An Example Where Orbital Relaxation Is an Important Contribution to the Fukui Function

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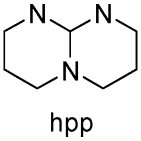
Density-functional electronic structure calculations are performed on the molecules $Cr_2(hpp)_4$, $Mo_2(hpp)_4$, and $W_2(hpp)_4$, where the bridging ligand, hpp, is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]-pyrimidine. The calculated electronic densities are used to determine the Fukui functions. These molecules are unique not only in their ability as electron donors but also because orbital relaxation plays a decisive role in their reactivity. Unlike other examples in the literature, the reactivity of these compounds cannot be expressed solely in terms of the highest occupied and lowest unoccupied Kohn−Sham orbitals but only using the Fukui function, which includes the effects of orbital relaxation.

Introduction

While density-functional theory (DFT) has gained wide acceptance as a computational tool,[1−3] its merits as a conceptual tool are somewhat less appreciated.[1,4] However, DFT provides the full complement of tools required to describe chemical reactions and has had numerous successes. Some tools of “conceptual DFT” are merely recapitulations of age-old chemical concepts (e.g., the electronic chemical potential is just the neagtive of the electronegativity[5]); some tools were previously known but lacked an adequate theoretical basis before the advent of conceptual DFT (e.g., the hardness[6]); some tools are improvements of other, well-accepted, results (e.g., the Fukui functions, which correct frontier molecular orbital theory with orbital relaxation effects[7,8]); and some tools were seemingly unknown before the advent of DFT (e.g., the local softness[9] and the associated local hard/soft acid/base principle[10]).

In this paper, we wish to focus on the Fukui functions, which provide information about site reactivity (regioselectivity).[1,7,11] Specifically, we wish to use the Fukui function to study the paddlewheel molecules $M_2(hpp)_4$, where M = Cr, Mo, and W and the bridging ligand, hpp, is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidine.



These three molecules have exceptionally low ionization energies; the tungsten complex has the lowest known ionization energy of any stable neutral molecule.[12,13] Consequently, these molecules are extremely good Lewis bases. The molybdenum complex will, for example, strip a chlorine atom from dichloromethane to form the $[Mo_2(hpp)_4]^+Cl^-$ salt.[13,14] On the basis of this example, electrophilic reagents seem to attack the metal complex “end on”, attacking one of the two metal atoms on the ends and not the bond connecting the metal atoms.[13] The goal of this paper is to ascertain whether the reactivity preference for this reaction could be predicted using the Fukui function. Besides the obvious importance of these complexes, we are motivated by the fact that, on the basis of the molecular orbital diagram previously presented for these molecules, frontier molecular orbital theory (incorrectly) predicts that electrophiles would attack the metal−metal bond.[12] We set out to determine, then, whether this might be a case where the tools of conceptual DFT (and, in particular, the Fukui function) would have an advantage over their molecular orbital theoretic predecessors. Foreshadowing our results, we find that, for these molecules, orbital relaxation effects play a decisive role in determining regioselectivity, and thus, the Fukui function (which accounts for orbital relaxation) can describe the observed reactivity preference even though simple frontier molecular orbital theory cannot.

Theoretical Background

To motivate the Fukui function, consider that if we transfer a fraction of an electron, δ, to an N electron molecule, it will tend to distribute itself so as to minimize the energy of the resulting $N + \delta$ electron system.[15] The resulting change in density is called the Fukui function from above and is denoted[7]

$$f_N^+(\boldsymbol{r}) = (\partial\rho(\boldsymbol{r})/\partial N)_{v(\boldsymbol{r})}^+ = \rho_{N+1}(\boldsymbol{r}) - \rho_N(\boldsymbol{r}) \qquad (1)$$

where $\rho_{N+1}(\boldsymbol{r})$ and $\rho_N(\boldsymbol{r})$ are the electron densities of the $N + 1$ and N electron systems evaluated at the geometry, $v(\boldsymbol{r})$, of the N electron system; the superscript plus sign on the derivative indicates that we are considering the derivative from above (right-hand derivative). (The finite difference approximation to the derivative is exact in the zero temperature limit.[11,16,17]) Since $f_N^+(\boldsymbol{r})$ will be large at molecular sites that can stabilize additional electrons and small elsewhere, we infer that places where $f_N^+(\boldsymbol{r})$ is large are subject to nucleophilic attack.

