**Supplementary Material**

N. Stamenković 1, J. Cerkovnik 2 \*

1 University of Ljubljana, Biotechnical Faculty, Department of Food Science and Technology, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

2 University of Ljubljana, Faculty of Chemistry and Chemical Technology, Department of Chemistry and Biochemistry, Več na pot 113, 1000 Ljubljana, Slovenia.

*Title of the manuscript*:

Electrophilic Aromatic Substitution: theoretical insight into halonium ion self-existence in catalytic system

*Contents of the SM*:

Cartesian coordinates of optimized structures shown throughout the manuscript and additional coordinates on structures and transition states on iron(V) species

**Phenylborane**

Charge = 0 Multiplicity = 1

C 0. 0. 0.98331

C 0. 1.21365 0.28261

C 0. -1.21365 0.28261

C 0. 1.21365 -1.11879

H 0. 2.1403 0.81761

B 0. 0. 2.63331

C 0. -1.21365 -1.11879

H 0. -2.1403 0.81761

C 0. 0. -1.81949

H 0. 2.1403 -1.65379

H -1.02191 0. 3.22331

H 1.02191 0. 3.22331

H 0. -2.1403 -1.65379

H 0. 0. -2.88949

**Aniline**

Charge = 0 Multiplicity = 1

C 0.91959 0.05803 0.01987

C 0.2704 -1.18404 0.00441

C 0.16717 1.24042 0.00371

C -1.12972 -1.24374 -0.00194

H 0.84413 -2.08719 -0.00219

N 2.38796 0.12055 -0.0095

C -1.23295 1.18088 -0.00264

H 0.66205 2.18907 -0.00342

C -1.88146 -0.06124 -0.00293

H -1.62471 -2.19234 -0.00639

H 2.75727 -0.33533 0.80031

H 2.72469 -0.33718 -0.83236

H -1.8068 2.08398 -0.00763

H -2.95049 -0.10676 -0.00465

**Phenyllithium**

Charge = 0 Multiplicity = 1

C 0. 0. 1.22565

C 0. 1.21365 0.52495

C 0. -1.21365 0.52495

C 0. 1.21365 -0.87645

H 0. 2.1403 1.05995

Li 0. 0. 3.22565

C 0. -1.21365 -0.87645

H 0. -2.1403 1.05995

C 0. 0. -1.57715

H 0. 2.1403 -1.41145

H 0. -2.1403 -1.41145

H 0. 0. -2.64715

**Phenol**

Charge = 0 Multiplicity = 1

C -0.03874 -0.93415 0.

C -0.02327 -0.23362 1.21365

C -0.02327 -0.23362 -1.21365

C 0.00768 1.16744 1.21365

H -0.03508 -0.76849 2.1403

O -0.07033 -2.3638 0.

C 0.00768 1.16744 -1.21365

H -0.03508 -0.76849 -2.1403

C 0.02316 1.86797 0.

H 0.0195 1.70231 2.1403

H 0.82748 -2.70371 0.

H 0.0195 1.70231 -2.1403

H 0.04679 2.93771 0.

Potential Energy Scan coordinates

**Oxygen(II)-fluoride (oxyfluoride)**

Charge = 0 Multiplicity = 1

O 0. 0. -0.49563

F 0. 1.01246 0.22028

F 0. -1.01246 0.22028

**FeBr3-FOF complex**

Charge = 0 Multiplicity = 6

Fe 0.08157 -1.03567 0.50821

Br -0.7134 0.93541 -0.37091

Br 2.36835 -1.11236 0.27415

Br -0.86342 -2.80989 -0.60945

O 0.1567 -0.36941 3.6796

F 1.35507 -0.65176 3.53198

F -0.53893 -1.17205 3.0397

**FeBr3OF-F complex**

Charge = 0 Multiplicity = 6

Br 0.06483 -1.54694 1.61148

Br 1.78554 1.58336 0.45085

Br 0.441 -0.86262 -2.06233

Fe 0.09194 0.09391 0.

