**Supplementary Material**

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

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**General remarks on quantum theory in electrophilic aromatic substitution and catalytic mechanistic considerations**

*Physicochemical outcome of interactivity patterns in general and EAS chemistry*

The chemistry behind EAS depends strictly on the choice of the range of catalytic and electrophilic systems. Electrophiles discussed within EAS theory are somewhat more chemically subtle than typical electrophiles used in materials syntheses or even total syntheses, and can be ascribed as multiple species that are usually in tandem arrangement. Moreover, novel electrophiles are optimized to resemble the tandem reactivity pattern not only among themselves (i.e., they are not dimers or polymers, in the so-called intra-reactivity setup), but also within the catalytic-electrophilic reactivity type (so-called inter-reactivity set-up). From a mechanistic point of view, the first reactivity pattern can be referred to as an autocatalytic reactivity pattern and the second as a heterogeneous catalytic reactivity pattern. The choice of the nucleophile is limited to the presence/absence of a functional group on the aromatic compound.

The nature of aromatic compounds has already been discussed in terms of the π-electrons responsible for the initiation process in EAS. Note that, in particular, π-electrons are (much) more mobile than corresponding σ-electrons, which leads directly to the key idea that the kinetic energies of π-electrons (also called π-kinetic energies) are gradually higher than those of corresponding σ-electrons. Moreover, due to the higher values of the kinetic energy of π-electrons, the mobility gradient analysis can show that there is a small discrepancy within the different types of π-electrons based on their topological definition [1]. The analysis of orbital shifts [2], on the other hand, can be a very striking and efficient tool in the tracking of π-electrons, suggesting that it is more than a phenomenon of increased electron mobility. Indeed, (fast) electron displacement in a given space is called a resonance phenomenon. In contrast, σ-electrons are axially bound to an atom, which prevents significant electron shift. Their σ-kinetic energies are lower than the π-kinetic energies because the space in which they can be located is significantly reduced. The resulting sum of the π- and σ-kinetic energies can be viewed as a simple mathematical relation called the total kinetic energy of a system (eq. 1), and their difference can be simply referred to as a kind of Electron-to-Space Interaction factor (ESI, eqs. 2a and 2b):

$E\_{k}=E\_{π}+E\_{σ}$ (1)

$ESI=E\_{π}-E\_{σ}$ (2a)

Since in aromatic compounds Eπ ≫ Eσ is a valid approximation, ESI can be approximated

$ESI\_{Ar}\~E\_{π}$ (2b)

Where Eπ is referred to here as the π-kinetic energy and Eσ as the σ-kinetic energy. ESI is a newly introduced quantity that can predict trends in macroscopic properties - binding energies and physical characterization of systems with highly functionalized topologies - on the one hand, and microscopic properties - consistent differentiation of zero-point energies, entropy gradients, and definitions of the localized electron density function - on the other [3]. In given aromatic systems, ESI can be applied specifically with respect to Negative Electrostatic Potential Map (NEPM) and thus predict the volume and electron density, which provides the opportunity to determine the electron density gradient, which can be important for the study of both binding processes and principles of reactivity in solution. Figure 1 shows the location of the NEPM over typical substituted monoaromatic compounds, which may correspond to an (increasing) ability in binding forces to eventually interpret the binding scheme between such compounds.



**Figure 1.** NEPM calculated for some simple monosubstituted aromatic compounds. The partial maps shown in structures 1 and 3 mainly indicate where the negative charge is concentrated, and therefore suggest where on the aromatic compound the binding process is most likely to start. Structures 2 show an important feature of this type of map - the density level. NEPM can be used to predict positions in EAS with relevant qualitative accuracy, as well as to predict electronic effects of substituents. Further analogies can be derived for other types of compounds. The kinetic energies (Ek) of aromatic compounds depend on the type and nature of the substituent, i.e., from phenol (π-electrons are most mobile) to phenyllithium (π-electrons are concentrated over negatively charged ipso carbons, which are least mobile). On the other hand, phenyllithium is the most reactive in both kinetic and thermodynamic sense, while phenylborane is the least reactive due to the orbital arrangement on the molecular map. NEPM can determine the mobility of n- and π-electrons since their physicochemical nature is similar, unlike σ-electrons, which is reflected in the n- and π-mobility coefficients, which are (much) larger than σ-electrons. All calculations were performed at the M062X/Def2QZVPPD//M062X/6-311G(2df,2pd) level of theory.