Analogous to the Fukui function from above is the Fukui function from below,[7]

$$f_N^-(\boldsymbol{r}) = (\partial\rho(\boldsymbol{r})/\partial N)_{v(\boldsymbol{r})}^- = \rho_N(\boldsymbol{r}) - \rho_{N-1}(\boldsymbol{r}) \qquad (2)$$

which is determined by calculating the best way to take an electron from a molecule.[15] As before, $\rho_{N-1}(\boldsymbol{r})$ is the electron

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density of the $N - 1$ electron system evaluated at the same geometry as the N electron system and the superscript minus sign on the derivative indicates that we are considering the derivative from below (left-hand derivative). Clearly, $f_N^-(\boldsymbol{r})$ will be large at places in the molecule that are minimally destabilized by the removal of electrons; these places are susceptible to electrophilic attack.

The reader will note similarities between the interpretation of the Fukui functions and the frontier molecular orbital theory proposed by Fukui and his collaborators.[18-20] In particular, as an index related to nucleophilic attack, $f_N^+(\boldsymbol{r})$ seems related to the lowest unoccupied molecular orbital (LUMO). Indeed, in the simplest molecular orbital theory model, additional electrons will occupy the LUMO, and thus, we expect $f_N^+(\boldsymbol{r})$ to be more or less related to the orbital density of the LUMO, $|\phi_{\mathrm{LUMO}}(\boldsymbol{r})|^2$. Similarly, as an index related to electrophilic attack, $f_N^-(\boldsymbol{r})$ seems related to the highest occupied molecular orbital (HOMO). The link between frontier molecular orbital theory and the Fukui function goes so deep, in fact, that one sometimes extends the analogy to define a third Fukui function, appropriate for radical attack.[7]

$$f_N^0(\boldsymbol{r}) = \frac{f_N^+(\boldsymbol{r}) + f_N^-(\boldsymbol{r})}{2} \tag{3}$$

$f_N^0(\boldsymbol{r})$ does not rest on the same firm theoretical footing as $f_N^+(\boldsymbol{r})$ and $f_N^-(\boldsymbol{r})$, however.

While it encapsulates key concepts from frontier molecular orbital theory, the Fukui function does not depend on molecular orbital theory arguments for its validity. This has its advantages. For example, when one expands the Fukui functions in terms of the Kohn−Sham spin orbitals (which are listed in increasing order of energy, so that $\phi_N(\boldsymbol{r})$ is the HOMO and $\phi_{N+1}(\boldsymbol{r})$ is the LUMO), one obtains[8;21] and

$$f_N^+(\boldsymbol{r}) = |\phi_{N+1}(\boldsymbol{r})|^2 + \sum_{i=1}^{N}\left(\frac{\partial|\phi_i(\boldsymbol{r})|^2}{\partial N}\right)_{v(\mathbf{r})}^{+} \tag{4}$$

$$f_N^-(\boldsymbol{r}) = |\phi_N(\boldsymbol{r})|^2 + \sum_{i=1}^{N}\left(\frac{\partial|\phi_i(\boldsymbol{r})|^2}{\partial N}\right)_{v(\boldsymbol{r})}^{-} \tag{5}$$

It is clear that the Fukui function includes information about not only the frontier molecular orbitals but also orbital relaxation, the change in orbital shape that accompanies the addition (eq 4) or removal (eq 5) of electrons from the system. When the second term in eqs 4 and 5 is small compared to the first term, it can be neglected for qualitative purposes and the frontier molecular orbital theory of Fukui et al. obtained anew.

As mentioned in the Introduction, the $M_2(hpp)_4$ systems are intriguing because their HOMOs would suggest that an electrophile will attack the metal−metal bond, in contrast with experiment.[12,13] This suggests that orbital relaxation may play an important role for these molecules. Referring to eq 5, one can see that the Fukui functions differ from the frontier orbitals only in that the Fukui functions include orbital relaxation. Consequently, by comparing the Fukui functions with the frontier orbital contributions, we can characterize the effects of orbital relaxation on a molecule's reactivity. Specifically, if orbital relaxation plays a decisive role in determining the site at which an electrophile attacks $M_2(hpp)_4$, then $f_N^-(\boldsymbol{r})$ should be larger at the "ends" of the metal dimer (the experimentally observed reactive site)[13] than it is in the "middle".