O -3.12066 0.52579 0.

F -4.20731 1.12311 0.

F -2.19528 1.35118 0.

**FeBr3-OF2 complex**

Charge = 0 Multiplicity = 6

O -2.4046 1.32204 0.

Br 0.20073 -1.24983 1.87794

F -3.04059 0.99331 1.01246

F -3.04059 0.99331 -1.01246

Br 1.69773 1.6379 0.

Br 0.20073 -1.24983 -1.87794

Fe 0.01908 0.0656 0.

**FeBr3OF-F complex**

Charge = 0 Multiplicity = 6

O -0.07389 -0.65517 0.

Br 1.89172 -2.73356 1.84094

F -1.11335 -1.5697 0.29876

F -0.45649 -0.10027 -1.24314

Br 3.04774 0.17832 -0.60095

Br 1.54438 -3.25481 -2.08174

Fe 2.02798 -1.87682 -0.3003

**FeBr3-Cl2 complex**

Charge = 0 Multiplicity = 6

Br -0.41393 -1.19871 1.87794

Br -0.41393 -1.19871 -1.87794

Br -2.35623 1.41041 0.

Fe -0.44639 0.1288 0.

Cl 1.7595 1.77092 0.

Cl 3.40362 0.66762 0.

**FeBr3Cl-Cl complex**

Charge = 0 Multiplicity = 6

Br -0.71429 -0.67488 0.

Br -0.76306 -0.76654 -3.99813

Br -2.46162 2.30834 -2.06812

Fe -1.14196 0.36166 -2.01895

Cl 0.6705 2.16085 -2.06735

Cl 2.53707 1.31711 -2.06054

**FeBr3-Br2 complex**

Charge = 0 Multiplicity = 6

Br -0.65527 -1.3279 1.87794

Br -0.65527 -1.3279 -1.87794

Br -2.525 1.3337 0.

Br 1.72183 1.667 0.

Br 3.57937 0.3449 0.

Fe -0.65117 0. 0.

**FeBr3Br-Br complex**

Charge = 0 Multiplicity = 6

Br 0.50739 -0.24138 0.

Br 0.37127 -0.34908 -3.9456

Br -1.17346 2.83729 -2.00928

Br 2.06123 2.67989 -2.05599

Br 4.13573 1.56736 -2.02706

Fe 0.11143 0.86134 -1.99338

**Iodine(I)-chloride (iodine-monochloride)**

Charge = 0 Multiplicity = 1

I 0. 0. 0.56343

Cl 0. 0. -1.75657

**FeBr3-ClI complex**

Charge = 0 Multiplicity = 6

Br -0.72688 -1.53503 1.8706

Br -0.72786 -1.52065 -1.88525

Br -2.91733 0.87715 0.00246

Fe -0.89049 -0.21 -0.00224

Cl 0.76574 1.29813 0.0031

I 2.81021 0.20152 -0.00163

**FeBr3Cl-I complex**

Charge = 0 Multiplicity = 6

Br 0.18227 -0.94089 0.

Br 0.18128 -0.9265 -3.75586

Br -2.00819 1.4713 -1.86814

Fe 0.01865 0.38414 -1.87284

Cl 1.67489 1.89227 -1.8675

I 3.71935 0.79567 -1.87223

Pretransition state cooridnates

**FeBr3-FOF complex**

Charge = 0 Multiplicity = 6

Fe 0. 0. 0.

Br 0. 0. 3.14076

Br 2.28924 0. 0.2262

Br -2.2842 0.21556 0.18565

O -0.52732 -1.09643 1.68293

F 0.25642 -2.30075 1.77611

F -0.0772 -1.81627 -0.73268

**FeBr3-OF-F complex**

Charge = 0 Multiplicity = 6

O 0. 0. 0.