Although the kinetic energy of an electron is an important element in the evaluation methodology of binding processes, there is another factor that additionally determines the total energy of an electron in a given state - the potential energy. The potential energy refers to the interactions between electrons and can be represented as either a Coulomb or an overlap integral. These integrals ultimately yield a value, theoretically represented as a density matrix, from which one can read whether and how strongly the electrons interact from an electrostatic point of view. The larger the value of a determinant of such matrix - the better the coverage. The sum of the contributions of potential and kinetic energy is equal to the total energy of a system (electronic energy of a system), represented in eq. 3:

$E\_{total}=E\_{k}+E\_{p}$ (3)

Here Etotal is called the total (electronic) energy of a system, Ek is the kinetic energy and Ep is the potential energy. If we take into account the presence of σ- and π-electrons, which contribute (significantly) to the modified reactivity in EAS or other types of retrons [3,4], eq. 3 can be extended to eq. 4:

$E\_{total}=E\_{π}+E\_{σ}+E\_{p}$ (4)

So there remains the space to define the mathematical meaning of the kinetic energy of an electron, as a particle. As free π-electrons can move between nearby orbitals, shift their position and maintain momentum over time, which confirms the Heisenberg relation as constant, since the velocity of an electron as a particle reaches values much smaller than the speed of light, which is shown in the following equations as follows [5]:

*Combining Heisenberg basic postulate (eq. 5) with the relativistic momentum equation in the formalism of classical mechanics (eq. 6), one obtains the velocity-modified Heisenberg principle (eq. 7), which refers to the kinetic property of a particle (e.g. electron):*

$∆σ\_{x}∆σ\_{p}\geq \frac{ℏ}{2}$ (5)

$∆p\_{e}=m\_{e}∆v\_{e}$ (6)

$∆σ\_{x\_{e}}∆σ\_{v\_{e}}\geq \frac{ℏ}{2m\_{e}}$ (7)

Where $∆σ\_{x\_{e}}$ is the momentum value of an electron at a given time reference function, $∆σ\_{v\_{e}}$ is the velocity momentum value at a given time reference function, where me and $∆v\_{e}$ denote the electron mass (in kg) and velocity change (in ms-1), respectively. Reduce the eventual probability of electron motion within a narrow electron distance (cf. reduced Planck constant to a full single frequency corresponding to 2π, or radius distance that can be approximated for a spin [electron]). Furthermore, if the velocity of the π-electrons is assumed to be constant, eq. 7 can be simplified in terms of the kinetic velocity of the electrons, further defining eq. 7:

$∆E\_{k}\left(e\right)=\frac{1}{2}m\_{e}∆v\_{e}^{2}$ (8)

$∆σ\_{v\_{e}}=α∆v\_{e}=α\sqrt{\frac{2∆E\_{k}\left(e\right)}{m\_{e}}}$ (9)

$∆σ\_{x\_{e}}α\sqrt{\frac{2∆E\_{k}\left(e\right)}{m\_{e}}}\geq \frac{ℏ}{2m\_{e}}$ (10)

$∆σ\_{x\_{e}}\geq \frac{ℏ}{α}\sqrt{\frac{1}{8∆E\_{k}\left(e\right)}}$ (11)

Here $∆E\_{k}\left(e\right)$ is denoted as the change in the kinetic energy of the electron solely as a function of the kinetic velocity of the electron, and α is a term corresponding to the frequency of change in electron velocity, which is inversely proportional to the frequency of collision with other electrons (in systems with many electrons) and the medium in which the electron is located. If the electron is in the axial bond orbital, then the value of the density overlap matrix is assumed to be high, which means that the value of the Coulomb integral is also increased. Since the electrons in the bonding orbital repel each other, the orbitals themselves must have opposite sign to attract each other for the electrons to move in the given overlap space. On the other hand, if an electron is in a secondary bonding orbital, the density matrix can vary depending on the type of orbital and the number of electrons in it. Usually, the value of the density overlap matrix in this case is a time-dependent quantity because the value of the Coulomb integral is smaller than for axial bond orbitals and the electrons have the opportunity to diffuse through the multiply occupied space. Since the orbital is defined as the square of the probability that an electron is at a particular point in the system "x", defined via the wave equation formulated in the Schrödinger equation [3,6], it can be postulated that the momentum of an electron can be determined as the limiting value(s) of the space traversed by the electron, as a function of time and position, defined as in Equation 12:

$∆σ\_{x\_{e}}=\lim\_{n,k\to L}\sum\_{i,j=0}^{n}\sum\_{α,β=0}^{k}\left.c\_{ij}r\_{ψ^{2}}c\_{αβ}r\_{ψ^{2}}\right|\left.x,y,z,t\right⟩$ (12)

$r\_{ψ^{2}}=\sqrt{\sum\_{x,y,z}^{}\left(∆x\right)^{2}\left(∆y\right)^{2}\left(∆z\right)^{2}}∮\_{V}^{}ψ^{2}dψ$ (13)

Here $r\_{ψ^{2}}$is defined as the eigenvector of an orbital containing an electron, and is defined as a contour integral as a function of the volume of the corresponding orbital described by the corresponding wave function ψ, and its coordinate number set described as a sum of linear vector functions by the x, y, and z coordinates. $r\_{max}^{L}$ is defined as the most intense eigenvector at the given value of L. L is the angular momentum of the analysed electron energy, while *cij* and *cαβ* are electron coefficients that occupy given alpha and beta HOMO and LUMO, defined as eigenvectors. Assigning physical meanings to eqs. 12 and 13, one can conclude that *cij/cαβ* is proportional to the designated orbital energy level, i.e., it defines the frontier molecular orbital image of an analysed system containing a given electron(s), which, in turn, must also follow subsequent formalisms, such as estimation of Fock matrix etc. Moreover, by solving eq. 12, it is a simple observation that the comparison of the solutions for π- and σ-electrons of the same quantum level indicates that $∆σ\_{x\_{e}}$ is larger for π-electrons than for σ-electrons, which also suggests that $∆σ\_{x\_{e}}$ can be considered as a parameter of electron mobility.

*Energy as a function of Electron Mobility parameter in PES theory*

Energy is a ubiquitous phenomenon when it comes to the physical aspect of a system and can be represented as an internal driving force. When considering binding processes, only the energy of the relevant electrons is considered, and the energy of the system in such a transition state (here the terms transition and transition states are disambiguated, the former denoting any process in which the electron density is minimally perturbed as a function of orbital and geometrical properties and time; and the latter - denotes the exact electron movement from one to another reactive site, which brings the interacting subsystems out of equilibrium, usually leading to quite an increase in energy, which can be diagnosed by analysing the density overlap matrices, which have only an imaginary frequency), increased by the entropy decrease. This type of energy (electronic energy) is thus responsible for the stability of the whole system and its chemical reactivity, and is essentially composed of a thermodynamic parameter (enthalpy) and a physical parameter (work). When chemical interactions are taken into account, another additional but important factor can be the geometrical parameter (entropy) of the subsystem, which is additionally determined by kinetic analyses.

PES analyses are a widely used theoretical tool in the study of transition states (TS) [7] and is a fundamental method for other modern algorithms at TS search paths, such as Nudged Elastic Band (NEB) theory [8], Quadratic Synchronous Transit methods (QST) [9], Linear Synchronous Transit (LST), Berny's approximation algorithm, and Synchronous Transit-Guided Quasi Newton method (STQN). PES analyses are invoked by defining relaxed scan reaction coordinates. This scan can be defined on one or more reaction coordinates at a time, which defines the ability for the prediction algorithm to create the potential energy surface on one coordinate (1D), two coordinates (2D), or three coordinates (3D). 3D potential energy surfaces are the most time-consuming to create, but are the most accurate and are better suited for predicting systems with multiple reactive sites than for systems with only one reactive site (e.g., reactive methyl compounds). Nevertheless, the ratio of predicted relative errors to time required is much better for 1D scans than for 3D scans, and - assuming a good theory used in these algorithms - 1D scans can be quite good even for large and complex reactive systems with up to several hundred atoms involved. In a theoretical sense, when using methods based on the wave function or electron density integral, the energy change of a system along the chosen reaction coordinate should follow a uniform energy change, which in turn depends strongly on the proximity of electrons defined by both the bond eigenvectors and the map of the uniform molecular electrostatic potential.

