Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Spin-resolved Charge Displacement Analysis as Intuitive Tool for the Evaluation of cPCET and HAT scenarios

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I. Methods

I.1 Computational Details

All the DFT calculations were performed using the ADF[1,2] program. Molecular orbitals (MOs) were expanded using two uncontracted sets of Slater-type orbitals (STOs) of triple-ζ quality basis set with double polarization functions (TZ2P). Core electrons were treated by the frozen core (FC) approximation.[3] Scalar relativistic corrections were included self-consistently using the Zeroth Order Regular Approximation[4] (ZORA). Single point calculations were carried out, on top of the available optimized geometries,[5] with the S12G functional[6] and TZ2P basis set (S12G/TZ2P) under the unrestricted formalism.
The coordinates of the TSs were taken from the SI of ref. 5 and used without further adjustment.

I.2 Charge-Displacement Function (CDF) Analysis

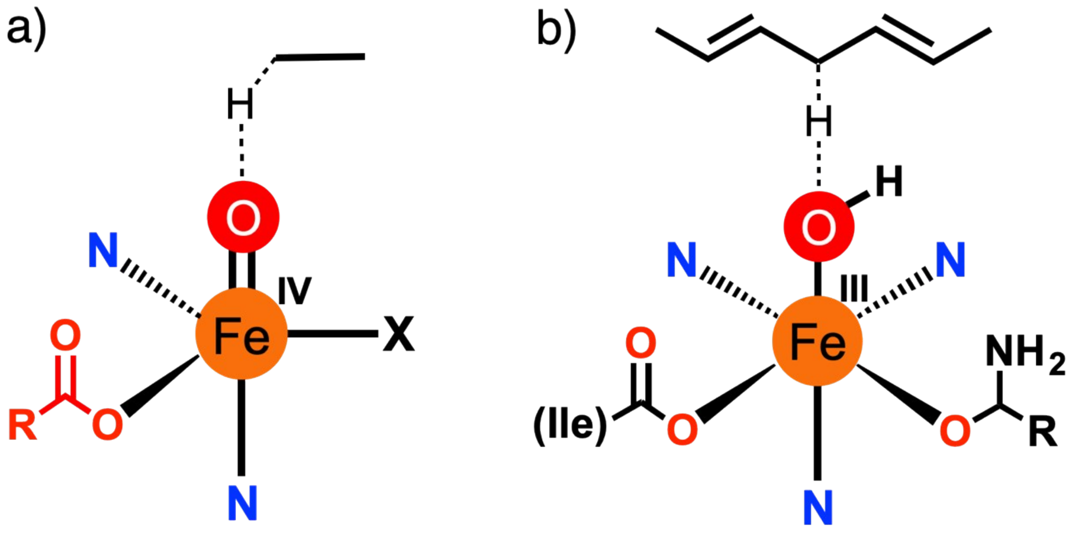
The electron density changes occurring upon the chemical bond formation between two fragments A and B can be analyzed through the charge-displacement function (CDF)[7]

$$\Delta q(z) = \int_{-\infty}^{z} dz' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta\rho(x,y,z')\, dx\, dy \qquad (1)$$