From the definition, it is clear that the Fukui function measures the linear response of the electron density to the charge transfer from an approaching reagent; as such, it is a reliable indicator only in the linear-response regime, which occurs when the reagent molecule is still far from the molecule. On the basis of this, one might expect that the Fukui function would only be a reliable indicator for reactions with early transition states. However, the Fukui function seems to be a rather robust reactivity indicator, an observation that has been attributed to the success of "hill-climbing" algorithms for finding transition states in chemical reactions.[11,22]

Computational Methods

The electronic structure calculations were performed with DMol3,[23-25] a numerical-based density-functional computer program. The Becke−Tsuneda−Hirao[26,27] (BOP) gradient corrected functional was used to approximate the exchange-correlation energy-density functional. The basis set employed was a double numerical plus polarization (DNP) basis developed in our laboratory. This basis set includes as polarization functions a p-function on hydrogen, d-functions on carbon, oxygen, and nitrogen, and f-functions on chromium, molybdenum, and tungsten. The finite basis-set cutoff was set to 20 b, and a fine numerical integration grid was utilized for all calculations. All calculations partially included relativistic effects through the use of the scalar relativity all electron Darwin and mass−velocity correction.[28] The self-consistent field (SCF) convergence criterion was set to 1.0×10^{-8}, and the geometry optimization convergence criteria were 1.0×10^{-5} hartree for the energy and 1.0×10^{-3} hartree/b for the gradient. Symmetry was not imposed on any calculations. For the charged molecular systems, we performed spin-unrestricted calculations.

The electronic densities from electronic structure calculations were used to determine the Fukui functions for the Cr, Mo, and W paddlewheel molecules. The Fukui functions $f_{N-1}^+(\boldsymbol{r})$ and $f_N^-(\boldsymbol{r})$ were calculated using eqs 1 and 2, respectively. As is implicit in the definition of the Fukui function, all densities were computed at the optimum geometry of the reference system. Specifically, when computing $f_N^-(\boldsymbol{r})$ for the neutral systems, $M_2(hpp)_4$, we optimized the geometry of the neutral system and then evaluated $f_N^-(\boldsymbol{r})$ using eq 2, where the density of the cation was evaluated at the geometry for the optimum geometry for the neutral molecule. When computing $f_{N-1}^+(\boldsymbol{r})$ for the cations, $M_2(hpp)_4{}^+$, we optimized the geometry of the cation and then evaluated $f_{N-1}^+(\boldsymbol{r})$ using eq 1, where the density of the neutral system was calculated at the optimum geometry for the cation.

Results and Discussion

The optimized gas phase structures for the Cr, Mo, and W paddlewheel molecules are presented in Figure 1. All three molecules exhibit C_4 symmetry,[29] and the calculated metal−metal distances (Table 1) are in reasonable agreement with the corresponding experimental measurements.[14,30] The calculations predict the extraordinarily low ionization potentials of this family of molecules and also the general trend, with the ionization potential decreasing with increasing size of the metal. Indeed, the calculated vertical ionization potentials (Table 2) are even smaller than the experimental values.[12] The tendency for hybrid density functionals to underestimate the ionization potentials had been previously observed,[12] and the GGA-type functionals we use seem to be a bit worse. However, unlike the previous calculations,[12] our computational approach successfully reproduces the difference between the ionization potentials of W_2-

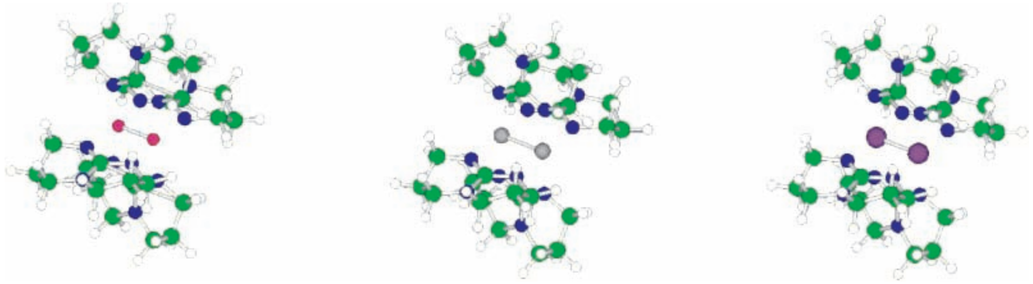

Figure 1. Ball-and-tube model of the three $M_2(hpp)_4$ complexes (M = Cr, Mo, and W, respectively).