Br 0. 0. 2.65782

F 1.30385 0. -0.59417

F -0.80063 0.03014 -1.18626

Br -1.01101 3.16874 -0.49423

Br 2.01545 2.5094 1.18876

Fe -0.27846 1.70667 1.12503

**FeBr3-Cl2 complex**

Charge = 0 Multiplicity = 6

Br 0. 0. 0.

Br 0. 0. 4.61358

Br 2.61579 0. 2.29051

Fe 0.21903 0.05453 2.30035

Cl 0.15672 2.59031 2.26419

Cl -1.36435 3.17766 3.71469

**FeBr3-Br2 complex**

Charge = 0 Multiplicity = 6

Br 0. 0. 0.

Br 0. 0. 3.54428

Br 3.50454 0. 2.95178

Br 1.62483 2.53517 1.72822

Br -0.66459 3.11497 1.78679

Fe 1.57427 0.22226 1.69472

**FeBr3-ClI complex**

Charge = 0 Multiplicity = 6

Br 0. 0. 0.

Br 0. 0. 3.24772

Br 3.24107 0. 3.4313

Fe 1.70401 0.17555 1.63792

Cl 3.05928 0.25041 0.35614

I 1.58019 3.14668 1.75129

Pseudotransition state coordinates

**FeBr3FO-F complex**

Charge = 0 Multiplicity = 6

Br -0.36772 -1.55205 1.46777

Br 1.60691 1.5064 0.54396

Br 0.1907 -0.69822 -2.14689

Fe -0.16765 0.1676 -0.04643

O -2.60461 0.3626 0.11724

F -4.53406 1.60707 0.11312

F -1.62988 1.11072 -0.04955

**FeBr3OF-F complex**

Charge = 0 Multiplicity = 6

O 0.69729 -0.32134 -1.23007

Br 3.19575 -2.66609 0.0518

F -0.45245 -0.87866 0.24085

F 0.37593 -0.95254 -2.43622

Br 1.9155 0.0729 1.54093

Br 0.00765 -3.55587 -0.54589

Fe 1.12843 -1.71043 0.29217

**FeBr3Cl-Cl complex**

Charge = 0 Multiplicity = 6

Br 0. 0. 0.