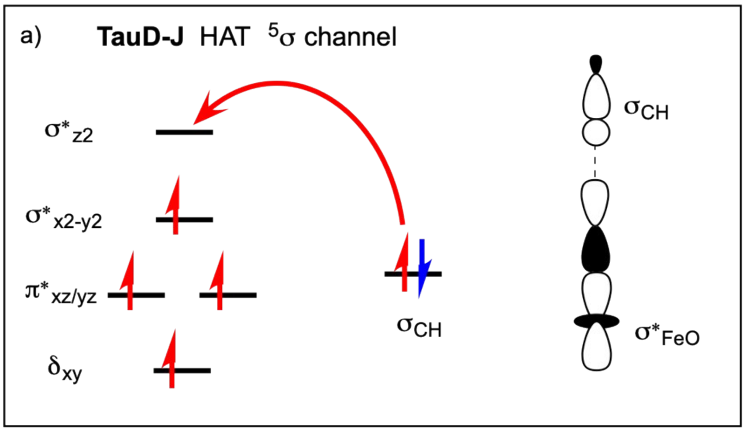
In this equation $\Delta\rho(x,y,z')$ is the electron density difference between the electron density of the complex AB and that of the two noninteracting fragments A and B in the geometries they have in the overall complex. A partial progressive integration of $\Delta\rho(x,y,z')$ along a suitable chosen bond axis z yields the charge-displacement function $\Delta q(z)$ (eq 1). This function measures at each point z along a chosen axis (typically the axis joining A and B fragments) the amount of electrons that, upon bond formation, moves across a plane perpendicular to this axis passing through z. Positive (negative) values of $\Delta q(z)$ correspond to electrons flowing in the direction of decreasing (increasing) z. A positive (negative) slope indicates regions of charge accumulation (depletion). In this study, the overal complex corresponds to the transition state structure of (i) the TauD-*J* + ethane substrate to model the HAT reaction, and (ii) the lipoxygenase + 2,5-heptadiene substrate to model the cPCET reaction. In each case, the two A and B fragments are represented by the high valent iron complex and its relative substrate and the z reference axis joins the O atom of the Fe moiety and the H atom of the substrate which undergo cleavage, so that the newely O–H formed is under investigation. The CDF provides a thorough, spatially detailed picture of the total charge flow between the iron complex and the substrate fragments. The CDF analysis has proven to be a stable method with respect to computational settings such as basis set quality and exchange-correlation functional.[8]

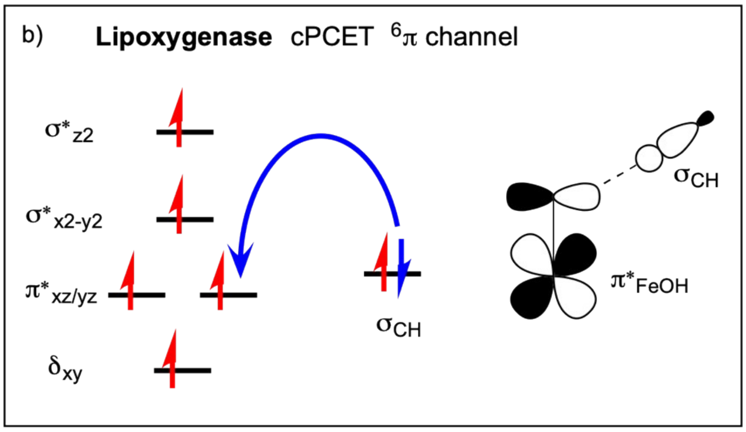
II. Reaction mechanisms

II.1 TS structures of the model complexes considered in this study: a) TauD-J intermediate; b) Lipoxygenase