TABLE 1: Metal−Metal Distances for $M_2(hpp)_4$ in angstroms

	M = Cr	M = Mo	M = W
calculated	1.778	2.089	2.206
experimental	1.852[a]	2.067[a]	2.250[b]

[a] Taken from ref 30. [b] Taken from ref 31.

TABLE 2: Vertical Ionization Potentials for $M_2(hpp)_4$ in electronvolts[a]

	M = Cr	M = Mo	M = W
calculated	3.93	3.61	3.00
experimental	5.00	4.33	3.76

[a] The experimental data are from ref 12.

(hpp)$_4$ and $Mo_2(hpp)_4$. We are confident that our computational results are accurate enough so that the following analysis—which depends only on the qualititative features of electron density, Fukui functions, and frontier orbitals—is reliable.

The most exceptional feature of this family of $M_2(hpp)_4$ molecules is their extremely low ionization potentials. Consequently, we start by studying $f_N^-(\boldsymbol{r})$, which provides information about the location in the molecule where the electron is lost during ionization. As discussed previously, $f_N^-(\boldsymbol{r})$ tends to be large in locations that are susceptible to electrophilic attack.

Figure 2 shows $f_N^-(\boldsymbol{r})$ for the three metal complexes. In Figure 2, the Fukui function is mapped onto a surface of the electron density with an isovalue of 0.002. This surface just encloses the van der Waals volumes of the individual atoms in the molecule and is thus a good representation of the van der Waals surface for the metal complex. As discussed in the section entitled “Theoretical Background”, $f_N^-(\boldsymbol{r})$ measures the linear response of the density as electrons are donated to the electrophile, and its reliability is greatest when the reagent is far from the molecule. The 0.002 isosurface, then, can be interpreted as a reactive surface because if the electrophile were located on this isosurface, the electron densities of the electrophile and metal complex would overlap enough to enable the process of charge transfer to begin, but the reactants would still be distant enough for the Fukui function to be a reliable indicator of the charge-transfer preferences of the metal complex. Consequently, plotting the Fukui function on the 0.002 isosurface provides an excellent method for displaying the important features of the Fukui function.

In Figure 2, the values of $f_N^-(\boldsymbol{r})$ on this surface are colored from red (largest value of $f_N^-(\boldsymbol{r})$ on the surface) to blue (smallest value of $f_N^-(\boldsymbol{r})$). The red region clearly indicates that, upon ionization, the electron comes from the ends of the molecule containing the metals aligned on the C_4 axis. This is consistent with the reactivity of these metal complexes, which tend to be oxidized on the ends of the molecule, along the C_4 axis.[13,14,30,31]

That an anion such as Cl^- bonds with the metal along the C_4 axis is also predicted by the Fukui function $f_{N-1}^+(\boldsymbol{r})$ for the cation metal complex, $M_2(hpp)_4{}^+$. $f_{N-1}^+(\boldsymbol{r})$ provides a measure for the willingness for the cation to accept electrons from an approaching reagent. Figure 3 shows $f_{N-1}^+(\boldsymbol{r})$ for the three metal complexes. Again, $f_{N-1}^+(\boldsymbol{r})$ is mapped onto an isosurface of the electron density of the cation; the color code is the same as that in Figure 2. The most positive value of $f_{N-1}^+(\boldsymbol{r})$ is located at the ends of the molecule along the C_4 axis containing the metal−metal bond. The fact that the cations, $M_2(hpp)_4{}^+$, react with a nucleophile at the same location that the neutral species, $M_2(hpp)_4$, react with an electrophile is a useful indication of internal consistency.[32]

The orbital densities of the HOMOs for the neutral metal complexes are shown in Figure 4. In agreement with the results of Cotton and co-workers,[12] electrons in the HOMO (red) are concentrated between the two metals along the delta bond. *The square of the HOMO does not provide an index of chemical reactivity for these complexes.*

The orbital densities of the LUMOs for the positively charged metal complexes, $M_2(hpp)_4{}^+$, are shown in Figure 5. The LUMO is concentrated between the two metals along the delta bond, as was the case for the HOMO in the neutral complexes. Again, the square of the LUMO is a poor indicator of chemical reactivity.