Assuming that the electronic energy is equal to Hamiltonian, eq. 12 can be rewritten as follows as a starting point, since it can be either regarded as time-independent Schrödinger equation (related only to ab initio functionals):

$\hat{H}=\hat{T}+\hat{V}$ (14)

If $\hat{T}$ is a kinetic energy operator and $\hat{V}$ is a potential energy operator, then the Hamiltonian operator is equal to the electronic energy as given earlier in eq. 3. The kinetic energy operator can be further transformed into a relation defined by the momentum coordinate:

$\hat{T}=-\frac{ℏ^{2}}{2m}∇^{2}=-\frac{ℏ^{2}}{2m}\left(\frac{∂^{2}ψ}{∂x^{2}}+\frac{∂^{2}ψ}{∂y^{2}}+\frac{∂^{2}ψ}{∂z^{2}}\right)$ (15)

$\hat{V}=E\_{p}=\hat{V}\left(r,t\right)$ (16)

Where *r* and *t* are the corresponding eigenvector and time period defining the intensity of the electron potential energy, further defined by the wave equation or electron density integral. When the number of reaction coordinates is reduced from three to one, the computational cost is also reduced proportionally, since the mathematical complexity of calculating the derivative is reduced, as can be seen from eq. 15, and thus the Hessian can be calculated more quickly:

$\hat{T}=-\frac{ℏ^{2}}{2m}∇^{2}=-\frac{ℏ^{2}}{2m}\frac{∂^{2}ψ}{∂x^{2}}$ (kinetic operator form in one-dimensional PES method) (17)

Eq. 13 remains intact since the orbital eigenvector is strictly defined in the Cartesian coordinate system, where all three coordinate vector intensities are known, due to the orbital displacement in space. On the other hand, Electron Mobility parameter can be considered according to the two basic definitions of Schrödinger equation, which allows us to exclude the time-independent form of eq. 18:

$∆σ\_{x\_{e}}=\lim\_{\begin{array}{c}n\to L\\k\to r\_{max}^{L}\end{array}}\sum\_{i=0}^{n}\sum\_{j=0}^{k}\left.c\_{i}r\_{ψ^{2}}c\_{j}r\_{ψ^{2}}\frac{∂}{∂x}\right|\left.y,z\right⟩$ (18)

The degree of freedom is also involved in the computational procedure and may also dictate the total computational time with respect to the possible structures analysed along the chosen reaction coordinate. Furthermore, it defines to what extent the reaction coordinates are involved in the further energy definition in the method PES and how the symmetry element affects the behaviour of the algorithm of the method PES as a function of time.

**Cartesian coordinates of optimized structures of aromatic compounds, iron adducts and electrophiloids**

Aromatic compounds’ coordinates

**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 (PES) coordinates

(inital scan step coordinates are provided)

**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

**FeBr3FO-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 (preTS) 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 (pseudoTS) 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

**First-Order Derivative (FOD) plots for iron adducts**

**(**„CDR-free“ refers to plots where all spotted CDR points were removed from the corresponding full PES plots!)

Pretransition (preTS) state PES

Fe–X bond scanned (X=F, O, Cl, Br, I)



**Figure S1.** FOD derived from full PES for FeBr3-FOF complex (Fe–F bond scanned)



**Figure S2.** FOD derived from CDR-free PES for FeBr3-FOF complex (Fe–F bond scanned)



**Figure S3.** FOD derived from full PES for FeBr3-OF-F complex (Fe–O bond scanned)



**Figure S4.** FOD derived from CDR-free PES for FeBr3-OF-F complex (Fe–O bond scanned)



**Figure S5.** FOD derived from full PES for FeBr3-Cl2 complex



**Figure S6.** FOD derived from full PES for FeBr3-Br2 complex



**Figure S7.** FOD derived from CDR-free PES for FeBr3-Br2 complex



**Figure S8.** FOD derived from full PES for FeBr3-ClI complex (Fe–Cl bond scanned)

Pseudotransition (pseudoTS) state PES

X–X bond scanned (X=F, O, Cl, Br, I)



**Figure S9.** FOD derived from full PES for FeBr3FO-F complex (O(5)–F(6) bond scanned)



**Figure S10.** FOD derived from full PES for FeBr3OF-F complex (O(1)–F(3) bond scanned)



**Figure S11.** FOD derived from CDR-free PES for FeBr3OF-F complex (O(1)–F(3) bond scanned)



**Figure S12.** FOD derived from full PES for FeBr3Cl-Cl complex



**Figure S13.** FOD derived from full PES for FeBr3Br-Br complex



**Figure S14.** FOD derived from full PES for FeBr3Cl-I complex



**Figure S15.** FOD derived from CDR-free PES for FeBr3Cl-I complex

**Supplementary references**

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