
| F | -0.889788000 | 0.038291000 | 1.754891000 |
| F | 1.950569000 | -0.059401000 | 0.254496000 |
| F | -0.480370000 | 1.616593000 | -1.014274000 |

$PbH_4$
E+ZPE: -195.020077 a. u.

| | | | |
|---|---|---|---|
| Pb | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 1.010242000 | 1.010242000 | 1.010242000 |
| H | -1.010242000 | -1.010242000 | 1.010242000 |
| H | -1.010242000 | 1.010242000 | -1.010242000 |
| H | 1.010242000 | -1.010242000 | -1.010242000 |

$TeI_6^{2-}$
E+ZPE: -2054.015425 a. u.

| | | | |
|---|---|---|---|
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | 2.954216000 |
| I | 0.000000000 | 2.954216000 | 0.000000000 |
| I | 2.954216000 | 0.000000000 | 0.000000000 |
| I | 0.000000000 | -2.954216000 | 0.000000000 |
| I | 0.000000000 | 0.000000000 | -2.954216000 |
| I | -2.954216000 | 0.000000000 | 0.000000000 |

$SbI_5^-$
E+ZPE: -1728.643048 a. u.

| | | | |
|---|---|---|---|
| Sb | 0.329295000 | -0.000561000 | 0.000000000 |
| I | 0.534890000 | -3.047926000 | 0.000000000 |
| I | 0.534490000 | 3.046659000 | 0.000000000 |
| I | 0.534890000 | 0.001065000 | 3.046810000 |
| I | -2.456028000 | -0.000324000 | 0.000000000 |
| I | 0.534890000 | 0.001065000 | -3.046810000 |

Scheme S1: Distortion from tetrahedral geometry results in a second-order interaction between two antibonding orbitals and results in a low-lying antibonding MO.