II.2 Favored reaction pathway for: a) TauD-J intermediate; b) Lipoxygenase

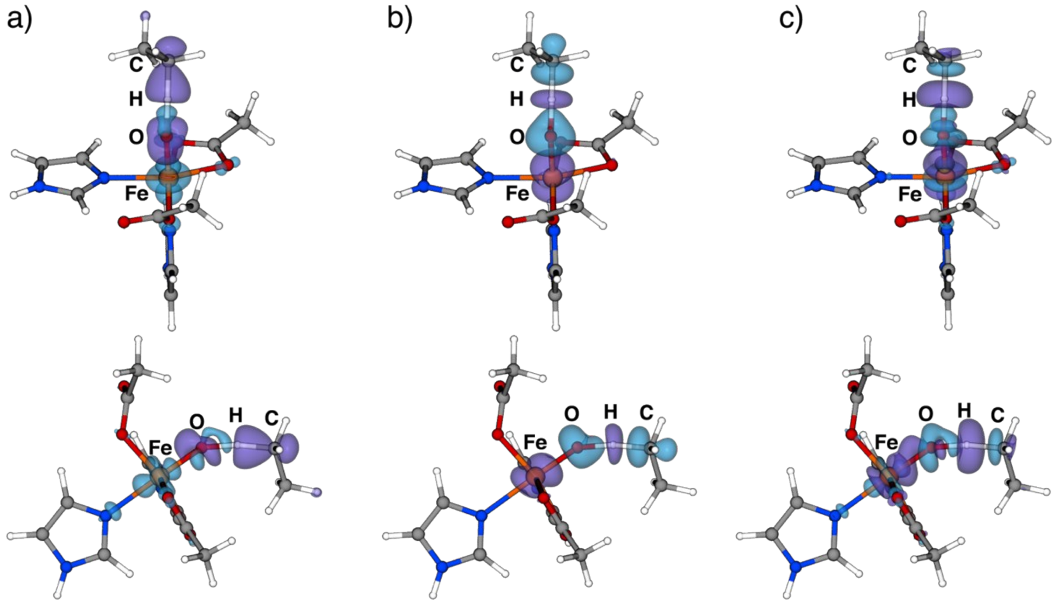




II.3 Alternative views of the 3D contour plots (± 0.035 e au^{-3}) of the Δρ for the FeO–H(substrate) bond in the TS of the TauD-J model complex

a) α spin-density difference; b) β spin-density difference; c) total density difference

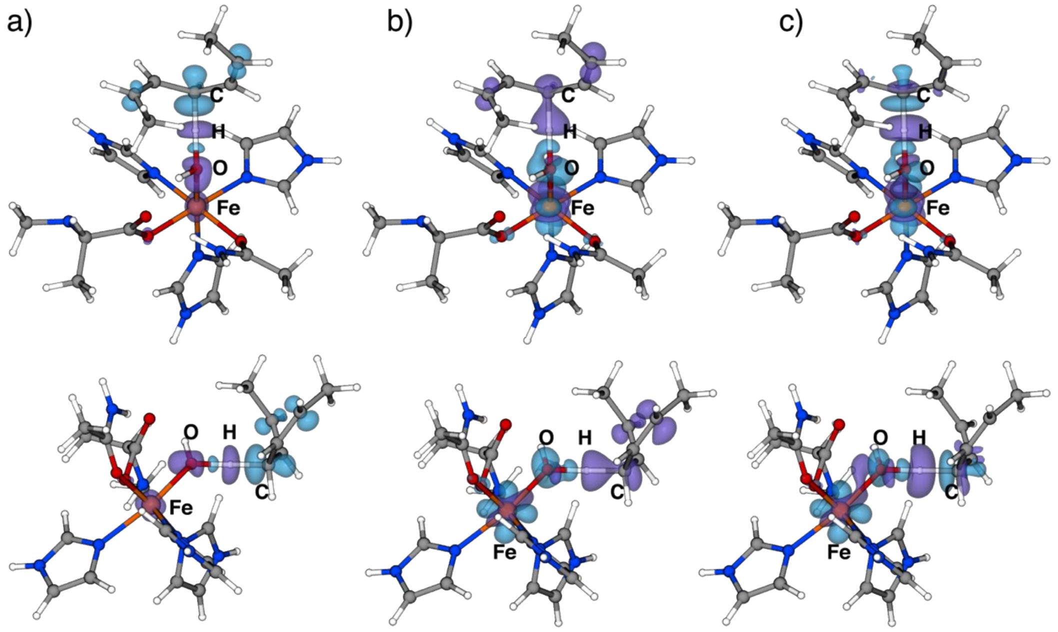
cyan (violet) ribbon color corresponds to regions of charge accumulation (depletion)



II.4 Alternative views of the 3D contour plots (± 0.035 e au^{-3}) of the Δρ for the FeO–H(substrate) bond in the TS of the Lipoxygenase model complex:

a) α spin-density difference; b) β spin-density difference; c) total density difference

cyan (violet) ribbon color corresponds to regions of charge accumulation (depletion)