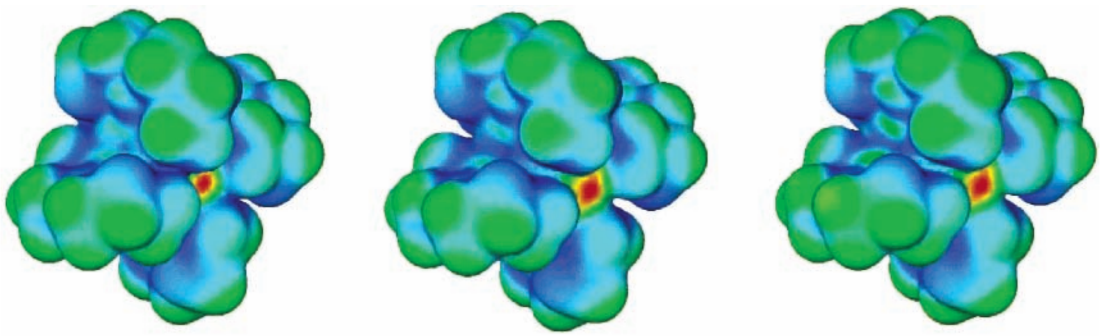

Figure 2. Fukui function $f_N^-(\boldsymbol{r})$ for the three $M_2(hpp)_4$ complexes (M = Cr, Mo, and W, respectively).

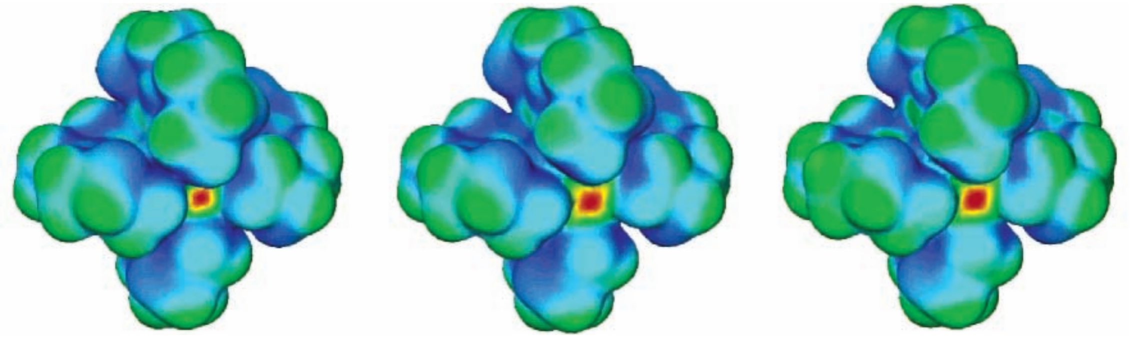

Figure 3. Fukui function $f^{+}_{N-1}(\boldsymbol{r})$ for the positively charged complexes, $M_2(hpp)_4{}^{+}$ (M = Cr, Mo, and W, respectively).

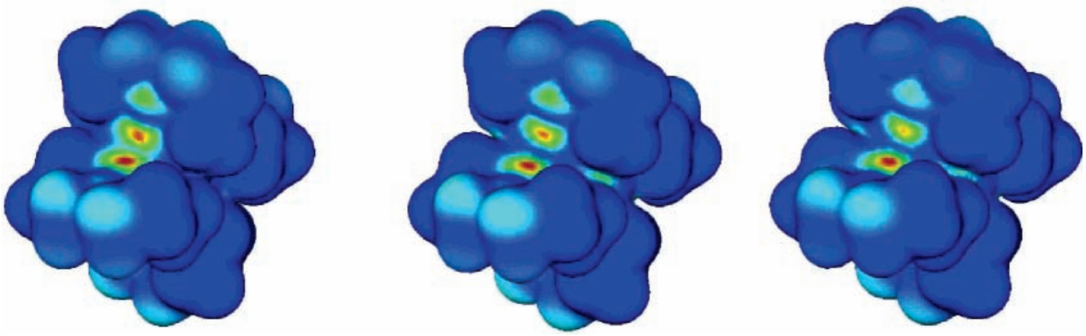

Figure 4. Orbital density of the HOMO for $M_2(hpp)_4$ complexes (M = Cr, Mo, and W, respectively).