Br 0. 0. 3.31234

Br 3.31263 0. 3.21518

Fe 1.60873 0.31597 1.65713

Cl 3.01169 1.03636 0.2127

Cl 1.37126 2.66863 1.89055

**FeBr3Br-Br complex**

Charge = 0 Multiplicity = 6

Br 0.58294 0.0419 -0.1822

Br -0.0354 -0.17 -3.88077

Br -1.67899 2.53117 -1.85371

Br 2.02285 2.6416 -2.47892

Br 4.22999 1.42004 -1.75603

Fe 0.22285 1.26117 -2.0989

**FeBr3-ClI complex**

Charge = 0 Multiplicity = 6

Br -0.07537 -1.34685 0.19225

Br 1.18275 -0.856 -3.11194

Br -1.13738 1.88196 -2.90059

Fe -0.35387 0.41074 -1.28262

Cl 1.27926 1.61457 -0.59684

I 2.87286 0.97157 -3.53683

Transition states - Iron(V) species

**Tribromooxyfluoroiron(V)-fluoride via O-F cleavage**

Charge = 0 Multiplicity = 6

Fe -0.62059 -2.15121 -0.03521

Br -2.79602 -2.33421 -0.75911

Br 0.44326 -4.17506 -0.28476

Br 0.46964 -0.55341 -1.27956

O -0.6037 -1.66928 1.71974

F 0.46473 -2.02821 2.23668

F -0.76899 0.17827 1.85695

**Tribromooxyfluoroiron(V)-fluoride via Fe-F formation**

Charge = 0 Multiplicity = 6

Fe -1.08163 -0.33169 0.1989

Br -2.99924 -1.12355 -0.79395

Br -0.21735 -2.46311 0.20663

Br 0.66057 0.40546 -1.10928

O -0.90569 -0.24841 2.00846

F 0.28021 -0.43736 2.31757

F -2.14528 2.05172 0.20842

**Tribromochloroiron(V)-chloride via Fe-Cl formation**

Charge = 0 Multiplicity = 6

Fe -3.27663 1.43384 1.04664

Cl -3.04974 -0.58444 1.75205

Br -2.00867 0.92929 -0.80476

Br -1.7495 3.04286 1.65403

Br -5.04648 1.98391 -0.31537

Cl -5.05454 2.14129 3.64264

**Tribromooxyfluoroiron(V)-fluoride via Fe-Cl-Cl concerted mechanism**

Charge = 0 Multiplicity = 6

Fe -3.19268 1.05035 0.99343

Cl -1.92571 -0.61282 0.23155

Cl -2.99659 -1.62451 2.76082

Br -3.22021 2.55378 2.73382

Br -5.35061 1.20226 0.21224

Br -2.28721 2.67361 -0.36125

**Tribromooxyfluoroiron(V)-fluoride via Fe-Cl formation**

Charge = 0 Multiplicity = 6

Fe -3.26449 1.65145 0.74264

Cl -2.90424 -2.12816 2.78292

Cl -2.38009 -1.43903 1.00226

Br -2.27481 2.57865 -1.115

Br -2.59768 2.80006 2.62043

Br -5.55171 1.77971 0.53735

Iron(V) species

**FeBr3OF**

Charge = -1 Multiplicity = 6

Fe 0.3175 -0.0135 0.

Br -0.63381 0.91298 -1.87794

Br -0.63381 0.91298 1.87794

Br -0.04143 -2.28532 0.

O 2.10706 0.31796 0.

F 2.30057 1.54276 0.

**FeBr3Cl**

Charge = -1 Multiplicity = 6

Fe 0.3175 -0.0135 0.

Br -0.63381 0.91298 -1.87794

Br -0.63381 0.91298 1.87794

Br -0.04143 -2.28532 0.

Cl 2.43154 0.37805 0.

**FeBr3Cl2**

Charge = 0 Multiplicity = 6

Fe 0. 0. -0.26636

Br 2.3 0. -0.26637

Br 0. 0. 2.03364

Br -2.3 0. -0.26637

Cl 0. -1.86195 -1.34137

Cl 0. 1.86195 -1.34137

**FeBr3OF2**

Charge = 0 Multiplicity = 6

Fe -0.11896 -0.01438 -0.00853

O 0.56124 -1.70249 -0.00929

Br -2.41648 -0.11358 0.0309

F 1.45585 -1.78803 0.84509

F 1.03197 -1.95794 -1.12766

Br 0.63171 1.11382 1.84988

Br 0.56829 1.08996 -1.9054

**FeFBr3O**

Charge = -1 Multiplicity = 6

Fe -0.44178 0.00898 0.

F -1.32044 -1.49287 0.

O -1.34269 1.59036 0.

Br 1.85818 -0.00427 0.

Br -0.44178 0.00898 -2.3

Br -0.44178 0.00898 2.3

**FeFBr3OF**

Charge = 0 Multiplicity = 6

Fe -0.38822 -0.20104 0.00544

F -1.02419 -1.82065 0.00992

O -1.53712 1.21048 0.0122

F -0.89209 2.2682 0.06472

Br -0.39773 -0.18508 -2.29449

Br 1.88594 0.14013 -0.03673

Br -0.35572 -0.19746 2.3052

**FeBr3O**

Charge = -2 Multiplicity = 6

Fe 0.3175 -0.0135 0.

Br -0.63381 0.91298 -1.87794

Br -0.63381 0.91298 1.87794

Br -0.04143 -2.28532 0.

O 2.10706 0.31796 0.

**Cl2**

Charge = 0 Multiplicity = 1

Cl 0. 0. 0.99

Cl 0. 0. -0.99