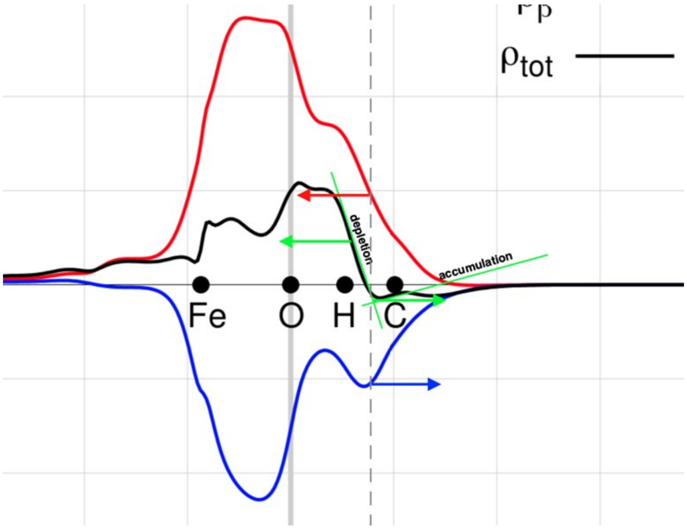
II.5 Breaking of the C-H bond

The relevant changes for the breaking of the C-H bond are not immediately obvious from the total osCDF in Figures 1b/2b, which is influenced by the choice of substrates that we used. The rearrangement of electrons during the HAT/cPCET process, resulting in the radical formation on carbon involves movement of charge from the substrate towards the carbon. This can be seen directly by focusing on the region to the right of the carbon, where in the ethane of Fig 1b there is hardly any change, while in the case of the heptadiene of Fig 2b there is a significant flow of electrons within the substrate. The origin of this is most easily seen in the alternative view from SI sections II.3/II.4 (vide supra). For TauD-*J*, the flow of electrons in the substrate involves exclusively the C-H region, while in the case of lipoxygenase also other parts of the substrate are affected. This additional flow in the substrate makes that the total osCDF at the CH region includes not just changes in the CH bond region, but also from other parts of the substrate.

For understanding/visualizing the breaking of the C-H bond, one should take into account not so much the value of the osCDF, but instead its slope. As reported in the text ("*Positive values of Δq(z) correspond to electrons flowing in the direction of decreasing z, and negative values to electrons moving to increasing z. A positive slope indicates regions of charge accumulation, and vice versa a negative slope indicates depletion.19*"), this slope determines if there is density accumulation or density depletion. By looking carefully at the region around the C-H bond, there is indeed in the middle of the C-H bond a turning point with overall density accumulation going to the right towards C and overall depletion to the left towards H.

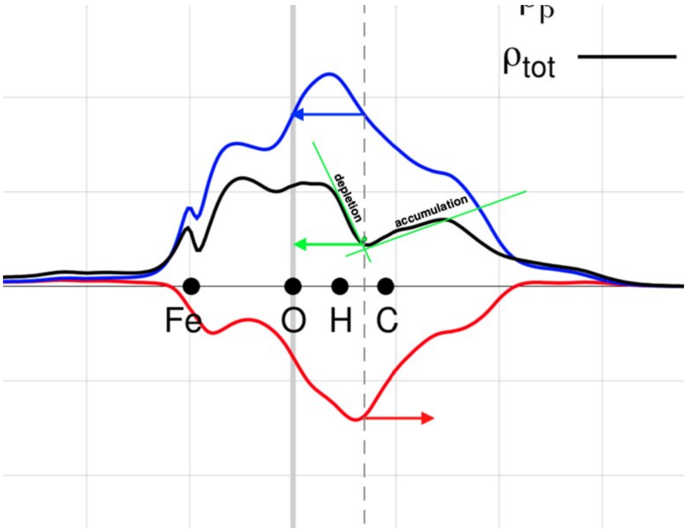
In TauD-J in the C-H region there exists an α-electron flow (red arrow) from the right to the left and a β-electron flow (blue arrow) from the left to the right, in accordance with scheme 2. However, the same scheme does not take into account the total electron flow (Δq_tot), which is the sum of the α and the β electron flows (black curve of the CDF plot). Here, in the proximity of the H atom we observe an electron depletion (negative slope) with Δq_tot>0, meaning that electrons are moving from right to the left (green arrow), whereas in the proximity of the C atom we observe an opposite trend i.e. electron accumulation (positive slope) and Δq_tot<=0 (electrons moving from the left to the right, green arrow).

Modified Fig. 1b with trendlines (green) that indicate the slope of the total osCDF in the H··C region



Likewise, for lipoxygenase, the α-electron flow (red arrow) and β-electron flow (blue arrow) is in agreement with scheme 3 and it's worth noting that the total electron accumulation and depletion around the H··C region follows the same trend as for TauD-J (i.e. a depletion around H followed by an accumulation around C). However, here, Δq_tot>0 over the whole plot, including the CH region.

Modified Fig. 2b with trendlines (green) that indicate the slope of the total osCDF in the H··C region



III. References

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