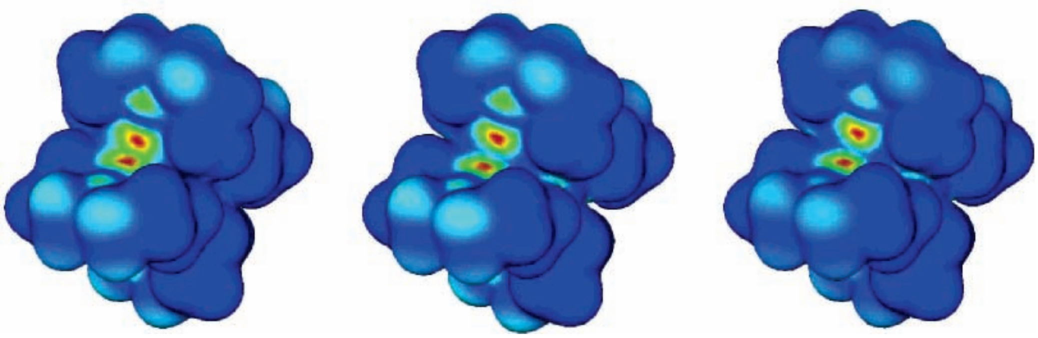

Figure 5. Orbital density of the LUMO for the positively charged complexes, $M_2(hpp)_4{}^{+}$ (M = Cr, Mo, and W, respectively).

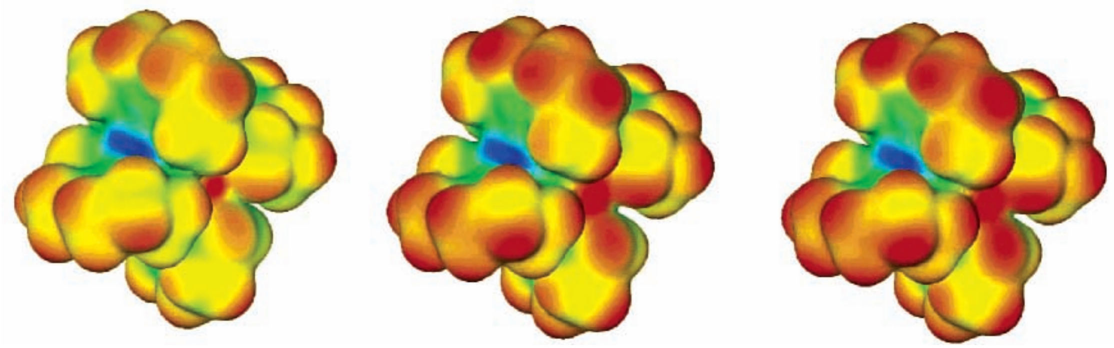

Figure 6. Electrostatic potential $\Phi_N(\boldsymbol{r})$ for the three $M_2(hpp)_4$ complexes (M = Cr, Mo, and W, respectively).

Klopman has argued that chemical reactions can be categorized as being one of two types: "frontier-controlled" reactions occur where the HOMO or LUMO density is largest, and "charge-controlled" reactions occur where the electrostatic potential

$$\Phi_N(\boldsymbol{r}) = \sum_{\alpha=1}^{P} \frac{Z_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|} - \int \frac{\rho_N(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' \qquad (6)$$

is most positive (nucleophiles) or negative (electrophiles).[33−35] (In eq 6, $\{Z_\alpha\}$ and $\{\boldsymbol{R}_\alpha\}$ denote the atomic numbers and nuclear positions for the molecule.) Figure 6 plots the electrostatic potential $\Phi_N(\boldsymbol{r})$ for the neutral molecules, $M_2(hpp)_4$. The scale ranges from negative values of the electrostatic potential (blue) to positive values (red). Oxidation should occur in electron-rich regions of the molecule, which are associated with negatively charged regions of the molecule. However, the blue regions in Figure 6, like the favorable regions in Figures 4 and 5, are not located at the ends of the molecule but instead are located along the delta bond. Electrophilic attack (oxidation)

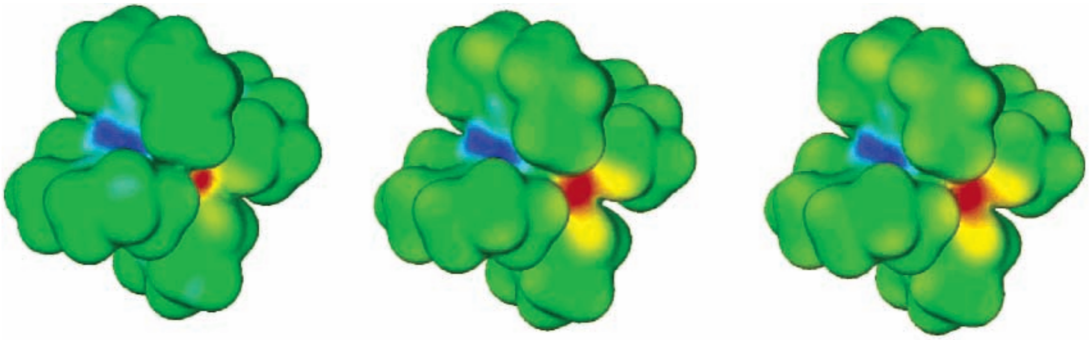

Figure 7. Electrostatic potential $\Phi_{N-1}(\boldsymbol{r})$ for the positively charged complexes, $M_2(hpp)_4^+$ (M = Cr, Mo, and W, respectively).

of these $M_2(hpp)_4$ complexes is neither frontier-molecular-orbital-controlled nor charge-controlled. Rather, it is "orbital-relaxation-controlled" or—discarding the molecular orbital language altogether in favor of the simpler and more inclusive density-functional-theory term—"Fukui-function-controlled".[36]

We also examined the electrostatic potential for the cations, $M_2(hpp)_4^+$, which are plotted in Figure 7. A nucleophile like the chloride anion should attack the cation in the regions where it is positively charged. In this case, $\Phi_{N-1}(\boldsymbol{r})$ correctly predicts the site of attack. Thus, the site of nucleophilic attack on the cations, $M_2(hpp)_4^+$, is consistent with this being a charge-controlled reaction, while electrophilic attack on the neutral complexes is not.

Conventional wisdom in density-functional theory would argue that, for the very soft metal complexes, $M_2(hpp)_4$, the Fukui function would be the appropriate indicator of chemical reactivity.[22,37] We observe that this is the case, albeit with a twist: in this case, it is the orbital relaxation contributions to the Fukui function, and not the frontier molecular orbital contribution, that are decisive. Though there are some other cases in the literature where orbital relaxation makes an important contribution to the Fukui function,[38,39] the authors are not aware of any cases where the qualitative difference in reactivity preference is this dramatic. Though the HOMO is sometimes not an adequate approximation for $f_N^-(\boldsymbol{r})$, we are unaware of any other cases where the HOMO has no significant density on the preferred site. The widely used approximations, $f_N^-(\boldsymbol{r}) \approx |\phi_{\mathrm{HOMO}}(\boldsymbol{r})|^2$ and $f_N^+(\boldsymbol{r}) \approx |\phi_{\mathrm{LUMO}}(\boldsymbol{r})|^2$, are totally invalid here. (While characterizing the precise nature of orbital relaxation in this system eludes us, it should be noted that the HOMO of the neutral molecule and the LUMO of the cation resemble each other (compare Figures 4 and 5). This suggests that the relaxation of $\phi_{\mathrm{HOMO}}(\boldsymbol{r})$ during the course of ionization is not determinative. Consequently, the dominant terms in eq 5 for $f_N^-(\boldsymbol{r})$ must be those associated with the relaxation of the lower-lying (HOMO-1, HOMO-2, etc.) orbitals.)

While the cations, $M_2(hpp)_4^+$, are not really hard Lewis acids, they are significantly harder species than the neutral complexes, so it is unsurprising that the electrostatic potential (which is an appropriate descriptor for hard acid/hard base interactions[22,37]) is a more reliable reactivity indicator for the cations than it was for the neutral species. It is reassuring that, in this case, both the Fukui function and the electrostatic potential predict the same regioselectivity.

In summary, we present computational evidence for the decisive importance of orbital relaxation effects in oxidation reactions of $M_2(hpp)_4$ compounds (M = Cr, Mo, and W). Even though frontier molecular orbital theory (based on the HOMO of the neutral metal complexes or the LUMO of their cations) fails to predict the appropriate regioselectivity for these species, the DFT-based Fukui function, which includes the effects of orbital relaxation, does. These studies reveal the inadequacy of the frontier-controlled versus charge-controlled dichotomy for describing chemical reactivity and provide evidence of the utility of conceptual density-functional theory for describing and predicting chemical reactivity.

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